MAGNETIC ORDER AND SUPERCONDUCTIVITY IN RUTHENATES,
RUTHENOCUPRATES, AND OTHER LAYERED OXIDES

A Dissertation

Submitted to the Graduate School
of the University of Notre Dame
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy

by

Matthew Passmore Smylie

Howard Blackstead, Director

Graduate Program in Physics

Notre Dame, Indiana

April 2010
MAGNETIC ORDER AND SUPERCONDUCTIVITY IN RUTHENATES, RUTHENOCUPRATES, AND OTHER LAYERED OXIDES

Abstract

by

Matthew Passmore Smylie

There exist several classes of materials that simultaneously exhibit superconductivity and anomalous magnetic order, where both effects are homogeneous throughout the material. No cohesive explanation for this "apparent ferromagnetism" has ever been published. In the $A_{1-x}Ce_xSr_2Cu_2MO_{10}$ and in the $ASr_2Cu_2RuO_8$ ($A=Ln,Y; M=Ru,Nb$) families of materials, it is shown via diffraction, SQUID magnetometry, and electron spin resonance that the metamagnetism in these materials is due to CuO$_2$ ferromagnetic order in the $ab$-plane, with adjacent layers stacked ferromagnetically; this CuO$_2$ magnetic order coexists with superconductivity in these materials. The implications of this on models of high-$T_c$ superconductivity may be profound.

Another controversial class of superconducting material, $Ba_2ARu_{1-x}Cu_xO_6$ ($A=Ln,Y$) is examined and the compound $Ba_2YRu_{1-x}Cu_xO_6$ is shown to be superconducting with simultaneous Cu magnetic order at temperatures near that of YBCO, without CuO$_2$ planes. The magnetic and crystal structures of several members of the Ln series are examined by SQUID magnetometry, electron spin resonance, and x-ray and neutron diffraction, with discovery of simultaneous superconductivity and Cu magnetic order in only $Ba_2DyRu_{1-x}Cu_xO_6$. 
A third related class of materials, $\text{La}_2\text{CuMO}_6$ (M=Ru,Nb,Ti,Ir,Sn) is also examined for superconductivity. The magnetic structure of these materials is investigated by diffraction and SQUID magnetometry, and new high-temperature synthesis techniques are performed that dramatically improve the structural and magnetic properties of the compound $\text{La}_2\text{CuRuO}_6$; electron spin resonance has identified Cu antiferromagnetism in this material for the first time. Hole doping (with Ba or Sr) and electron doping (with Ce or Th) fails to generate superconductivity in this material. The high-temperature synthesis techniques are unsuccessful in processing of other members of the $\text{La}_2\text{CuMO}_6$ family due to the stability of $\text{La}_2\text{M}_2\text{O}_7$-type compounds at high temperatures. The compound $\text{La}_2\text{CuSnO}_6$ forms distinct CuO$_2$ and SnO$_2$ chemical layers, yet shows no superconductivity.
For my family, especially my grandparents, who have done more for me than they will ever know.
CONTENTS

FIGURES ................................................................................................................... v

ACKNOWLEDGMENTS ............................................................................................... xvii

CHAPTER 1: INTRODUCTION ............................................................................. 1
  1.1 Motivation ........................................................................................................ 1
  1.2 A Short History of Superconductivity ............................................................. 2
  1.3 Outline of Thesis ............................................................................................ 3

CHAPTER 2: MAGNETISM AND SUPERCONDUCTIVITY IN RUTHENOCUPRATES ............................................................................ 5
  2.1 Background ........................................................................................................ 5
  2.2 Ln2−xCexSr2Cu2RuO10 ..................................................................................... 13
  2.3 Y1−xCe0.5Sr2Cu2RuO10 .................................................................................. 16
  2.4 Y1.5Ce0.5Sr2Cu2NbO10 ................................................................................. 28
  2.5 O10 Family Conclusions .................................................................................. 36
  2.6 LnSr2Cu2RuO8 ................................................................................................ 38
  2.7 YSr2Cu2RuO8 .................................................................................................. 49
  2.8 YSr2Cu2NbO8 .................................................................................................. 57
  2.9 O8 Family Conclusions .................................................................................. 66

CHAPTER 3: MAGNETISM AND SUPERCONDUCTIVITY IN RUTHENATES ......................................................................................... 69
  3.1 Ba2YRu1−xCu2O6 ............................................................................................... 69
  3.2 Broadening the Search: Ba2LnRu1−xCu2O6 ..................................................... 84
  3.3 Ba2DyRu1−xCu2O6 ........................................................................................... 87
  3.4 Ba2NdRu1−xCu2O6 ........................................................................................... 120
  3.5 Ba2SmRu1−xCu2O6 .......................................................................................... 142
  3.6 O8 Family Conclusions .................................................................................. 150
FIGURES

Figure 2.1: One half of the unit cell of superconducting Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$. CuO$_2$ planes are shifted by one half of a unit cell in the ab-plane across the fluorite-like rare earth layer. ................................................................. 8

Figure 2.2: Typical temperature dependence of magnetic susceptibility with H=10 Oe for superconducting Y$_{1-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$. The “apparent ferromagnetism” coexists with the superconductivity. ......................................................... 10

Figure 2.3: The unit cell of superconducting GdSr$_2$Cu$_2$RuO$_8$. The chain CuO layers in YBCO have been replaced with RuO$_2$ layers. ................................................................. 11

Figure 2.4: Typical temperature dependence of magnetic susceptibility with H=100 Oe for superconducting YSr$_2$Cu$_2$RuO$_8$. The “apparent ferromagnetism” coexists with the superconductivity. ......................................................... 13

Figure 2.5: Temperature dependence of magnetic susceptibility for Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$RuO$_{10}$ with H=10 Oe ................................................................. 18

Figure 2.6: Powder neutron diffraction at 16 K and Rietveld refinement on Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$RuO$_{10}$. The fit is in good agreement with ferromagnetic in-planar order, stacked antiferromagnetically. ........................................ 20

Figure 2.7: Magnetic resonance at 12.885 GHz with H$_r$ perpendicular to H$_d$ in superconducting Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$RuO$_{10}$ ................................................................. 23

Figure 2.8: Magnetic resonance at 12.885 GHz with H$_r$ parallel to H$_d$ in superconducting Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$RuO$_{10}$ ................................................................. 24

Figure 2.9: Magnetic resonance at 20.3 GHz with H$_r$ perpendicular to H$_d$ in superconducting Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$RuO$_{10}$ ................................................................. 25

Figure 2.10: Magnetic resonance at 20.3 GHz with H$_r$ parallel to H$_d$ in superconducting Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$RuO$_{10}$ ................................................................. 26
Figure 2.11: Magnetic resonance at 35.27 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting $Y_{1.5}Ce_{0.5}Sr_2Cu_2RuO_{10}$  .......................................................... 27

Figure 2.12: Magnetic resonance at 35.27 GHz with $H_{rf}$ parallel to $H_{dc}$ in superconducting $Y_{1.5}Ce_{0.5}Sr_2Cu_2RuO_{10}$  .......................................................... 28

Figure 2.13: Temperature dependence of magnetic susceptibility for superconducting $Y_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ with $H=10$ Oe  ......................................................................................................................... 30

Figure 2.14: Expansion of temperature dependence of magnetic susceptibility for superconducting $Y_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ with $H=10$ Oe. A magnetic transition is visible at 273 K. The diamagnetism and ferromagnetism rapidly go off-scale below 27.5 K. ........................................................................................................ 31

Figure 2.15: Field dependence of magnetic susceptibility for superconducting $Y_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$. Metamagnetism is observed at all temperatures up to room temperature. The superconductivity at 3 K is off-scale. ................. 32

Figure 2.16: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting $Y_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$  .......................................................... 35

Figure 2.17: Magnetic resonance at 20.3 GHz with $H_{rf}$ parallel to $H_{dc}$ in superconducting $Y_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$  .......................................................... 36

Figure 2.18: Magnetic resonance at 13.2 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting $GdSr_2Cu_2RuO_8$  .................................................................... 44

Figure 2.19: Magnetic resonance at 13.2 GHz with $H_{rf}$ parallel to $H_{dc}$ in superconducting $GdSr_2Cu_2RuO_8$  .................................................................... 45

Figure 2.20: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting $GdSr_2Cu_2RuO_8$  .................................................................... 46

Figure 2.21: Magnetic resonance at 20.3 GHz with $H_{rf}$ parallel to $H_{dc}$ in superconducting $GdSr_2Cu_2RuO_8$  .................................................................... 47

Figure 2.22: Magnetic resonance at 35.27 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting $GdSr_2Cu_2RuO_8$  .................................................................... 48

Figure 2.23: Magnetic resonance at 35.27 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting $GdSr_2Cu_2RuO_8$  .................................................................... 49

Figure 2.24: Temperature dependence of magnetic susceptibility for $Y_{0.7}Cu_{2.1}Ru_{0.9}O_{7.9}$ with $H=10$ Oe  ........................................................................................................ 51
Figure 2.25: Low-angle powder neutron diffraction at 16 K on YSr$_2$Cu$_{2.1}$Ru$_{0.9}$O$_{7.9}$. The refinement agrees well with ab-planar ferromagnetism stacked antiferromagnetically.

Figure 2.26: Full neutron diffraction and Rietveld fit for nuclear and magnetic reflections at 16 K on YSr$_2$Cu$_{2.1}$Ru$_{0.9}$O$_{7.9}$. The fit is in good agreement with the proposed model of ferromagnetic CuO$_2$ layers stacked antiferromagnetically.

Figure 2.27: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting YSr$_2$Cu$_{2.1}$Ru$_{0.9}$O$_{7.9}$. The only difference from the Gd homologue is the lack of magnetic metal ions besides Cu.

Figure 2.28: Magnetic resonance at 20.3 GHz with $H_{rf}$ parallel to $H_{dc}$ in superconducting YSr$_2$Cu$_{2.1}$Ru$_{0.9}$O$_{7.9}$.

Figure 2.29: The unit cell of superconducting YSr$_2$Cu$_2$NbO$_8$. The magnetic transition at 257 K is more pronounced.

Figure 2.30: Temperature dependence of magnetic susceptibility for superconducting YSr$_2$Cu$_{2.1}$Nb$_{0.9}$O$_8$ with $H=10$ Oe. Transitions are visible at low and high temperature, indicating high temperature Cu magnetic order.

Figure 2.31: Temperature dependence of magnetic susceptibility for superconducting YSr$_2$Cu$_{2.1}$Nb$_{0.9}$O$_8$ with $H=100$ Oe. The magnetic transition at 257 K is more pronounced.

Figure 2.32: Temperature dependence of magnetic susceptibility for superconducting YSr$_2$Cu$_{2.1}$Nb$_{0.9}$O$_8$ with $H=1000$ Oe. The superconductivity can no longer screen the magnetism, and at lowest temperatures the antiferromagnetically stacked CuO$_2$ collapse into ferromagnetism.

Figure 3.1: Temperature dependence of magnetic susceptibility for Ba$_2$YRu$_{0.85}$Cu$_{0.15}$O$_6$ with $H=10$ Oe. The Ru magnetic transition is screened by the diamagnetism.

Figure 3.2: Unit cell of Ba$_2$YRu$_{1.4}$Cu$_6$O$_6$. There are alternating, stacked layers of magnetic YRuO$_4$ and nonmagnetic 4BaO. Good spatial arrangement of Y and Ru is essential to superconductivity in the system.
Figure 3.3: Low-angle neutron diffraction on Ba$_2$YRu$_{0.9}$Cu$_{0.1}$O$_6$. The ~$10^\circ$ scattering peak persists to at least 85 K, and is consistent with a spin-density wave. The green line serves as a guide to the eye. ............................................................

Figure 3.4: Low-field magnetic resonance at 32.7 GHz in Ba$_2$YRu$_{0.85}$Cu$_{0.15}$O$_6$ with $H_{rf}$ perpendicular to $H_{dc}$. At lowest temperatures, the low-field Cu resonance is visible against the superconducting dissipation. ............................................

Figure 3.5: Low-field magnetic resonance at 32.7 GHz in Ba$_2$YRu$_{0.85}$Cu$_{0.15}$O$_6$ with $H_{rf}$ parallel to $H_{dc}$. At lowest temperatures, the low-field Cu resonance is visible against the superconducting dissipation. ......................................................

Figure 3.6: Magnetic resonance at 20.3 GHz in Ba$_2$GdRuO$_6$ with 5% by weight of GdBa$_2$Cu$_3$O$_7$ sintered for 12 h at 1380 °C. No paramagnetic Gd resonance is observed below $T_{N-Ru} = 48$ K. ......................................................

Figure 3.7: Powder x-ray diffraction on undoped Ba$_2$DyRuO$_6$ sintered at 1400 °C. All peaks belong to the O$_6$-phase, and no impurity phases are detectable. ...... 89

Figure 3.8: Temperature dependence of magnetic susceptibility for Ba$_2$DyRuO$_6$ with $H=10$ Oe .....................................................................................................

Figure 3.9: Field dependence of magnetic susceptibility with $T = 2$ K for Ba$_2$DyRuO$_6$ ..............................................................................................................

Figure 3.10: Magnetic resonance at 12.885 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in Ba$_2$DyRuO$_6$ ..............................................................................................................

Figure 3.11: Magnetic resonance at 12.885 GHz with $H_{rf}$ parallel to $H_{dc}$ in Ba$_2$DyRuO$_6$ ..............................................................................................................

Figure 3.12: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in Ba$_2$DyRuO$_6$. A small paramagnetic impurity is observed that was also seen in an empty cavity. ...............................................................

Figure 3.13: Magnetic resonance at 20.3 GHz with $H_{rf}$ parallel to $H_{dc}$ in Ba$_2$DyRuO$_6$. ......................................................

Figure 3.14: Magnetic resonance at 20.3 GHz near $T_N$ with $H_{rf}$ perpendicular to $H_{dc}$ in Ba$_2$DyRuO$_6$. No resonance is observed. ......................................................

Figure 3.15: Powder x-ray diffraction on Ba$_2$DyRu$_{0.9}$Cu$_{0.1}$O$_6$ at different sintering temperatures. The indexed peaks are all O$_6$-phase. The red stars indicate very small impurity peaks not observed in the undoped material. .................
Figure 3.16: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1100 °C ...................................................... 101

Figure 3.17: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1200 °C ...................................................... 102

Figure 3.18: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1300 °C. Inset: Expansion detailing transition at 11 K. ................................................................. 103

Figure 3.19: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1400 °C ...................................................... 105

Figure 3.20: Field dependence of magnetic susceptibility with $T = 2$ K for $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1400 °C ...................................................... 106

Figure 3.21: Magnetic resonance at 20.3 GHz with $H_{\text{rf}}$ perpendicular to $H_{\text{dc}}$ in $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1200 °C as a function of temperature ...... 108

Figure 3.22: Magnetic resonance at 20.3 GHz with $H_{\text{rf}}$ parallel to $H_{\text{dc}}$ in $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1200 °C as a function of temperature ...... 109

Figure 3.23: Magnetic resonance at 20.3 GHz with $H_{\text{rf}}$ perpendicular to $H_{\text{dc}}$ in $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1400 °C as a function of temperature ...... 110

Figure 3.24: Magnetic resonance at 20.3 GHz with $H_{\text{rf}}$ parallel to $H_{\text{dc}}$ in $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1400 °C as a function of temperature ...... 111

Figure 3.25: Susceptibility as a function of temperature of mixed $\text{Ba}_2\text{DyRuO}_6 + 6\%$ $\text{DyBa}_2\text{Cu}_3\text{O}_7$ with $H = 10$ Oe ................................................................. 114

Figure 3.26: Susceptibility as a function of temperature of $\text{Ba}_2\text{DyRuO}_6 + 6\%$ $\text{DyBa}_2\text{Cu}_3\text{O}_7$ after 970 °C heat treatment, with $H = 10$ Oe ........................................... 116

Figure 3.27: Susceptibility as a function of temperature of $\text{Ba}_2\text{DyRuO}_6 + 6\%$ $\text{DyBa}_2\text{Cu}_3\text{O}_7$ after 1400 °C heat treatment, with $H = 10$ Oe ....................... 117

Figure 3.28: ZFC susceptibility as a function of temperature of $\text{Ba}_2\text{DyRuO}_6 + 6\%$ $\text{DyBa}_2\text{Cu}_3\text{O}_7$ following various heat treatments, with $H = 10$ Oe ....................... 119

Figure 3.29: Comparison of powder x-ray diffraction of $\text{Ba}_2\text{DyRuO}_6 + 6\%$ $\text{DyBa}_2\text{Cu}_3\text{O}_7$ following mixing and heat treatment to pure $\text{Ba}_2\text{DyRuO}_6$. The indexed peaks are $\text{DyBa}_2\text{Cu}_3\text{O}_7$. ................................................................. 120
Figure 3.30: Powder x-ray diffraction on undoped Ba$_2$NdRuO$_6$ sintered at 1400 °C. All peaks belong to the O$_6$-phase, and no impurity phases are detectable. .... 121

Figure 3.31: Temperature dependence of magnetic susceptibility for Ba$_2$NdRuO$_6$ with H=10 Oe ................................................................. 123

Figure 3.32: Temperature dependence of magnetic susceptibility for Ba$_2$NdRuO$_6$ with H=1000 Oe ................................................................. 125

Figure 3.33: Temperature dependence of magnetic susceptibility for Ba$_2$NdRuO$_6$ in various high fields. Closed circles are zero-field cooled measurements; open circles, field cooled. ........................................ 126

Figure 3.34: Field dependence of magnetic susceptibility at various temperatures for Ba$_2$NdRuO$_6$ ................................................................. 128

Figure 3.35: Powder x-ray diffraction on Ba$_2$NdRu$_{0.9}$Cu$_{0.1}$O$_6$ at different sintering temperatures. The indexed peaks are all O$_6$-phase. Impurity peaks are marked with red stars, and are not found in the undoped material. ............ 130

Figure 3.36: Temperature dependence of magnetic susceptibility with H = 10 Oe for Ba$_2$NdRu$_{0.9}$Cu$_{0.1}$O$_6$ sintered at 1100 °C ........................................ 131

Figure 3.37: Temperature dependence of magnetic susceptibility with H = 10 Oe for Ba$_2$NdRu$_{0.9}$Cu$_{0.1}$O$_6$ sintered at 1200 °C ........................................ 132

Figure 3.38: Temperature dependence of magnetic susceptibility with H = 10 Oe for Ba$_2$NdRu$_{0.9}$Cu$_{0.1}$O$_6$ sintered at 1300 °C ........................................ 133

Figure 3.39: Temperature dependence of magnetic susceptibility with H = 10 Oe for Ba$_2$NdRu$_{0.9}$Cu$_{0.1}$O$_6$ sintered at 1400 °C ........................................ 135

Figure 3.40: Expansion of temperature dependence of magnetic susceptibility with H = 10 Oe for Ba$_2$NdRu$_{0.9}$Cu$_{0.1}$O$_6$ sintered at 1400 °C ........................................ 136

Figure 3.41: Field dependence of magnetic susceptibility at various temperatures for Ba$_2$NdRu$_{0.9}$Cu$_{0.1}$O$_6$ sintered at 1400 °C ........................................ 137

Figure 3.42: Magnetic resonance at 20.3 GHz with H$_{rf}$ perpendicular to H$_{dc}$ in Ba$_2$NdRu$_{0.9}$Cu$_{0.1}$O$_6$ sintered at 1400 °C as a function of temperature ....... 139

Figure 3.43: Magnetic resonance at 20.3 GHz with H$_{rf}$ parallel to H$_{dc}$ in Ba$_2$NdRu$_{0.9}$Cu$_{0.1}$O$_6$ sintered at 1400 °C as a function of temperature ....... 140
Figure 3.44: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{NdRu}_{0.8}\text{Cu}_{0.2}\text{O}_6$ sintered at 1400 °C ......................................................141

Figure 3.45: Powder x-ray diffraction on undoped $\text{Ba}_2\text{SmRuO}_6$ sintered at 1400 °C. All peaks belong to the $\text{O}_6$-phase, and no impurity phases are detectable. ...... 143

Figure 3.46: Temperature dependence of magnetic susceptibility for $\text{Ba}_2\text{SmRuO}_6$ with $H=10$ Oe. The inset shows a blowup of the ZFC and FC susceptibility near the magnetic transition. .................................................................144

Figure 3.47: Powder x-ray diffraction on $\text{Ba}_2\text{SmRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ at different sintering temperatures. The indexed peaks are all $\text{O}_6$-phase. Impurity peaks are marked with red stars, and are not seen in the undoped material. .............. 146

Figure 3.48: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{SmRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1300 °C. The inset shows a blowup of the ZFC and FC susceptibility near the magnetic transition. .........................147

Figure 3.49: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{SmRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1400 °C. The inset shows a blowup of the ZFC and FC susceptibility near the magnetic transition. ..........................148

Figure 3.50: Temperature dependence of magnetic susceptibility with $H = 1000$ Oe for $\text{Ba}_2\text{SmRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1400 °C. The inset shows a blowup of the ZFC and FC susceptibility near the magnetic transition. .........................149

Figure 4.1: One quarter of the unit cell of $\text{La}_2\text{CuRuO}_6$. Optimally formed material has the Cu and Ru occupying adjacent sites of a rock salt lattice; poor quality samples will have some Ru/Cu site mixing. .................................................154

Figure 4.2: Powder x-ray diffraction on $\text{La}_2\text{CuRuO}_6$ at different sintering temperatures. The indexed peaks are all $\text{O}_6$-phase. Impurity peaks are only observed for low sintering temperatures. .................................................................157

Figure 4.3: Powder x-ray diffraction on single-phase $\text{La}_2\text{CuO}_4$ optimally processed at 900 °C and $\text{La}_2\text{CuO}_4$ sintered at 1400 °C. Clearly no $\text{La}_2\text{CuO}_4$ survived high temperature processing. .................................................................158

Figure 4.4: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_2\text{CuRuO}_6$ sintered at 1100 °C. The inset shows an expansion of the vertical scale, highlighting the transitions. .................................................................160

Figure 4.5: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_2\text{CuRuO}_6$ sintered at 1200 °C .................................................................161
Figure 4.6: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_2\text{CuRuO}_6$ sintered at $1300 \degree \text{C}$ .............................................................. 162

Figure 4.7: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_2\text{CuRuO}_6$ sintered at $1350 \degree \text{C}$ .............................................................. 163

Figure 4.8: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_2\text{CuRuO}_6$ sintered at $1400 \degree \text{C}$ .............................................................. 164

Figure 4.9: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_2\text{CuRuO}_6$ sintered at $1450 \degree \text{C}$ .............................................................. 165

Figure 4.10: Temperature dependence of ZFC magnetic susceptibility with $H = 10$ Oe in all samples of $\text{La}_2\text{CuRuO}_6$ .............................................................. 166

Figure 4.11: Temperature dependence of magnetic susceptibility with $H = 7$ T for $\text{La}_2\text{CuRuO}_6$ sintered at $1400 \degree \text{C}$. No transitions are evident at higher temperatures. .............................................................. 167

Figure 4.12: Temperature dependence of magnetic susceptibility with $H = 100$ Oe for $\text{La}_2\text{CuRuO}_6$ sintered at $1400 \degree \text{C}$ .............................................................. 168

Figure 4.13: Temperature dependence of magnetic susceptibility with $H = 1000$ Oe for $\text{La}_2\text{CuRuO}_6$ sintered at $1400 \degree \text{C}$ .............................................................. 169

Figure 4.14: Temperature dependence of magnetic susceptibility with $H = 1$ T for $\text{La}_2\text{CuRuO}_6$ sintered at $1400 \degree \text{C}$ .............................................................. 170

Figure 4.15: Field dependence of magnetic susceptibility for $\text{La}_2\text{CuRuO}_6$ sintered at $1400 \degree \text{C}$. In both measurements there is a trend towards ferromagnetic saturation. .............................................................. 171

Figure 4.16: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in $\text{La}_2\text{CuRuO}_6$ sintered at $1300 \degree \text{C}$ as a function of temperature. No high temperature resonance is observed. .............................................................. 173

Figure 4.17: Magnetic resonance at 20.3 GHz with $H_{rf}$ parallel to $H_{dc}$ in $\text{La}_2\text{CuRuO}_6$ sintered at $1300 \degree \text{C}$ as a function of temperature. No high temperature resonance is observed. .............................................................. 174

Figure 4.18: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in $\text{La}_2\text{CuRuO}_6$ sintered at $1400 \degree \text{C}$ as a function of temperature ........................................... 175
Figure 4.19: Magnetic resonance at 20.3 GHz with $H_{rf}$ parallel to $H_{dc}$ in $La_2CuRuO_6$ sintered at 1400 °C as a function of temperature ........................................... 176

Figure 4.20: Powder x-ray diffraction on $La_{1.9}Sr_{0.1}CuRuO_6$ at different sintering temperatures. No $SrCO_3$ is observable ...................................................... 179

Figure 4.21: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.9}Sr_{0.1}CuRuO_6$ sintered at 1300 °C ...................................................... 180

Figure 4.22: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.9}Sr_{0.1}CuRuO_6$ sintered at 1350 °C ...................................................... 180

Figure 4.23: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.9}Sr_{0.1}CuRuO_6$ sintered at 1400 °C ...................................................... 181

Figure 4.24: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.9}Sr_{0.1}CuRuO_6$ sintered at 1450 °C ...................................................... 181

Figure 4.25: Powder x-ray diffraction on $La_{1.8}Sr_{0.2}CuRuO_6$ at different sintering temperatures. No $BaCO_3$ is observable. ...................................................... 182

Figure 4.26: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.8}Ba_{0.2}CuRuO_6$ sintered at 1300 °C ...................................................... 183

Figure 4.27: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.8}Ba_{0.2}CuRuO_6$ sintered at 1350 °C ...................................................... 184

Figure 4.28: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.8}Ba_{0.2}CuRuO_6$ sintered at 1400 °C ...................................................... 184

Figure 4.29: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.8}Ba_{0.2}CuRuO_6$ sintered at 1450 °C ...................................................... 185

Figure 4.30: Powder x-ray diffraction on $La_{1.8}Ce_{0.2}CuRuO_6$ at different sintering temperatures. The indexed peaks are those distinctly belonging to the monoclinic phase $O_6$. No $CeO_2$ is observable. ...................................................... 187

Figure 4.31: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.8}Ce_{0.2}CuRuO_6$ sintered at 1300 °C ...................................................... 188

Figure 4.32: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.8}Ce_{0.2}CuRuO_6$ sintered at 1400 °C ...................................................... 189

xiii
Figure 4.33: Temperature dependence of magnetic susceptibility with $H = 1000$ Oe for $\text{La}_{1.8}\text{Ce}_{0.2}\text{CuRuO}_6$ sintered at $1400$ °C.

Figure 4.34: Powder x-ray diffraction on $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ at different sintering temperatures. The indexed peaks are those distinctly belonging to the monoclinic phase $O_6$. The stars indicate peaks belonging to ThO$_2$, indicating the doping was a failure.

Figure 4.35: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at $1300$ °C.

Figure 4.36: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at $1350$ °C.

Figure 4.37: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at $1450$ °C.

Figure 4.38: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at $1400$ °C. No transitions are observable above $\sim 19$ K. The inset shows an expansion of the low-temperature region, showing the net negative magnetization.

Figure 4.39: Temperature dependence of zero-field cooled magnetic susceptibility with $H = 10$ Oe for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at $1400$ °C with very careful calibration of the background field to less than $0.1$ Oe. The net negative magnetization no longer occurs.

Figure 4.40: Temperature dependence of magnetic susceptibility with $H = 7$ T for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at $1400$ °C. The antiferromagnetic state has collapsed into ferromagnetism, and no additional transitions are visible.

Figure 5.1: Powder x-ray diffraction on $\text{La}_2\text{CuTiO}_6$ sintered at $1400$ °C. The indexed peaks are all orthorhombic $O_6$-phase. No impurity peaks are observed.

Figure 5.2: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_2\text{CuTiO}_6$ sintered at $1400$ °C, showing the paramagnetic character of the material. The FCW data is noise-level for the instrument.

Figure 5.3: Powder x-ray diffraction on $\text{La}_2\text{CuIrO}_6$ sintered at different temperatures. The indexed peaks are all monoclinic $O_6$-phase. No impurity peaks are observed.
Figure 5.4: The unit cell of La$_2$CuSnO$_6$. Optimally formed material has the Cu and Sn forming separate planes; poor quality samples will have some Sn/Cu site mixing. This cell has one quarter of the atoms of the unit cell of La$_2$CuRuO$_6$. 208

Figure 5.5: Powder x-ray diffraction on La$_2$CuSnO$_6$ sintered at different temperatures, showing the destruction of La$_2$CuSnO$_6$ and synthesis of La$_2$Sn$_2$O$_7$ as sintering temperatures are raised. The red stars indicate peaks belonging to O$_7$-phase; this includes all of the largest peaks in the sample sintered at 1400 °C. ................................................................. 210

Figure 5.6: Blowup of powder x-ray diffraction on La$_2$CuSnO$_6$ sintered at different temperatures, clearly indicating the destruction of La$_2$CuSnO$_6$ peaks and creation of La$_2$Sn$_2$O$_7$ peaks at higher sintering temperatures. The indexed peaks all belong to monoclinic O$_6$-phase, whereas the red stars indicate peaks belonging to O$_7$-phase. ............................................................................ 211

Figure 5.7: Temperature dependence of magnetic susceptibility with H = 10 Oe for La$_2$CuSnO$_6$ sintered at 1100 °C ................................................................. 212

Figure 5.8: Temperature dependence of magnetic susceptibility with H = 10 Oe for La$_2$CuSnO$_6$ sintered at 1200 °C ................................................................. 213

Figure 5.9: Temperature dependence of magnetic susceptibility with H = 10 Oe for La$_2$CuSnO$_6$ sintered at 1250 °C ................................................................. 213

Figure 5.10: Temperature dependence of magnetic susceptibility with H = 10 Oe for La$_2$CuSnO$_6$ sintered at 1300 °C ................................................................. 214

Figure 5.11: Temperature dependence of magnetic susceptibility with H = 10 Oe for La$_2$CuSnO$_6$ sintered at 1400 °C ................................................................. 214

Figure 5.12: Temperature dependence of magnetic susceptibility with H = 10 Oe for La$_2$CuSn$_{0.9}$In$_{0.1}$O$_6$ sintered at 1350 °C. No diamagnetism is visible. ...... 216

Figure B.1: Simple cubic ................................................................. 233

Figure B.2: Body-centered cubic ................................................................. 233

Figure B.3: Face-centered cubic ................................................................. 233

Figure B.4: Hexagonal ................................................................. 234

Figure B.5: Simple tetragonal ................................................................. 234
Figure B.6: Body-centered tetragonal ................................................................. 234
Figure B.7: Rhombohedral ................................................................................. 234
Figure B.8: Simple orthorhombic ................................................................. 235
Figure B.9: Base-centered orthorhombic ................................................................. 235
Figure B.10: Body-centered orthorhombic ................................................................. 235
Figure B.11: Face-centered orthorhombic ................................................................. 236
Figure B.12: Simple monoclinic ................................................................................. 236
Figure B.13: Base-centered monoclinic ................................................................. 236
Figure B.14: Triclinic .................................................................................. 236
Figure B.15: Block diagram of x-ray diffractometer ........................................ 251
Figure C.1: Block diagram of SQUID cryostat .................................................. 273
Figure C.2: Longitudinal SQUID System Schematic ........................................... 276
Figure C.3: Schematic view of an rf SQUID ....................................................... 283
Figure C.4: Total flux $\Phi$ through an rf SQUID loop versus the applied flux $\Phi_a$. The hysteresis loops remove energy from the LC tank circuit. ...................... 286
Figure C.5: rf SQUID current-voltage for two different values of input flux ...... 288
Figure C.6: Dependence of output rf voltage $V_0$ on the applied flux $\Phi_a$ ........ 289
Figure E.1: Block diagram of example ESR spectrometer .............................. 317
ACKNOWLEDGMENTS

Two faculty in my academic history deserve special recognition, for without them I never would have discovered my career calling. My undergraduate research advisor, Dr. Nancy M. Haegel, opened my eyes to a career in science, and my thesis advisor, Dr. Howard A. Blackstead, developed me into a scientist. I owe these two very much.

The staff of the Dept. of Physics at Notre Dame have watched over me with much care over the last six years, and without their help and support my professional education would have been much harder; they deserve much more credit than I feel they ever get.

Much of my work would not have been possible without cooperation from collaborators and colleagues both at the University of Notre Dame, and at the University of Missouri. Dr. William Yelon's group at Missouri, including Dr. Q. Cai and Mr. J. Lamsal, have been helpful. My collaborators at Notre Dame, notably Dr. J. Densmore and Dr. M. Kornecki as well as Mr. B. Benapfl, were of great help. I must also acknowledge Dr. Paul McGinn and Dr. Alexander Mukasyan of the Dept. of Chemical and Biomolecular Engineering at Notre Dame for scientific advice and equipment use.

Additionally I must acknowledge all of my friends both in and out of the field of physics who have acted as sounding boards for new ideas, or as sources of comfort for failed ideas; there are too many names to list.
CHAPTER 1: 
INTRODUCTION

1.1 Motivation

Almost 25 years following the discovery of high-temperature superconductivity, there still exists no generalized theory describing this remarkable effect. This is in part due to the magnitude of the problem, but may also in part be due to the lack of variety in known superconducting systems. Since the late 1990's, new superconducting families exhibiting simultaneous superconductivity and bulk magnetic order have been discovered that defy the conventional (but incomplete) understanding of HTSC's which is based on CuO\(_2\) planar superconductivity. This work details further discovery, investigation, and characterization of some of these materials. An understanding of the most complicated systems that demonstrate superconductivity will be essential to an ultimate understanding of the mechanism or perhaps mechanisms of high-temperature superconductivity.
1.2 A Short History of Superconductivity

It was not until the BCS theory [13] in 1957 that an adequate theoretical picture of the superconductivity was accepted. This BCS theoretical description of superconductivity suggested a low limit (~30 K) to the highest possible superconducting temperature in any material due to the relative weakness of the electron-phonon coupling interaction, and for nearly 40 years, this theoretical prediction was accurate. In 1986, Bednorz and Muller [16] discovered superconductivity in Sr-doped La$_2$CuO$_4$ at 35 K, which was 12 K higher than a nearly 15 year old record temperature, and more importantly, was above the maximum critical temperature allowed by BCS theory.

This discovery generated enormous interest in the field, and Bednorz and Muller were awarded the 1987 Nobel prize, in less than a year following their discovery. Shortly after this discovery of the first cuprate superconductor, M.K. Wu et al. [141] found that the material YBa$_2$Cu$_3$O$_7$, a variation on La$_2$CuO$_4$, was a superconductor with $T_c$=93 K. Further experimentation with different variations on La$_2$CuO$_4$’s structure continued to generate additional superconductors, with the record temperature at ambient pressure of $T_c$=138 K. Despite the great success of experimental work in discovering new superconductors, the theoretical picture did not make great strides, and nearly 25 years later, still is incomplete.

Currently, the question of the mechanism of carrier pairing in the high-temperature superconductors is open. There are many theories, but none encompass all known superconducting materials, and some have very limited applicability; the discovery of magnetically ordered materials that are also superconducting [17,45,140]...
has opened up a new avenue of investigation that may lead to a better understanding of the mechanism behind high-temperature superconductivity, as these materials do not fit with most proposed theories.

1.3 Outline of Thesis

This work details investigations into four classes of materials: Ln$_{2}$Cs$_{x}$Sr$_{2}$Cu$_{2}$RuO$_{10}$, LnSr$_{2}$CuRuO$_{8}$, Ba$_{2}$LnRuO$_{6}$, and La$_{2}$CuMO$_{6}$ (Ln=Y, Ln and M=Ru, Ir, Sn, Ti, Nb). The first two families of material are known as ferromagnetic superconductors in the literature due to their unusual magnetic behavior, and these are discussed in Chapter 2. There has been controversy over superconductivity in the third family of material, Ba$_{2}$LnRuO$_{6}$; the magnetism and superconductivity of the material family is discussed in Chapter 3. Chapter 4 describes the synthesis and characterization of substantially higher-quality La$_{2}$CuRuO$_{6}$ than is known in the literature, and several attempts to dope the material in order to find superconductivity. Chapter 5 describes the synthesis and characterization of several other materials in the La$_{2}$CuMO$_{6}$ family as well as attempts to find superconductivity.

Chapter 6 discusses a summary of the results and features common to all of the classes of materials. Appendices A-E contain a condensed theoretical background on the experimental techniques used, as well as descriptions of equipment and experimental procedures. Appendix A discusses sample preparation. Appendix B discusses structural
analysis via powder x-ray diffraction as well as powder neutron diffraction. Appendix C
discusses magnetism, magnetic order, superconductivity, and SQUID magnetometry.
Appendix D describes resistivity measurements. Appendix E discusses electron spin
resonance and microwave spectrometers.
2.1 Background

With the discovery of superconductivity in the La$_2$CuO$_4$ system by Bednorz and Muller in 1986 [16], the field of superconductivity was changed forever. Prior to this, superconductivity was limited to low temperature systems, and was adequately explained by the famous BCS model [13] of electron pairing. Shortly after the discovery of superconductivity in the La$_2$CuO$_4$ family, Wu [141] found that yttrium substitution led to a transition temperature above 90 K; they had discovered YBa$_2$Cu$_3$O$_7$, the first material to superconduct above the temperature of liquid nitrogen. Following this breakthrough, there was a veritable gold rush of discovery, with different groups investigating variations on and substitutions in the chemical structures of the O$_4$ and O$_7$ structures. Two key facts gradually arose: stacked CuO$_2$ planar structures were common to all, and magnetic ions could be substituted into some, but not all, crystal sites without decreasing the transition temperature. Development has continued in this field to the present day where there are materials with $T_c$ above 150 K. A coherent explanation of the mechanism, however, still eludes theorists and experimentalists alike.
Hundreds, if not thousands, of variations were tried, and several related classes of compounds were discovered, typically involving adding additional chemical layers to the $O_7$ crystal structure. It was not until the realization that RuO$_2$ layers have the same oxygen coordination and have a comparable bond length to the CuO$_2$ layers prevalent in the high-$T_c$'s that the ruthenocuprates and their derivatives were first investigated; materials with alternating RuO$_2$ and CuO$_2$ layers were possible. Initial work had startling results: the materials are magnetically ordered, then become superconducting while remaining magnetically ordered.

Magnetic order in the high-$T_c$'s is uncommon, but not exceptional; materials such as RNi$_2$B$_2$C order antiferromagnetically at temperatures of a fraction of $T_c$; also, in LnBa$_2$Cu$_3$O$_7$, the rare earth site orders antiferromagnetically at ~2 K, independent of choice of magnetic lanthanide. This antiferromagnetic order coexists with superconductivity, with no detrimental effect; evidence has suggested over the last 20 years that this is possible as the ordered layers are spatially separated from the superconducting layers. Prior to the discovery of the ruthenocuprates, there were no known high-temperature superconducting materials that exhibited magnetic order and superconductivity at the same time, with the onset of magnetic order at a temperature above that of the onset of superconductivity.

The materials Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ and Eu$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ were the first ruthenocuprates synthesized to show both magnetic order and superconductivity [45] and followed the successful synthesis of superconducting Nd$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$NbO$_{10}$ [34]. The difference between the ruthenium material and the niobium material is the lack of
magnetic order due to the replacement of magnetic ruthenium with nonmagnetic niobium. The O$_{10}$ class of materials differ from the stacked YBCO structure by replacing the yttrium oxide layer with a fluorite-type layer of Ln$_{1.5}$Ce$_{0.5}$O$_2$, shifting alternating layers by $(a+b)/2$ in the unit cell (Figure 2.1), and replacing one of the now-distinct copper oxide layers with a different metal oxide layer.
Figure 2.1: One half of the unit cell of superconducting \( \text{Gd}_{2-x}\text{Ce}_x\text{Sr}_2\text{Cu}_2\text{RuO}_{10} \). CuO\(_2\) planes are shifted by one half of a unit cell in the ab-plane across the fluorite-like rare earth layer.
The materials exhibit different types of magnetization when cooled in a magnetic field versus when cooled in zero magnetic field (Figure 2.2), acting antiferromagnetically when zero field-cooled ("ZFC", a magnetization measurement performed with the sample cooled in no applied field) and ferromagnetically when field-cooled ("FC", a magnetization measurement performed with the sample cooled in an applied field), as well as ferromagnetically in a field-cooled warming or remnant magnetization ("FCW", a measurement performed in no applied field following field-cooling) and in each case becoming superconducting at a temperature below the magnetic ordering temperature. The difference between the field-cooled and field-cooled warming measurements is due to the lack of diamagnetism in the measurement with zero applied field; turning off the field means that no diamagnetism will be observed, but the ferromagnetic-like behavior will remain visible in zero applied field; thus, the susceptibility increases. The quicker dropoff of the field-cooled warming susceptibility is characteristic of a ferromagnet.

Preliminary reports by Mössbauer spectroscopy and magnetization measurements indicated weak ferromagnetic ordering of ruthenium [45], whereas later neutron diffraction measurements on Nd$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$RuO$_{10}$ [86] found no magnetic order, and extensive neutron diffraction measurements on the Eu homologue found no antiferromagnetic ruthenium and specifically excluded ferromagnetic ruthenium [90]. The origins of this “apparent ferromagnetism”, this difference in magnetic state when field-cooled versus zero field-cooled, were not clear.
Another superconducting, magnetically ordered material first synthesized shortly after the discovery of the O\textsubscript{10} family was GdSr\textsubscript{2}Cu\textsubscript{2}RuO\textsubscript{8}, containing (Figure 2.3) bilayers of CuO\textsubscript{2} and monolayers of RuO\textsubscript{2} [17]. The structure of the O\textsubscript{8} family of materials is similar to the YBCO structure, with the chains of CuO replaced with RuO\textsubscript{2} planes.

Figure 2.2: Typical temperature dependence of magnetic susceptibility with $H=10$ Oe for superconducting $Y_{2-x}Ce_xSr_2Cu_2RuO_{10}$. The “apparent ferromagnetism” coexists with the superconductivity.
Figure 2.3: The unit cell of superconducting $\text{GdSr}_2\text{Cu}_2\text{RuO}_8$. The chain CuO layers in YBCO have been replaced with RuO$_2$ layers.
These materials were found to exhibit magnetic order well above the onset of superconductivity, with the magnetic order not affected by the onset of superconductivity. As in the O$_{10}$ materials, these O$_8$ materials show different types of magnetization when cooled in zero magnetic field versus when field-cooled; the “apparent ferromagnetism” occurs at a temperature well above the diamagnetic onset (Figure 2.4). Initial reports claimed ferromagnetic ruthenium order by means of muon spectroscopy [17]; however, later neutron diffraction measurements performed with isotopically selected Gd (to avoid the very large $^{157}$Gd neutron capture cross section [100] found only antiferromagnetic order; again, the origins of the “apparent ferromagnetism” were not clear, and high-resolution neutron diffraction results meant it could not directly be attributable to canting of ruthenium moments or other weak ferromagnetic arrangements. Investigations [19] over the last several years have conclusively shown the anomalous magnetization to have a very surprising source.
Polycrystalline samples of the \( \text{Ln}_{2-x} \text{Ce}_x \text{Sr}_2 \text{Cu}_2 \text{RuO}_{10} \) family of compounds may be prepared by a solid state chemical reaction at standard pressure as first described by Felner et al. [46]. The reaction may be written as

\[
(1-0.5x) \text{Gd}_2 \text{O}_3 + x \text{CeO}_2 + 2 \text{SrCO}_3 + 2 \text{CuO} + \text{RuO}_2 \rightarrow \text{Gd}_{2-x} \text{Ce}_x \text{Sr}_2 \text{Cu}_2 \text{RuO}_{10}
\]
(with Ln=Gd) where the excess carbon and oxygen is exhaust gas. The processing procedure follows the techniques outlined in Appendix A: precursor oxides and carbonates are dried at 300 °C prior to use, stoichiometric quantities are weighed out, and then thoroughly mixed in an agate mortar and pestle. The mixed material is then heated in an alumina crucible to 1000 °C and held for ~80 hours [34] with intermediate coolings and regrinds, then pressed into pellets and sintered at ~1100 °C in an alumina tube furnace under flowing O$_2$ gas for 60 hours. These parameters result in single-phase material and exhibit the largest superconducting volume fraction. The class of materials can be categorized as tetragonal with space group $I4/mmm$, and lattice parameters [10] are approximately $a=b=3.83$ Å and $c=28.39$ Å, with slight variations for different cerium concentrations and for different choices of Ln$^{3+}$ ion. Doping of the material is performed by the introduction of the Ce; adding Ce makes the material superconducting as the higher valence Ce$^{4+}$ provides holes; superconductivity only occurs for $x$ values between 0.4-0.8, and the highest $T_c$ is obtained for a Ce content of $x=0.6$ [104].

Magnetic order in the O$_{10}$ class of materials has been under debate since the discovery of superconductivity in the ruthenocuprates in 1997. The materials have been widely reported on in the literature [32,45,95,138]. Depending on sample quality, preparation technique, and oxygen concentration, the O$_{10}$ materials show a magnetic transition at 125-180 K as well as a superconducting onset at ~50 K. The nature of the magnetic transition depends on the type of measurement performed. When cooled in zero field (zero field-cooled), the transition is antiferromagnetic; when cooled in an applied field (field-cooled), the transition appears ferromagnetic—thus the rise of the
name, “apparent ferromagnetism”. With Ce doping outside the critical range, the magnetic behavior is identical, minus the observation of a diamagnetic transition. Shengelaya et al. [121] performed muon spectroscopy on the material with Ln=Eu, finding bulk homogenous magnetism and superconductivity coexisting. The ferromagnetic-like behavior of the materials below ~125-180 K has previously been attributed to canting of antiferromagnetically ordered ruthenium ions [104], and much work was done by several groups in attempts to confirm this; however, more recent investigations described in this work and elsewhere [19] has firmly established that the CuO$_2$ planes, and not the RuO$_2$ planes, are responsible for most of the observed metamagnetism or "apparent ferromagnetism".

Neutron diffraction data collected by Knee and Weller [80] on the $^{160}$Gd$_{1.3}$Ce$_{0.7}$Sr$_2$Cu$_2$RuO$_{10}$ compound did not identify any magnetic order above 40 K. Similar measurements performed by Kuz'micheva [86] on Nd$_{1.4}$Ce$_{0.6}$Sr$_2$Cu$_2$RuO$_{10}$ found no evidence for magnetic order down to 1.4 K. Neutron diffraction data collected on the SuperD2B instrument at ILL, Grenoble, by McLaughlin et al. [96] on the Nd$_{0.9}$Y$_{0.2}$Ce$_{0.2}$Sr$_2$Cu$_2$RuO$_{10}$ compound observed very weak intensity for the [0.5 0.5 0], [0.5 0.5 0.5] and [1.5 1.5 2] nuclear reflections, implying a doubling of the unit cell by antiferromagnetic order. Rietveld refinement indicates c-axis antiferromagnetic Ru order at ~140 K, and no canting of Ru order is observable. Even though the authors specifically eliminate Ru canting, they still claim it must be there to explain the magnetization measurements. Below 140 K, additional diffraction peaks from a [0.5 0.5 0.5] reflection can be fit with Ru c-axis antiferromagnetism; below 60 K, increased
intensity on the [0.5 0.5 0] is claimed as evidence of \textit{ab}-plane Cu antiferromagnetism, but the counting statistics are not high enough to resolve the [0.5 0.5 0] and [0.5 0.5 0.5] peaks, casting doubt on this interpretation. A reason for the wide disagreement between neutron diffraction experiments is the very long \textit{c}-axis, requiring very sensitive detection and low noise at low angles. Another, more easily solvable issue is the high neutron absorption cross-section of naturally abundant Eu, Gd, and Nd; replacing this with a nonmagnetic ion greatly facilitates structural analysis.

2.3 $Y_{1.5}Ce_{0.5}Sr_2Cu_2RuO_{10}$

Replacement of the Ln$^{3+}$ ion with nonmagnetic Y removes the issue of the large magnetic moments of the lanthanides. This compound does not form readily [95] at atmospheric pressures due to the size mismatch between Y and the Ln it replaces; a high temperature, high pressure process is required. Stoichiometric amounts of precursor chemicals are weighed out and mixed in an agate mortar and pestle set in a glove box under Ar atmosphere as per the chemical reaction

$$0.75 \ Y_2 \ O_3 + 0.5 \ CeO_2 + SrO_2 + SrCuO_2 + 0.75 \ CuO + 0.25 \ Cu + RuO_2 \rightarrow Y_{1.5}Ce_{0.5}Sr_2Cu_2RuO_{10}$$

with the Ar necessary to maintain the O$_{10}$ stoichiometry. To synthesize pellets, 500 mg of sample was loaded and sealed in a gold capsule, then heated to 1450 °C under 6 GPa of pressure, and held for 2 hours then cooled rapidly. The capsule showed no mass gain or loss implying no change in the oxygen stoichiometry. This processing procedure creates
a high-quality bulk O$_{10}$ phase with a few percent (at most) of unknown secondary phase.

The magnetization of the Y homologue is similar to that of the parent compound, without the large paramagnetism at lowest temperatures. SQUID magnetization data collected at 10 Oe (Figure 2.5) show a diamagnetic transition at \(\sim 40\) K, going net diamagnetic at \(\sim 32\) K. There is an additional magnetic transition at \(\sim 100\) K; once again, the nature of the transition depends on the type of measurement performed. In a zero field-cooled measurement, the transition is antiferromagnetic; in a field-cooled measurement, the transition is ferromagnetic. No additional magnetic transitions were observed in fields up to 7 T for temperatures up to 400 K, and a fit to high field data yield an effective moment of 0.857 \(\mu_B\), too small to be Ru but a reasonable value for two Cu moments, implying ferromagnetic exchange dominating the Cu-Cu interactions, and a Weiss \(\theta\) for the Ru that is sufficiently large to suppress its contribution to the paramagnetism. Interestingly, in the field-cooled data, the magnetization does not decrease at \(T_C\); instead, there is a slight increase. The field-cooled warming, or remnant magnetization, data are larger than the field-cooled data below \(T_C\), indicating superconducting behavior as removing the field increases the magnetization due to diamagnetism no longer is present.
Neutron diffraction experiments conducted by collaborators at the University of Missouri (Figure 2.6) performed at 16 K confirm the structure as tetragonal with very similar lattice parameters to published values. Additional scattering not seen at room temperature at ~16° is either due to scattering at [0.5 0.5 0] or [0.5 0.5 0.5]; due to the long c-axis in the material, it was not possible to unambiguously index the peak. Rietveld refinement indicates c-axis Ru antiferromagnetic order, but with adjacent RuO$_2$ layers not coupled; this is likely due to the addition of the fluorite block. The addition of the (Y,Ce)$_2$O$_2$ block causes a large increase of the superexchange path due to the substantial increase in planar separation, as well as geometric frustration as the Ru ion

Figure 2.5: Temperature dependence of magnetic susceptibility for Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$RuO$_{10}$ with $H=10$ Oe

Neutron diffraction experiments conducted by collaborators at the University of Missouri (Figure 2.6) performed at 16 K confirm the structure as tetragonal with very similar lattice parameters to published values. Additional scattering not seen at room temperature at ~16° is either due to scattering at [0.5 0.5 0] or [0.5 0.5 0.5]; due to the long c-axis in the material, it was not possible to unambiguously index the peak. Rietveld refinement indicates c-axis Ru antiferromagnetic order, but with adjacent RuO$_2$ layers not coupled; this is likely due to the addition of the fluorite block. The addition of the (Y,Ce)$_2$O$_2$ block causes a large increase of the superexchange path due to the substantial increase in planar separation, as well as geometric frustration as the Ru ion
sites are shifted by \((a/2, a/2)\) in nearest-neighbor RuO\(_2\) planes. Surprisingly, the ~16° peak persists nearly to, or perhaps above, room temperature; counting statistics above 225 K are not high enough to accurately determine the temperature at which this nuclear reflection disappears; however, the implication that Ru antiferromagnetic order persists until above 225 K cannot be overlooked. No change in magnetic scattering was observed near ~100 K, the temperature at which a magnetic ordering was clearly observed in SQUID magnetization data. If this transition were due to antiferromagnetically ordered RuO\(_2\) planes coupling antiferromagnetically across the unit cell, the nuclear reflection at ~16° would dramatically change in intensity, and other low-angle nuclear peaks would increase in intensity; this is not observed. Ferromagnetic RuO\(_2\) planes stacking antiferromagnetically at this temperature is unlikely and is not supported by neutron diffraction in this material nor in diffraction data on all variations of the Ln parent compound. As only minor enhancements of the intensities of nuclear reflections is observed, only two possibilities exist, both requiring magnetic order of the four CuO\(_2\) planes per unit cell: either adjacent CuO\(_2\) layers order ferromagnetically in-plane and stack antiferromagnetically at ~100 K, or adjacent ferromagnetically in-plane ordered CuO\(_2\) layers stack ferromagnetically with the nearest neighbor plane, but couple antiferromagnetically with the other pair of CuO\(_2\) planes in the unit cell with the \(c\)-axis coupling starting at ~100 K. Other combinations of magnetic ordering would double the magnetic unit cell, and as such, would be visible via neutron diffraction. The diffraction data also indicate the presence of an impurity phase consisting of a few percent of the bulk sample; this could not be indexed as due to SrRuO\(_3\) or other known magnetically
ordered compounds formable from the precursor chemicals. SQUID magnetization studies performed on nonsuperconducting samples of the same material indicate distinguishable magnetic transitions that may be directly attributable to Cu planar ordering and layer coupling.

![Figure 2.6: Powder neutron diffraction at 16 K and Rietveld refinement on $Y_{1.5}Ce_{0.5}Sr_2Cu_2RuO_{10}$. The fit is in good agreement with ferromagnetic in-planar order, stacked antiferromagnetically.](image)

Thorough electron spin resonance data measurements using custom microwave spectrometers on polycrystalline samples of $Y_{1.5}Ce_{0.5}Sr_2Cu_2RuO_{10}$ support a complex magnetic model. Swapping Y for Gd in the material removes the issue of well-characterized Gd paramagnetic resonance [100]. Extensive electron spin resonance (ESR) studies have been performed that verify that Ru$^{5+}$ ions in octahedral coordination
are ESR silent [20]; thus any ESR signal observed must be due to Cu magnetism or superconductivity. With the sample at the bottom of a rectangular TE_{101} ESR spectrometer cavity, measurements were performed with both $H_{rf}$ perpendicular to $H_{dc}$ and $H_{rf}$ parallel to $H_{dc}$; measuring magnetic resonances in both angular configurations allows for characterization of magnetic ordering. Perpendicular fields allows excitation of paramagnetic, ferromagnetic, weakly ferromagnetic and antiferromagnetic resonance modes; parallel fields only allows excitations of weakly ferromagnetic and antiferromagnetic resonance modes [132]. Thus, any resonance visible in both angular configurations must be antiferromagnetic or due to weak ferromagnetism which is essentially canted antiferromagnetism. A sample of DPPH (2,2-Diphenyl-1-Picrylhydrazyl) was also mounted on a side wall in the ESR cavity as a calibration marker, as it has a very narrow paramagnetic resonance linewidth and a well-known temperature dependent resonance intensity—this is standard in ESR spectroscopy. At 12.885 GHz ($K_u$ band), in data (Figure 2.7) with $H_{rf}$ perpendicular to $H_{dc}$, a resonance is observed at low fields peaking at ~90 K and rapidly diminishing above the magnetic ordering temperature of ~100 K as established by SQUID magnetometry. No resonant response was observed at higher temperatures. As $T_C$ is approached, microwave dissipation of the form $\sim H^{1/2}$, characteristic of a superconductor, is observed, dominating the response and steepest near $T_C$, as expected [130]. In data (Figure 2.8) with $H_{rf}$ parallel to $H_{dc}$, the data are much the same. The low-field resonant response still peaks at ~90 K, and the superconducting dissipation dominates the response at lowest temperatures. This confirms that the magnetic transition at ~100 K, not observed via neutron diffraction, is
antiferromagnetic in nature, as weak ferromagnetism would have been visible via neutron diffraction; canting of Ru moments away from c-axis antiferromagnetism would have enhanced existing diffraction peaks, and no corresponding increase in the diffraction intensities is observed. Increasing the frequency to 20.3 GHz (K band) will raise magnetic resonances to higher peak fields to match the increased photon energy. In ESR data (Figure 2.9, Figure 2.10) at this higher frequency, the same features are observed: a low field magnetic resonance peaking at ~90 K is visible in both angular configurations, and dominant superconducting dissipation of form \( \sim H^{1/2} \) is visible below \( T_c \). Further increasing the frequency to 35.27 GHz (Figure 2.11, Figure 2.12) (R band) shows the same effects, with the low field magnetic resonance at the same temperatures visible in both angular configurations. An additional feature perhaps evident at ~8000 Oe is not statistically significant compared to background drift to consider as an actual signal.

From this resonance data, it must be concluded that the Cu is antiferromagnetically ordered, and based on the neutron diffraction data, the Cu must be ordered ferromagnetically in layers with adjacent layers coupling antiferromagnetically, or adjacent pairs coupling ferromagnetically with each other and coupling antiferromagnetically with the other two \( \text{CuO}_2 \) planes in the unit cell. However, this argument partially relies on the electronic environment of the Ru ions being similar to comparable compounds that show no ESR response; replacing the magnetic Ru with a nonmagnetic ion would remove this issue.
Figure 2.7: Magnetic resonance at 12.885 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting $Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}RuO_{10}$
Figure 2.8: Magnetic resonance at 12.885 GHz with $H_{rf}$ parallel to $H_{dc}$ in superconducting $Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}RuO_{10}$
Figure 2.9: Magnetic resonance at 20.3 GHz with $H_r$ perpendicular to $H_{dc}$ in superconducting $Y_{1.5}Ce_{0.5}Sr_2Cu_2RuO_{10}$
Figure 2.10: Magnetic resonance at 20.3 GHz with $H_f$ parallel to $H_{dc}$ in superconducting $Y_{1.3}Ce_{0.5}Sr_2Cu_2RuO_{10}$
Figure 2.11: Magnetic resonance at 35.27 GHz with $H_{\text{rf}}$ perpendicular to $H_{\text{dc}}$ in superconducting $Y_{1.5}\text{Ce}_0.5\text{Sr}_2\text{Cu}_2\text{RuO}_{10}$
The material \( Y_{1.5}Ce_{0.5}SrCu_{2}NbO_{10} \) is a homologue of the \( Ln_{1.5}Ce_{0.5}SrCu_{2}RuO_{10} \) family of materials with nonmagnetic \( Nb^{5+} \) replacing \( Ru^{5+} \), and nonmagnetic \( Y^{3+} \) replacing the magnetic lanthanide. Thus in this material, Cu is the only magnetic ion as \( Ce^{4+} \) and \( Sr^{2+} \) are nonmagnetic as well (as both have closed-shell electron configurations).

Figure 2.12: Magnetic resonance at 35.27 GHz with \( H_{rf} \) parallel to \( H_{dc} \) in superconducting \( Y_{1.5}Ce_{0.5}SrCu_{2}RuO_{10} \)
This material cannot be synthesized at atmospheric pressure, due to ion size mismatch causing too much lattice strain. As such, it must be synthesized via a high temperature, high pressure method. There are no published accounts of prior synthesis of this compound. Precursor chemicals as per the formula

\[
0.75 Y_2O_3 + 0.5 CeO_2 + 0.25 SrO_2 + 1.75 SrCuO_2 + 0.25 CuO + 0.5 Nb_2O_5 \rightarrow Y_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}
\]

were mixed in an agate mortar and pestle in a glove box under Ar gas to preserve the oxygen stoichiometry. 500 mg of sample was sealed in a gold capsule and then heated to 1450 °C under 6 GPa of pressure, and held for 2 hours then cooled rapidly. The capsule showed no mass gain or loss implying no change in the oxygen stoichiometry. This method produced largely single phase material, with an 11% impurity phase identified by neutron diffraction as the nonmagnetic compound SrNbO$_3$. An additional low concentration impurity is evident but has not been successfully identified.

The magnetic behavior of the Y-Nb material has features common to the O$_{10}$ family. The compound Nd$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$NbO$_{10}$ was first synthesized by Cava et al. [34] and was found to be superconducting at 28 K; however, the authors did not report observation of the “apparent ferromagnetism” evident in the Ru homologues. The Y-Nb material differs from this compound only by virtue of Y instead of Nd, and shows a diamagnetic transition at almost the same temperature, ~27.5 K; the Y-Nb material, however, clearly shows the “apparent ferromagnetism” common to the parent ruthenocuprate. As was the case in the parent compound, the magnetic transition at ~27.5 K is different depending on the type of SQUID magnetization measurement performed. In a zero field-cooled measurement (Figure 2.13), the transition is superconducting and
the sample becomes diamagnetic; in a field-cooled measurement, the transition appears superconducting. There is an additional transition at ~19 K, where the zero field-cooled magnetization becomes more negative, and the field-cooled and field-cooled warming (or remnant magnetization) data diverge. In addition, careful measurements at higher temperatures (Figure 2.14) have shown an additional transition occurring at 273 K, an order of magnitude larger than the other transition temperatures in the material. A comparable transition was extensively searched for in the Y-Ru homologue but has not yet been concretely identified. The field-cooled warming measurement shows small remnant magnetization persisting to this near room temperature transition, indicating that the transition is ferromagnetic (as an antiferromagnet traps no flux).

Figure 2.13: Temperature dependence of magnetic susceptibility for superconducting $Y_{1.5}Ce_{0.5}Sr_{2}Cu_{2}NbO_{10}$ with $H=10$ Oe
Extensive field-dependent magnetization data (Figure 2.15) at different temperatures show no evidence for the high-field saturation characteristic of ferromagnets in fields up to 7 T, but do show metamagnetic behavior for all temperatures studied up to 300 K. The implications of this are not clear. If there is a ferromagnetic ordering of the CuO$_2$ planes at ~273 K, above this temperature only linear, paramagnetic field dependence should be observable, and below this temperature, ferromagnetic saturation should be observable. The origin of this metamagnetic behavior at room temperature is not understood.

Figure 2.14: Expansion of temperature dependence of magnetic susceptibility for superconducting Y$_{1.5}$Ce$_{0.5}$Sr$_{2}$Cu$_{2}$NbO$_{10}$ with H=10 Oe. A magnetic transition is visible at 273 K. The diamagnetism and ferromagnetism rapidly go off-scale below 27.5 K.
Neutron diffraction measurements carried out at 16 K by collaborators at the University of Missouri show scattering peaks arising solely from nuclear scattering. This rules out magnetic structures that involve doubling of the unit cell such as simple antiferromagnetism. High statistics data taken over the low angle region at a variety of temperatures show only minimal change in diffraction peak intensities; there is no significant change in the diffraction profile at any of the transition temperatures in the material. As simple antiferromagnetism is excluded, two possibilities remain for the magnetic order of the 4 CuO$_2$ planes per unit cell: adjacent CuO$_2$ layers ordered
ferromagnetically and stacked antiferromagnetically, and adjacent CuO$_2$ layers ordered ferromagnetically and stacked in ferromagnetic pairs coupling antiferromagnetically with the other pair of CuO$_2$ planes in the unit cell. These combinations of ferromagnetism and antiferromagnetic stacking would only generate small intensity increases at the diffraction peaks due to the crystalline structure and are difficult to resolve. It is likely that the \( \sim 273 \) K transition corresponds with in-plane Cu ferromagnetic ordering, the adjacent CuO$_2$ planes couple either ferromagnetically or antiferromagnetically at \( T_c \) of \( \sim 27.5 \) K, and the sets of planes couple antiferromagnetically at 19 K. The increase in diamagnetism at 19 K can then be explained as a decrease in magnetization due to antiferromagnetic ordering; thus the net magnetization becomes more negative. The conclusion must be that Cu is responsible for the magnetism observed in the material, and the ordering is complex.

Electron spin resonance measurements also support Cu magnetic order. Removing the Ln and the Ru from the parent compound removes any possibility of other ions resonating, and as such, any magnetic resonances in the Y-Nb material must be due to magnetically ordered Cu ions. Measurements performed at 20.3 GHz (Figure 2.16, Figure 2.17) demonstrate two magnetic resonances. A sample of DPPH was placed on a cavity sidewall as a calibration marker. With \( H_{rf} \) perpendicular to \( H_{dc} \), a resonance centered at \( \sim 1000 \) Oe is observed starting at 24 K, peaking at \( \sim 17 \) K; an additional resonance, centered at a higher field of \( \sim 6400 \) Oe, then dominates below 10 K. No obvious superconducting dissipation \( \sim H^{1/2} \) was clearly observed, but slight signal may be masked by the large low-temperature resonance. The lack of clear observation of
superconductivity is likely due to exceeding $J_c$ in the material during the measurements. No microwave resonance, aside from a very small paramagnetic impurity, was observed at temperatures above 50 K. With $H_{rf}$ parallel to $H_{dc}$, only antiferromagnetic or weakly ferromagnetic modes are excitable; as the same resonances are observed at the same temperatures, these must be either antiferromagnetic or weakly ferromagnetic in origin. Superconducting dissipation is once again not clearly visible due to exceeding the critical current density in the sample. The resonance data thus clearly indicate magnetic ordering of the Cu ions, with the only consistent explanation being ferromagnetic CuO$_2$ planes coupling antiferromagnetically across the unit cell while the sample demonstrates superconductivity, as was the case in the Ru homologue where Mössbauer spectroscopy indicated bulk magnetic and bulk superconducting behavior [41,45]. Additional data collected at 35 GHz indicate similar behavior, but is substantially noisier and is omitted here.
Figure 2.16: Magnetic resonance at 20.3 GHz with $H_r$ perpendicular to $H_{dc}$ in superconducting $Y_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$
2.5 O\textsubscript{10} Family Conclusions

The data point to a consistent picture of magnetic structure across the Gd-Ru, Y-Ru, and Y-Nb-O\textsubscript{10} systems. The proposed model of magnetic order in the $Y_{1.5}Ce_{0.5}Sr_2Cu_2NbO_{10}$ is that the Cu ions order ferromagnetically at $\sim$273 K in the $ab$-plane; at a lower temperature, seemingly equal to the superconducting transition
temperature, nearest-neighbor ferromagnetically ordered planes start to interact antiferromagnetically across the fluorite \((Y,\text{Ce})_2\text{O}_2\) block layer, and at a lower temperature of \(\sim 17 \text{ K}\) the coupling between pairs of layers begins. The “apparent ferromagnetism” is caused by rotation of the pitch angle between CuO\(_2\) planes; canting of the Cu moments out of the \(ab\)-plane is excluded by neutron diffraction. There is a small but clear magnetic transition at \(\sim 273 \text{ K}\); this is ferromagnetic in nature and must be due to in-plane ferromagnetism of Cu. Two magnetic transitions that must be due to Cu spin reordering are observable, both below \(T_c\); these are most likely from ferromagnetic CuO\(_2\) planes stacking antiferromagnetically with each other. Other pictures are not consistent when SQUID magnetization, electron spin resonance, and neutron diffraction data are all taken into account. In the Y-Ru compound, the data also support ferromagnetic CuO\(_2\) layers stacked antiferromagnetically. The Ru moments are aligned along the \(c\)-axis antiferromagnetically, and may be so to nearly room temperature; however, no transitions were observable in high magnetic fields in the temperature range 100-350 K. The absence of obvious flux trapping above \(\sim 100 \text{ K}\) indicates that the CuO\(_2\) planes may order ferromagnetically in-plane at the same temperature they stack antiferromagnetically. The model also fits the data on the Gd-Ru material, with the origins of the “apparent ferromagnetism” in the entire class of materials being rotation about the \(c\)-axis of the direction of magnetization of the \(ab\)-planar ferromagnetic Cu ions, and having very little or nothing to do with the Ru ions. By several tests, the class of materials are bulk superconductors, and simultaneously bulk magnetically ordered, and it is the Cu ions that account for most of the interesting magnetic behavior.
Polycrystalline samples of the LnSr$_2$Cu$_2$RuO$_8$ family of compounds may be synthesized by conventional solid-state reaction as first performed by Bernhard [17]. The synthesis process is two-step to avoid creation of ferromagnetic SrRuO$_3$. Initially appropriate amounts of precursors are thoroughly mixed and decomposed at 960 °C in air. Then, following a regrind and densification, another heat treatment at 1010 °C in flowing nitrogen is performed. The first chemical reaction may be written as, in the case of Ln=Gd,

$$RuO_2 + 2SrCO_3 + 0.5Gd_2O_3 + 2CuO \rightarrow Sr_2GdRuO_6 + Cu_2O$$

This combination of Sr$_2$GdRuO$_6$ and Cu$_2$O is then reground and heated at 1050 °C in flowing oxygen, resulting in formation of single phase GdSr$_2$Cu$_2$RuO$_8$ as per x-ray diffraction analysis. The Ln=Gd material was the first synthesized, and has been investigated the most extensively; the material can only be formed at standard pressure for Ln = (Gd, Eu, Sm). The intermediate product Sr$_2$GdRuO$_6$ belongs to a very interesting class of double perovskite compounds of the form A$_2$BB'O$_6$ in which superconductivity has been observed, which is the focus of Chapter 3. Detailed measurements by Papageorgiou et al. [107] have shown that the magnetism is intrinsic to the bulk material and cannot be due to any Sr$_2$GdRuO$_6$ impurity. The compound GdSr$_2$Cu$_2$RuO$_8$ is tetragonal with space group $P4/mmm$ (Figure 2.3) and lattice parameters $a=b=3.839$ Å, $c=11.536$ Å [7], and substitution of the other lanthanides for Gd introduces a small, systematic variation in lattice parameters as a function of trivalent lanthanide radius as is the well-known case in the Ln123 family of materials. The actual
doping mechanism of these materials is still hotly debated [82,88,94,131] with many groups claiming a 50/50 mix of Ru$^{4+}$/Ru$^{5+}$ ions being key; however, Mössbauer [41] spectroscopy has recently shown unequivocally that the valence of the Ru ions in high-quality samples is 5+, eliminating the possibility of large amounts of Ru$^{4+}$ existing in samples. When formed stoichiometrically, the materials are charge-balanced insulators; most likely the doping is an issue of oxygenation, an idea still under investigation [38,62]. Magnetic order in the O$_8$ family is a contentious topic, as is in the case in the O$_{10}$ family. Neutron diffraction experiments are hampered by the large neutron absorption cross sections of naturally occurring Gd, Sm, and Eu [100].

When optimally formed, the materials show a magnetic transition near ~135 K, and show a superconducting transition as high as ~60 K; these materials have been quite thoroughly reported on in the literature [9,10,30,37,69,106,142]. The magnetic transition temperatures do depend on choice of synthesis parameters [49], and are the highest reported in the literature to date. The magnetic transition at 135 K is particularly interesting, as the nature of the magnetic ordering depends on if the sample was field-cooled or cooled in zero applied field. In a zero field-cooled SQUID magnetization measurement the material is antiferromagnetic; in a field-cooled measurement, the material is ferromagnetic. In both measurement types, the onset temperature of the diamagnetic transition is not affected; however, the net magnetization in the field-cooled measurement is less negative due to the offset of the ferromagnetic signal, and for increasing fields net negative magnetization may not be visible as the ferromagnetic-like component grows larger. The initially proposed magnetic structure by Bernhard et al.
that accounts for this magnetic behavior has the Ru ions aligned antiferromagnetically along the $c$-axis, with a canting into the $ab$-plane causing the ferromagnetic behavior, with the Cu not magnetically ordering. Bernhard makes the observation that muon spin rotation measurements indicate that the magnetic order is homogeneous on a microscopic scale and accounts for most of the sample volume; the material is explicitly not magnetically ordered in some grains and superconducting in others, the magnetic order and superconductivity occur throughout the material. More recent investigations [25,26,144] once again demonstrate though that the CuO$_2$ planes, and not the RuO$_2$ planes, are responsible for the metamagnetic behavior.

Neutron diffraction measurements on $^{160}$GdSr$_2$Cu$_2$RuO$_8$ by Chmaissem et al. [37] at IPNS at Argonne National Laboratory did not observe any magnetic scattering consistent with the initially proposed ferromagnetic canted ordering of Ru moments, seeing only $c$-axis Ru antiferromagnetic order, and set that the maximum ordered $ab$-plane ferromagnetic moment cannot be larger than $\sim$0.3 $\mu_B$. Chmaissem mentions that accuracy is limited mainly by the large background resulting from paramagnetic scattering from Gd spins. Neutron diffraction measurements performed by Takagiwa et al. [128] observe a [0.5 0.5 0.5] peak, suggesting $c$-axis antiferromagnetic Ru ordering, and also show a small increase in the intensity of the [001] peak; this only can be attributable to ferromagnetic order. Neutron diffraction measurements performed by Lynn et al. [90] at NIST is also inconsistent with the initially proposed ferromagnetic canted ordering of Ru moments, also seeing only $c$-axis Ru antiferromagnetic order. The NIST data set a maximum ferromagnetic Ru moment of 0.1 $\mu_B$; Lynn's interpretation after
extensive measurement with polarized beam measurements is that ferromagnetic canting of Ru spins may be dismissed. An interesting feature of Lynn's neutron diffraction data is that the [002] peak, corresponding to induced ferromagnetic Ru moments, is observed for applied fields under 0.4 T at 80 K. At fields above this value, the [0.5 0.5 0.5] peak (corresponding to antiferromagnetic order) decreases steadily and the [002] peak increases steadily, implying a collapse of the Ru antiferromagnetism. This would imply that canting of Ru moments is the cause of the “apparent ferromagnetism”, except that the apparent ferromagnetism is observed in SQUID magnetometry data in fields as small as 2.5 Oe. This strongly suggests that the Ru ions are not responsible for this weak ferromagnetic effect. Observation of \( ab \)-planar Cu magnetism is difficult due to the small moment of the Cu ion and the magnetic structure only enhancing existing neutron diffraction peaks, and not generating additional peaks below the ordering temperature.

Extensive electron spin resonance data collected in conjunction with J. Densmore on custom microwave spectrometers on large grain polycrystalline samples of GdSr\(_2\)Cu\(_2\)RuO\(_8\) further reinforce the notion that the Ru ions are not responsible for the weak ferromagnetism observed in SQUID magnetization data. The samples were very large grain polycrystals provided by C. Bernhard at the University of Fribourg, Switzerland. Measurements performed at three different microwave frequencies show interesting and consistent features. The presence of the \( l=0 \) Gd ion acts as a convenient reference and quality assurance, as the resonance of paramagnetic Gd is well understood [98]. At 13.2 GHz (K\(_u\) band), in data with \( H_{rf} \) perpendicular to \( H_{dc} \), the paramagnetic Gd resonance (Figure 2.18) peaking at ~4200 Oe dominates the response as temperature is
decreased, implying that the Gd does not magnetically order above the lowest temperature observed (10 K). The vertical scale is chosen as such to highlight the smaller features; if the entire Gd response was shown, the smaller features would not be visible. As temperature is decreased, the magnetization of paramagnetic Gd increases as $T^{-1}$, such that its resonance increases likewise. Again, a sample of DPPH was placed on the ESR cavity sidewall as a calibration marker. A second, smaller resonance is visible peaking near 0 Oe with a maximum intensity at 90 K. As $T_C$ is approached, power dissipation characteristic of superconductivity is observed, peaking just below $T_C$, with the paramagnetic Gd resonance superimposed over this. As investigations into magnetic resonance of Ru ions in octahedral coordination [30] has definitively demonstrated that octahedrally coordinated Ru is ESR-silent, this suggests that the resonance observed at low magnetic fields slightly below the magnetic ordering temperature of the material is related to Cu magnetic order and not Ru magnetic order. Examining the same sample with $H_{rf}$ parallel to $H_{dc}$ allows excitation of only antiferromagnetic and weakly ferromagnetic resonance modes. A small magnetic resonance (Figure 2.19) is still visible centered at ~4200 Oe; this is likely due to the extremely large crystal grains in the sample distorting the uniformity of $H_{rf}$ in the cavity, which could cause a small paramagnetic Gd resonance. The $H^{1/2}$ dissipation characteristic of a superconductor is again first observed at 50 K, comparable to the magnetic $T_C$ of the material. The low field resonance is again observed at temperatures near the magnetic ordering temperature of the sample; this thus must be antiferromagnetic, or at least, weakly ferromagnetic, Cu resonance as all other potential causes may be excluded. The same features are observed at 20.3 GHz (K band)
and 35.27 GHz (R band), with the resonant fields pushed higher in value to match the increase in photon energy. At 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ (Figure 2.20), the paramagnetic Gd response, now centered at ~6800 Oe, again dominates as temperature is decreased, but the superconducting $H^{1/2}$ dissipation is still visible near $T_C$, and the resonance attributable to magnetically ordered Cu stands out at low fields. With $H_{rf}$ parallel to $H_{dc}$ (Figure 2.21) the Gd resonance is almost entirely suppressed, the $H^{1/2}$ dissipation near $T_C$ increases, and the low field magnetic resonance is visible. At 35.27 GHz, with $H_{rf}$ perpendicular to $H_{dc}$ (Figure 2.22) the Gd resonance is pushed up to a peak value at ~12100 Oe, further separating it from the low-field resonance. This unfortunately masks some of the superconducting dissipation, but the $H^{1/2}$ behavior is still observable near $T_C$. At this higher frequency, the low-field resonance is clearly distinguishable from the background. With $H_{rf}$ parallel to $H_{dc}$ (Figure 2.23) the Gd resonance is again minimized and the $H^{1/2}$ behavior at lower temperatures is obvious; also, the low-field resonance is still clearly visible. The vertical scale in figures showing microwave resonance data measured at the same frequencies is identical. As superconducting dissipation goes as $(H^{1/2} / H_{C2})$, the dissipation should be largest near $T_C$, where $H_{C2}$ peaks. This multi-frequency observation of magnetic resonance in a material containing ESR-silent Ru strongly suggests that ordered Cu is responsible for the metamagnetic behavior of the material.
Figure 2.18: Magnetic resonance at 13.2 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting GdSr$_2$Cu$_2$RuO$_8$
Figure 2.19: Magnetic resonance at 13.2 GHz with $H_{rf}$ parallel to $H_{dc}$ in superconducting $GdSr_2Cu_2RuO_8$. 
Figure 2.20: Magnetic resonance at 20.3 GHz with $H_r$ perpendicular to $H_{dc}$ in superconducting $\text{GdSr}_2\text{Cu}_2\text{RuO}_8$
Figure 2.21: Magnetic resonance at 20.3 GHz with $H_r$ parallel to $H_{dc}$ in superconducting $GdSr_2Cu_2RuO_8$
Figure 2.22: Magnetic resonance at 35.27 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting GdSr$_2$Cu$_2$RuO$_8$. 
Figure 2.23: Magnetic resonance at 35.27 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting GdSr$_2$Cu$_2$RuO$_8$

2.7 YSr$_2$Cu$_2$RuO$_8$

Replacing the magnetic (and neutron-absorbing) Gd with nonmagnetic Y in the O8 materials has several advantages: neutron diffraction may be more easily performed as isotopically selected Y is not necessary, and the large paramagnetic moment of the Gd is no longer present, making ESR measurements as well as SQUID magnetization
measurements easier. As the Y homologue is not formable at standard pressure [143], it must be prepared via a high temperature, high pressure process undertaken by collaborators at the National Institute for Materials Science in Tsukuba, Japan. It was found that a small Cu excess was necessary to produce single phase material of high quality. Stoichiometric amounts of precursors as per the chemical formula

\[ 0.5 Y_2 O_3 + 0.5 SrO_2 + 1.5 SrCuO_2 + 0.6 CuO + 0.9 RuO_2 \rightarrow YSr_{2}Cu_{1.1}Ru_{0.9}O_{7.9} \]

which provides an oxygen concentration of exactly 7.9. The precursors were weighed out and mixed in an agate mortar in a glove box under an atmosphere of Ar to preserve the Oxygen content. An amount of 500 mg of ground material was sealed in a gold capsule, then processed at 6 GPa and 1450 °C for 2 hours and allowed to rapidly cool. Careful weighing before and after heat treatment allowed observation of no gain or loss in oxygen content due to the heat treatment. This procedure results in samples that are tetragonal with space group \( P4/mmm \), with lattice parameters \( a=b=3.818(1) \, \text{Å}, c=11.5222(3) \, \text{Å} \) [32], very similar to that of the parent Gd material.

SQUID Magnetization measurements (Figure 2.24) show the Y homologue to have similar magnetic behavior to the parent Gd material. The material has a diamagnetic onset with a \( T_C \) of \( \sim 45 \, \text{K} \), becoming net diamagnetic at \( \sim 25 \, \text{K} \). There is a magnetic transition at \( \sim 142 \, \text{K} \) that again depends on the type of measurement performed. In a zero field-cooled measurement, it is an antiferromagnetic transition; in a field-cooled measurement, it is strongly ferromagnetic. Extensive searches showed no evidence for any additional magnetic transitions for fields up to 7 T between \( \sim 150 \, \text{K} \) and 400 K. The diamagnetic transition temperature is not affected by cooling in a field, but the material
never becomes net diamagnetic in a field-cooled measurement. Perhaps most interesting is the field-cooled warming (or remnant magnetization) measurement. There is substantial flux trapping; this can be due to either superconductivity or ferromagnetism of some sort. The only way for the remnant magnetization to be *larger* than the field-cooled magnetization is that when the field is turned off, the diamagnetism no longer is observed—concrete evidence of superconductivity. This trapped flux persists to the magnetic transition temperature \( \sim 140 \text{ K} \), where the remnant magnetization then goes rapidly to zero; the material is superconducting and also ferromagnetic.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{temperature_dependence.pdf}
\caption{Temperature dependence of magnetic susceptibility for \( \text{YSr}_2\text{Cu}_2\text{Ru}_0.9\text{O}_7.9 \) with \( H=10 \text{ Oe} \)}
\end{figure}
Neutron diffraction measurements performed at the University of Missouri Research Reactor (MURR) with a wavelength of 1.4875 Å were used to determine the origins of the magnetization of this material. Partial data (Figure 2.25) covering the 2θ window of 9° to 29° were collected at a number of temperatures between 16 K and 150 K, and full spectra (Figure 2.26) covering 100° were taken at room temperature and at 16 K. Ten hour counting times were used for each measurement, much longer than typically employed, to provide much higher statistical accuracy of the final results. The low-angle data at several temperatures show the [0.5 0.5 0.5] and [0.5 0.5 1.5] nuclear reflections, which disappear near the magnetic transition at \(~142\) K, and the integrated intensities match well with a model of \(c\)-axis antiferromagnetically ordered Ru moments. Rietveld refinement on the neutron data performed by collaborators at the University of Missouri to a \(c\)-axis Ru antiferromagnetic model has a small residual at the [001] reflection, again suggesting some slight ferromagnetic component as the [001] reflection shares the periodicity of the crystal lattice. The Rietveld fit yields a magnetic Cu moment of \(~0.45\pm0.14\) \(\mu_B\); even higher counting times could increase the signal to noise ratio. Excluding the Ru as the source of this ferromagnetism leaves only the Cu to be responsible; the only structure that fits the data is ferromagnetic CuO\(_2\) planes, stacked antiferromagnetically. As there are two CuO\(_2\) planes per unit cell, this does not double the magnetic unit cell in the \(c\)-axis, and ferromagnetic planar order would not double the cell in the \(xy\)-plane.
Figure 2.25: Low-angle powder neutron diffraction at 16 K on $\text{YSr}_2\text{Cu}_{2.1}\text{Ru}_{0.9}\text{O}_{7.9}$. The refinement agrees well with ab-planar ferromagnetism stacked antiferromagnetically.
Figure 2.26: Full neutron diffraction and Rietveld fit for nuclear and magnetic reflections at 16 K on $\text{YSr}_2\text{Cu}_{2.1}\text{Ru}_{0.9}\text{O}_{7.9}$. The fit is in good agreement with the proposed model of ferromagnetic CuO$_2$ layers stacked antiferromagnetically.
Extensive electron spin resonance data collected on various polycrystalline samples provided by collaborators support the picture of ordered Cu planes coupled antiferromagnetically. As magnetic resonance attributable to Ru is not expected, observed magnetic resonances should be attributable to Cu ions. In data collected at 20.3 GHz (Figure 2.27) with $H_{rf}$ perpendicular to $H_{dc}$, there is a strong resonance observed peaking at 140 K, with a peak at a field of ~600 Oe. Once again, a sample of DPPH has been placed on a sidewall of the cavity as a calibration marker. The observation of the magnetic resonance is made substantially easier by having replaced Gd with Y in the material. At lowest temperatures, only very minor evidence of $H^{1/2}$ superconducting dissipation is visible; this is likely due to exceeding $J_c$ in a small sample. Other pieces of the same batch of sample consistently showed diamagnetic behavior via SQUID magnetometry. Comparing this resonance data to the same measurements (Figure 2.28) performed with $H_{rf}$ parallel to $H_{dc}$, which only allow excitations of antiferromagnetic or weakly ferromagnetic modes, shows consistent results: the low field resonance is still observed peaking near ~140 K. Slightly more superconducting dissipation is visible at lowest temperatures, which is to be expected with parallel fields [130]. As the Ru may be excluded as source of the resonance, the Cu must be magnetically ordered. The only picture consistent with the neutron diffraction, magnetization, and electron spin resonance data is that of Ru $c$-axis antiferromagnetic order, with $ab$-planar Cu ferromagnetism with adjacent CuO$_2$ planes stacked antiferromagnetically. It is easy to imagine that small applied fields rotates the Cu moments or tilts them out of the $ab$-plane, causing the “apparent ferromagnetism” observed in the magnetization data.
Figure 2.27: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in superconducting $\text{YSr}_2\text{Cu}_2\text{Ru}_0.8\text{O}_7$.
The next natural step is to remove the question of Ru magnetism altogether. The Nb homologue YSr$_2$Cu$_2$NbO$_8$ may only be formed via a high pressure and high temperature method due to ion size mismatch, as is the case in the Y$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$NbO$_{10}$ material and the YSr$_2$Cu$_2$RuO$_8$ material. Single-phase materials were prepared by V.P.S.
Awana at the National Physics Laboratory, New Delhi, India, under a pressure of 6 GPa and at a temperature of 1450 °C for two hours. The high-pressure anvil cell again requires the sample to be encased in a thin gold foil to prevent contact with the anvil plates and to prevent contamination entering or gas from escaping. The material was only single-phase when made with a Nb-poor starting stoichiometry, YSr$_2$Cu$_{2.1}$Nb$_{0.9}$O$_8$; nominal stoichiometric starting compositions result in secondary phase formation and off-site niobium. The appropriate chemical reaction may be written as

$$0.5 \text{Y}_2\text{O}_3 + 0.5 \text{SrO} + 1.5 \text{SrCuO}_2 + 0.15 \text{CuO} + 0.45 \text{Cu} + 0.45 \text{Nb}_2\text{O}_5 \rightarrow \text{YSr}_2\text{Cu}_{2.1}\text{Nb}_{0.9}\text{O}_8$$

which produces an oxygen concentration of exactly 8.0, as the sample is sealed against gas gain or loss. The material created by this procedure is single-phase, and is tetragonal with space group $P4/mmm$ with lattice parameters $a=b=3.8531(3)$ Å and $c=11.5471(8)$ Å, which is comparable to the ruthenium-based O$_8$'s (Figure 2.29).
Figure 2.29: The unit cell of superconducting YSr$_2$Cu$_2$NbO$_8$. The only difference from the Gd homologue is the lack of magnetic metal ions besides Cu.
SQUID magnetization measurements (Figure 2.30, Figure 2.31, Figure 2.32) in various fields on samples prepared by collaborators are very interesting. The material is superconducting with a $T_C$ of ~35 K, going fully diamagnetic at ~23 K. However; there is an additional magnetic transition at ~257 K, nearly a factor of two larger than any transition temperature in the Ru homologues. Measurements in fields up to 7 T to temperatures of 400 K show no additional magnetic transitions at higher temperatures. As is the case in the Ru homologues, the nature of the transition depends on the type of measurement performed. In a zero field-cooled measurement, the transition is antiferromagnetic; in a field-cooled measurement, it is ferromagnetic. There is an additional feature in this material not present in the Ru homologues. At $T_C$ in a field-cooled measurement, the diamagnetic transition appears to be either ferromagnetic with the diamagnetism eventually dominating at temperatures below ~16 K, or antiferromagnetic with $T_N$ of ~16 K. At lowest temperatures, a small paramagnetic upturn is visible; this is likely due to the small amount of Cu on Nb crystallographic sites. Examining the field-cooled warming or remnant magnetization data dismisses the suggestion that the ~16K transition is antiferromagnetic, as there is substantial trapped flux—an antiferromagnet will not remain magnetized in the absence of a field and thus does not trap flux. As was the case in the Y-Ru homologue, the remnant magnetization is larger than the field-cooled magnetization, which is clear evidence of diamagnetism. Above $T_C$, flux trapping persists until the magnetic transition at ~257 K, indicating ferromagnetism. As there is no other magnetic ion in the material besides Cu, the
“apparent ferromagnetism” must be attributable to a Cu magnetic order that is clearly antiferromagnetic but with ferromagnetic behaviors.

Figure 2.30: Temperature dependence of magnetic susceptibility for superconducting YSr$_2$Cu$_{2.1}$Nb$_{0.9}$O$_8$ with $H=10$ Oe. Transitions are visible at low and high temperature, indicating high temperature Cu magnetic order.
Figure 2.31: Temperature dependence of magnetic susceptibility for superconducting YSr$_2$Cu$_{2.1}$Nb$_{0.9}$O$_8$ with $H=100$ Oe. The magnetic transition at 257 K is more pronounced.
Neutron diffraction measurements again performed at the University of Missouri Research Reactor (MURR) with a wavelength of 1.4875 Å were used to determine the origins of the magnetization of this material. High-flux data were acquired at 16 K to perform structural analysis, and found no impurity phases to the 1% level. No evidence was found in the full data set for any doubling of the unit cell characteristic of antiferromagnetic order; measurements covering the low angle window with 10 times longer counting time were performed to check this and still found no evidence for antiferromagnetic order. The diffraction apparatus did not allow for observation at

\[ T \leq 63 \text{ K} \]

Figure 2.32: Temperature dependence of magnetic susceptibility for superconducting YSr$_2$Cu$_2$Nb$_{0.9}$O$_8$ with $H=1000$ Oe. The superconductivity can no longer screen the magnetism, and at lowest temperatures the antiferromagnetically stacked CuO$_2$ collapse into ferromagnetism.
sufficiently small angles for detection of enhancement of the [001] peak, so from neutron
diffraction alone it is not possible to uniquely assign ferromagnetism to the CuO$_2$ planes.

Extensive electron spin resonance data collected on polycrystalline samples
provided by V.P.S. Awana again support the picture of ferromagnetic Cu planes stacked
antiferromagnetically. With the sample placed at the bottom of a TE$_{101}$ microwave cavity
operating at 20.3 GHz, and with $H_{rf}$ perpendicular to $H_{dc}$, strong, continually increasing
resonance is observed (Figure 2.33) below $T_C$. A small paramagnetic resonance is
observed near ~6800 Oe, which is likely due to very small SrCuO$_2$ impurity. Again a
small sample of DPPH was placed inside the ESR cavity on a sidewall as a calibration
marker. No $H^{1/2}$ superconducting dissipation is observed, as was the case with the Y-Ru
homologue; again this may be due to exceeding $J_c$ in the material. Powder from the same
batch used in the ESR spectrometer cavity was also used for SQUID magnetometry
measurements, where net diamagnetism was consistently observed. No resonance was
observed for temperatures above 42 K; measurements near 250 K did not show any clear
responses. With the field rotated such that $H_{rf}$ is parallel to $H_{dc}$ (Figure 2.34), the
paramagnetic impurity resonance vanishes, but the low-field resonance is still
increasingly large below $T_C$. As this configuration only allows antiferromagnetic or
weakly ferromagnetic excitations, the large resonance must be either due to
antiferromagnetic order or weak ferromagnetism. Superconducting $H^{1/2}$ dissipation is
again not observed for the same reason as is the case with perpendicular fields. Once
again it is important to point out that the only magnetic ion in this compound is Cu; the
Cu must be responsible for the magnetic resonance, and must be responsible for the observed magnetism.

Figure 2.33: Magnetic resonance at 20.3 GHz with \( H_{\text{rf}} \) perpendicular to \( H_{\text{dc}} \) in superconducting \( \text{YSr}_2\text{Cu}_2\text{Nb}_0.9\text{O}_8 \).
2.9 O₈ Family Conclusions

The data point to a consistent picture of magnetic structure across the Gd-Ru, Y-Ru, and Y-Nb-O₈ systems as was the case in the O₁₀ family. The proposed model of magnetic order in the YSr₂Cu₂NbO₈ material is that the Cu ions order ferromagnetically at ~257 K in the ab-plane; at a lower temperature, interestingly equal to the

Figure 2.34: Magnetic resonance at 20.3 GHz with Hᵣ平行 to Hᵣc in superconducting YSr₂Cu₂₁Nb₉₉O₈
superconducting transition temperature, the ferromagnetically ordered planes start to interact across the Y layer, stacking antiferromagnetically. This suggests a connection between the magnetic state and the superconducting state, giving possible insight as to the pairing mechanism. The “apparent ferromagnetism” is caused by either rotation of the pitch angle between CuO$_2$ planes, or canting of the Cu moments out of the $ab$-plane. This is the only picture consistent with all data. Replacing nonmagnetic Nb with magnetic Ru changes the picture, but not dramatically. The Ru moments align antiferromagnetically along the $c$-axis, with nearest neighbors pointing in alternate directions at ~142 K, seemingly commensurate with the antiferromagnetic coupling of CuO$_2$ layers. Extensive searching via SQUID magnetometry was carried out to try to identify a magnetic transition at a high temperature, as was the case with the ~257 K transition in the Nb homologue; none was observable in fields up to 7 T. As no flux trapping occurs above ~142 K, it is most likely that the Cu ions order ferromagnetically in the $ab$-plane at the same temperature that the CuO$_2$ planes couple antiferromagnetically. The situation is the same in the Gd-Ru material, with the only difference being different transition temperatures. Just as was found to be the case in the $O_{10}$ family of materials, the $O_8$ family of materials are bulk superconductors and bulk magnetically ordered.

These materials, due to the multiple layers and very long $c$-axes and elaborate unit cells, are a very interesting proof of the coexistence of superconductivity and long-range magnetic order but are ultimately not very satisfying to many critics of so-called “magnetosuperconductors”, the class of magnetically ordered materials that are
simultaneously superconducting, and accurate theoretical descriptions are complicated by
the very long superexchange paths across the unit cells. As such, crystallographically
simpler structures would be nicer to study, but simpler structures are not found in the
layered ruthenocuprate oxides; the limiting structural forms of SrRuO$_3$, which is a
ferromagnet with $T_c$ of 162 K [35], and Sr$_2$RuO$_4$, which is the only known spin-triplet
superconductor [103] with $T_c$ of $\sim$1.5 K, do not demonstrate the coexisting
superconductivity and magnetic order that the ruthenocuprates do. A different class of
materials, however, does show these features, and has crystallographic similarities with
the ruthenocuprates: double perovskite ruthenate oxides.

68
CHAPTER 3:
MAGNETISM AND SUPERCONDUCTIVITY IN RUTHENATES

3.1 \( \text{Ba}_2\text{YRu}_{1-x}\text{Cu}_x\text{O}_6 \)

The discovery of superconductivity in the material \( \text{Sr}_2\text{YRu}_{1-x}\text{Cu}_x\text{O}_6 \) in 1996 by M.K. Wu \textit{et al.} \cite{139,140} generated a controversy. The \( x=0 \) undoped material is an antiferromagnetic insulator with transition temperature \( T_N=26 \) K. Doping the material with Cu yields superconductivity, but does \textit{not} destroy the antiferromagnetic order; this is the opposite of what occurs in the doping of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \). The compound \( \text{Sr}_2\text{YRu}_{1-x}\text{Cu}_x\text{O}_6 \) is both superconducting and magnetically ordered. In other compounds this is not a contentious issue, as the magnetic order and superconductivity have always been understood to occur in separate chemical layers; however, in this material, there are only two distinct chemical layers, \( \text{SrO} \) and \( \text{YRuO}_4 \), and there is no easy way around the issue of the interaction between magnetic order and superconducting pairing. Replacing Sr with Ba to form \( \text{Ba}_2\text{YRuO}_6 \) generates an antiferromagnetic compound with \( T_N=37 \) K, and doping this material with \( \sim10\% \) Cu on the Ru site causes superconductivity \cite{115} at \( \sim84 \) K \textit{without destroying the antiferromagnetism}. Although in a material \textit{without} \( \text{CuO}_2 \) planes, this \( T_c \) is comparable to that of \( \text{YBCO} \).
Extensive work over the last several years has solved several key problems in synthesis, and especially, repeatability of synthesis of superconducting samples, issues that other research groups have not solved. Independent production of comparable quality samples is one of the main reasons behind a years-old controversy [51] surrounding superconductivity in $\text{Ba}_2\text{YRu}_{1-x}\text{Cu}_x\text{O}_6$; the other is the observation that the compound contains Y, Ba, Cu, and O, the elemental ingredients of the well-known high-$T_c$ superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$. To synthesize the material, the precursor compounds must first be dried out immediately prior to usage, typically at $\sim 300 \, ^\circ\text{C}$. Then the precursor compounds are weighed out according to the standard solid state chemical reaction formula

$$2 \text{BaCO}_3 + 0.5 \text{Y}_2\text{O}_3 + (1-x)\text{RuO}_2 + x\text{CuO} \rightarrow \text{Ba}_2\text{YRu}_{1-x}\text{Cu}_x\text{O}_6$$

for arbitrary values of Cu doping $x$, and thoroughly mixed in a clean agate mortar and pestle. The limits on Cu solubility have been observed to be $\sim 20\%$ [21]; above this, and substantial secondary phase production occurs. The optimal doping concentration known is $\sim 15\%$; concentrations above this have yielded decreased superconducting volume fractions. The excess C is given off typically as CO$_2$ during heat treatment. This step, although appearing trivial, is essential; thorough grinding and mixing is vital at every step. Generally in materials synthesis, “longer is better” is the rule; however in the interest of expediency and usage of labor, the rule of 30 minutes per 4 grams of sample has been routinely adopted and yields consistent sample quality. As discussed in Appendix A, grinding is an acquired technique, and expert grinding is worth many more hours of novice grinding. A ball milling machine utilizing zirconia balls was also tried.
many times, but never produced samples as high in quality as those ground by hand. An ultra-high energy planetary ball milling machine at the University of Missouri was also repeatedly attempted, but samples ground in this machine were consistently inferior to even those ground in the simple ball milling machine. This is likely because mechanical grinding is *too energetic*; it is probable that when the (nonreactive) zirconia balls smash powder against the sidewalls of the grinding chamber, unwanted chemical reactions are induced, ruining the stoichiometry of the sample prior to any heat treatments in a furnace. As a result, mechanical milling was abandoned in favor of hand grinding of samples as a low-energy milling machine was not available. Following the mechanical grinding, the powder is placed in an alumina crucible with lid, and placed into a box furnace in atmosphere at 970 °C for 48 hours, quickly ramping up and cooling down. This step, known as calcination, burns out the carbon and begins the formation of product, observable by diffraction measurements. Vacuum calcination and calcination under N\textsubscript{2} gas have also been tried, but yielded inferior product (the vacuum calcination, a total failure: the CuO oxidized to CuO\textsubscript{2}). The calcined mixture is then again thoroughly ground; it must be repeatedly stressed that thorough mixing is vital to good product formation. The powder samples are then separated into 1 g batches, and densified under 10,000 PSI with a hydraulic press and 1 mm diameter cleaned stainless steel die. The densification squeezes air out and helps facilitate the sintering of isolated micrograins of material. Uniform stress during densification is important; higher mass pellets typically produce inferior product, and at some point the superconductivity is no longer observed in very large pellets. It is suspected that the small die does not stress very tall piles of
powder very uniformly, and this causes variations in the consistency of the material that
detrimentally affects the final product. The die is thoroughly cleaned with acetone prior
to use, and is lubricated with paraffin wax to ensure smooth motion. This wax is not a
contamination concern; at the processing temperatures used, organic materials will long
have since vaporized—paraffin wax has a boiling point of ~370 °C [75].

Several different methods of high-temperature processing have been tested. The
two largest challenges in processing this class of materials are the very high volatility of
Ru [65] at very high temperatures, and achieving site order between the Y$^{3+}$ and Ru$^{5+}$
ions. Unfortunately, these are mutually exclusive: very high temperatures have been
observed to be necessary to achieve the highest degree of Y-Ru site order, but very high
temperatures readily sublimates Ru out of the material. Thus, it is a contest to heat the
pressed pellets to as high a temperature as possible for as short a time as possible. This is
accomplished by placing a stack of 3 pressed pellets on a pile of unpressed (but calcined)
sample powder in an alumina boat, and placing the boat into a standard tube furnace. The
powder is to hinder diffusion and to prevent any reaction from occurring at the interface
of the pellet and the alumina boat. Pt foil was also used for the same purposes, but at
high temperatures the Pt reacts with the pellets in some unknown chemical reaction. No
systematic detrimental effect was observed, but with the cost of platinum foil, this
process was abandoned. Controlled amounts of various gases may be blown through the
tube during synthesis, and the best combinations of gas found so far is 70% Ar and 30%
O$_2$, mimicking atmosphere minus CO$_2$, water vapor, and N$_2$ gas. N$_2$ gas chemistry may
occur at very high temperatures, so nonreactive Ar is used. The best processing
procedure so far discovered is a quick ramp to 500 °C, a four hour ramp to 1450 °C, holding at 1450 °C for 12 hours, then a four hour ramp to 500 °C, and ambient cooling to room temperature. The tube is not opened, and thus the sample is not exposed to atmosphere, until completely cooled. The extensive data on sample quality versus processing parameters is not shown here as the investigation is ongoing; these parameters, however, seem to be optimal after dozens of experiments conducted over the last several years. Longer sintering times directly affect the Ru concentration; this has been verified by microprobe analysis performed by collaborators at the University of Missouri. Longer sintering times also lower the net diamagnetism observed in a material as well as yield secondary phases becoming visible in diffraction data. Alternative methods have been attempted to prevent Ru sublimation. BaO and BaO$_2$ were tried as precursors instead of carbonates, which should eliminate the need for the intermediate temperature processing step; however, these materials were always mechanically and magnetically inferior to those processed with BaCO$_3$. The “catbox” method involved burying the pellets completely in several grams of unpressed (but calcined) powder, thinking that diffusion through the powder would slow Ru sublimation, and allow longer sintering times; this only produced inferior samples. A sample prepared at Notre Dame was pressed at the University of North Dakota by K. Marasinghe at 7 GPa in a high pressure cell similar to the apparatus used in synthesis of YSr$_2$Cu$_{2.1}$Nb$_{0.9}$O$_8$ as discussed in Chapter 2.8. This sample was sintered as described above, and showed good superconducting properties but was inferior to samples pressed and sintered at Notre Dame. It is not currently clear why high pressure did not help produce a high-quality
sample. The best samples to date have been those prepared and sintered at Notre Dame as described above, with the center pellet of the stack of three typically chosen to cut samples out of for characterization. A more detailed survey of processing temperatures, times, and gas environments may produce higher quality material.

SQUID magnetization data (Figure 3.1) shows Ba$_2$YRu$_{0.85}$Cu$_{0.15}$O$_6$ to be fully superconducting, with a transition temperature of $\sim$85 K. The transition is unique in that it is extremely broad; typical superconducting transitions are as small as 1 K wide in well-formed Y123 [141] and 10 K wide in other well-known superconductors. There is no “apparent ferromagnetism” in this material, unlike in the ruthenocuprates; however, there are also no CuO$_2$ planes in this material. Data across a wide number of samples consistently shows superconductivity in zero field-cooled (ZFC) and field-cooled (FC) measurements as well as flux trapping persisting to $T_C$ in field-cooled warming (FCW) or remnant magnetization measurements. The magnitude of the magnetization strongly depends on sample quality. This statement sounds obvious, but other groups (M.K. Wu excepted) that could not consistently produce superconducting samples did not optimize their processing procedures as mentioned above; reports of failure to synthesize superconducting samples in the literature are usually quite unsurprising given the non-optimal parameters and techniques reported. Magnetization as a function of applied field at constant temperature shows no metamagnetic behavior in fields up to 7 T, unlike the ruthenocuprate materials; the Ru$^{5+}$ response is typical of an antiferromagnet, and interactions are too strong to allow canting even in large fields. Additional data indicate that magnetic Ru order coexists with superconductivity at temperatures below $T_{N,Ru}$. The
undoped parent compound, Ba$_2$YRuO$_6$, had been well studied as an example of geometrically frustrated magnetism prior to discovery of superconductivity in the material, and original magnetization data [1,15] is not reproduced here. The undoped compound has an antiferromagnetic transition at $T_N = 37$ K, visible in zero field-cooled and field-cooled measurements, and is directly attributable to the Ru moments. The data require a Weiss $\theta$ of $\sim 614$ K [20], implying very strong antiferromagnetic coupling between Ru$^{5+}$ ions. This antiferromagnetic transition is not visible in doped, superconducting samples; the diamagnetism entirely screens the magnetism of the ordered Ru$^{5+}$ moments. Any Cu magnetic order in the doped materials is likewise screened by diamagnetism. Neutron diffraction measurements have shown that the Ru$^{5+}$ ions are still ordered in the doped materials.
Neutron diffraction performed by collaborators at University of Missouri on several samples of Ba$_2$YRu$_{1-x}$Cu$_x$O$_6$ indicate an interesting magnetic structure. The crystal structure (Figure 3.2) is consistently observed to be “rock salt” face-centered cubic, with lattice parameter $a=8.3154$ Å a typically observed value in neutron diffraction experiments that is comparable to that in the literature [15,115]. This value is also consistent with multiple powder x-ray diffraction measurements. The material consists of only two chemical layers, YRuO$_4$ and BaO; XAFS measurements confirm the Ru to be in the 5+ oxidation state [97].

Figure 3.1: Temperature dependence of magnetic susceptibility for Ba$_2$YRu$_{0.85}$Cu$_{0.15}$O$_6$ with $H=10$ Oe. The Ru magnetic transition is screened by the diamagnetism.
Figure 3.2: Unit cell of $\text{Ba}_2\text{YRu}_{1-x}\text{Cu}_x\text{O}_6$. There are alternating, stacked layers of magnetic $\text{YRuO}_4$ and nonmagnetic $4\text{BaO}$. Good spatial arrangement of $\text{Y}$ and Ru is essential to superconductivity in the system.
The appearance of additional peaks in the neutron diffraction data below 40 K can be fit to high accuracy as originating from Ru magnetic structure. The data is consistent with the Ru ordered ferromagnetically in the $ab$-plane, with adjacent planes stacked antiferromagnetically. Low angle neutron diffraction data as a function of temperature (Figure 3.3) shows a very interesting feature: above the magnetic ordering temperature of the Ru$^{5+}$ ions, a very small but distinct diffraction peak is still observable at a magnetic-only scattering angle ($\sim 10^\circ$) until the superconducting transition temperature. This can be fit by Cu antiferromagnetic order of the same type as the Ru magnetic order (where ferromagnetic planes are stacked antiferromagnetically), setting in at the same temperature that the observed superconductivity does. The peak is broad and incommensurate, consistent with a spin-density wave. There is no observable evidence for distortion or canting away from ferromagnetic layers stacked antiferromagnetically, in either doped or undoped samples. Site occupancy is a major issue, and can be verified by Rietveld refinement of neutron diffraction. It has been repeatedly observed that doped but nonsuperconducting samples always have some degree of site disorder between the Y site and the Ru site, which are the B and B' sites in the double perovskite system $A_2BB'O_6$. Site disorder causes a deviation from the regular, rock salt structure that has nearest neighbor ions alternating between B and B'. Varying the spatial arrangement of ions will cause significant changes in the local magnetic environments and may in fact be a clue as to the pairing mechanism in this class of materials. The superconducting samples with the largest volume fraction of superconductor routinely have the least amount of site disorder; even a few percent site disorder seems to be crucial.
Figure 3.3: Low-angle neutron diffraction on $\text{Ba}_2\text{YRu}_{0.90}\text{Cu}_{0.10}\text{O}_6$. The $\sim 10^\circ$ scattering peak persists to at least 85 K, and is consistent with a spin-density wave. The green line serves as a guide to the eye.
Electron spin resonance data collected on a large number of samples of superconducting and nonsuperconducting Ba$_2$YRu$_{1-x}$Cu$_x$O$_6$ show interesting features. The undoped material, Ba$_2$YRuO$_6$, is ESR silent at all microwave frequencies tested (10-35 GHz), and this is apparently due to a large magnon energy gap associated with the Ru$^{5+}$ ions in octahedral coordination [20]. This makes the Cu-doped material a very sensitive test case for Cu resonance as well as superconducting $\sim\mathrm{H}^{1/2}$ dissipation. Data collected using a TE$_{101}$ cavity at 32.7 GHz (Figure 3.4, Figure 3.5) clearly show a magnetic resonance centered at $\sim$300 Oe with superimposed superconducting dissipation. The low field resonance is observable in both the configuration with $\mathbf{H}_{\text{rf}}$ parallel to $\mathbf{H}_{\text{dc}}$, and with $\mathbf{H}_{\text{rf}}$ perpendicular to $\mathbf{H}_{\text{dc}}$. This low field resonance persists to the transition temperature ($\sim$85 K) indicated by the neutron diffraction results, which is the same temperature as the diamagnetic transition. The unambiguous observation of magnetic resonance in both angular configurations leads to the conclusion that the Cu ions must be magnetically ordered, as the Ru is the only other magnetic ion in the material and is known to be ESR silent. As mentioned previously, magnetic resonance observable in both angular configurations requires the magnetic order to either be antiferromagnetic or weakly ferromagnetic. As the neutron diffraction data indicate Cu planar ferromagnetism stacked antiferromagnetically and not weak ferromagnetism, the origin of the magnetic resonance must be due to Cu antiferromagnetism. This is the first known case of a high temperature superconductor with magnetically ordered Cu that does not have CuO chains or CuO$_2$ planes: Cu dopant at 10-20% does not constitute a CuO$_2$ plane.
Figure 3.4: Low-field magnetic resonance at 32.7 GHz in Ba$_2$YRu$_{0.85}$Cu$_{0.15}$O$_6$ with $H_{rf}$ perpendicular to $H_{dc}$. At lowest temperatures, the low-field Cu resonance is visible against the superconducting dissipation.
The concern here though is in the materials themselves and not in a comprehensive theory of high temperature superconductivity. As this is no longer the only known high temperature superconductor without CuO$_2$ planes since the discovery [71] and characterization of the oxypnictide class of materials in the last few years, biased critics entrenched in the various theoretical approaches to YBCO and its derivatives should be prepared to yield ground. The processing difficulties referred to above have long been a stumbling block; with only two groups able to successfully

Figure 3.5: Low-field magnetic resonance at 32.7 GHz in Ba$_2$YRu$_{0.85}$Cu$_{0.15}$O$_6$ with $H_d$ parallel to $H_{dc}$. At lowest temperatures, the low-field Cu resonance is visible against the superconducting dissipation.

The concern here though is in the materials themselves and not in a comprehensive theory of high temperature superconductivity. As this is no longer the only known high temperature superconductor without CuO$_2$ planes since the discovery [71] and characterization of the oxypnictide class of materials in the last few years, biased critics entrenched in the various theoretical approaches to YBCO and its derivatives should be prepared to yield ground. The processing difficulties referred to above have long been a stumbling block; with only two groups able to successfully
synthesize superconducting Ba$_2$YRu$_{1-x}$Cu$_x$O$_6$ or its homologue Sr$_2$YRu$_{1-x}$Cu$_x$O$_6$, skepticism is understandable. Careful processing, however, continues to create superconducting samples; previous reports [51] invariably use far too low a sintering temperature and far too long a sintering time and thus cannot succeed. The most common complaint is that during synthesis of Ba$_2$YRu$_{1-x}$Cu$_x$O$_6$, YBCO is unintentionally formed, as the transition temperatures for the two materials are similar, and filaments of it are responsible for the superconductivity observed. There are many problems with this statement. The very broad diamagnetic transition is far from characteristic of the extremely narrow diamagnetic transition in YBCO. Additionally, YBCO undergoes a well-known peritectic decomposition [74] at ~1000 °C, and the resulting products (mainly Y$_2$BaCuO$_5$ or “green phase”, named so for its bright coloration) undergo a peritectic decomposition [102] at ~1270 °C. It is very unlikely that the tetragonal YBCO phase survives the elevated temperatures necessary for production of high-quality Ba$_2$YRuO$_6$. Additionally, the YBCO (or the YSrCO homologue) structure has never been observed in x-ray diffraction measurements, or in neutron diffraction experiments at the University of Missouri. This sets the limit to possible impurity phase of YBCO (or YSrCO) at about 1%, which is not enough to account for the amount of diamagnetism observed in Ba$_2$YRu$_{1-x}$Cu$_x$O$_6$ (or Sr$_2$YRu$_{1-x}$Cu$_x$O$_6$) [21]. Also, low temperature (300-500 °C) oxygen annealing increases the superconducting volume fraction of samples of YBCO, but lowers the superconducting volume fraction of Ba$_2$YRu$_{1-x}$Cu$_x$O$_6$.

To attempt to silence critics and verify that the bulk phase and not a minority phase is responsible for the superconductivity, a series of doping studies [22] were
performed in which YBCO was the dopant (~5% by weight) into fully-formed Ba$_2$YRuO$_6$. The mixed material was processed as if it was a precursor compounds, and an array of measurements were taken at every step. No evidence was ever found for the survival of the YBCO phase above the high processing temperature; in fact, the samples ended up being Cu doped by way of the decomposition of the YBCO compound, and showed superconductivity characteristic of the Ba$_2$YRuO$_6$ family. Microprobe studies performed by collaborators at the University of Missouri, confirmed the stoichiometry of a statistically large number of grains (31) to be that of superconducting Ba$_2$YRu$_{1-x}$Cu$_x$O$_6$, and found no sign of any stoichiometry similar to that of YBa$_2$Cu$_3$O$_7$.

3.2 Broadening the Search: Ba$_2$LnRu$_{1-x}$Cu$_x$O$_6$

Following the discovery and characterization [140] of the Y-based materials, it is natural to investigate the substitution of lanthanides for Y, as was the case with Ln substitution in YBCO forming the series LnBCO (or Ln123). Since all of the formable members of the family LnBCO superconduct, rich behavior would be expected in the family Ba$_2$LnRu$_{1-x}$Cu$_x$O$_6$. It was thought that with the wealth of sample processing experience obtained through a multi-year study of the Ba$_2$YRuO$_6$ system that substantial improvements could be made in the quality of samples in the Ba$_2$LnRuO$_6$ family. The members of the Ba$_2$LnRuO$_6$ series (Ln=Ce excepted) all share the same crystal structure as the Y homologue, with two distinct chemical layers, LnRuO$_4$ and BaO.
The most interesting system has Ln=Gd. The inclusion of the Gd$^{3+}$ ion allows for investigation of the magnetic environment in the material by electron spin resonance measurements. Synthesis of high-quality undoped material follows the method described above, with a lower sintering temperature (1380 °C) the only change. Ba$_2$GdRu$_{1-x}$Cu$_x$O$_6$ has never been shown to superconduct [27,111], whereas GdBa$_2$Cu$_3$O$_7$ is a well-known superconductor. The lack of observation of superconductivity in the Gd ruthenate was not for lack of effort; multiple attempts to make a superconducting sample using the methodology described above always have failed. With magnetic Ln ions in complete substitution on the Y site in YBCO, magnetic pair-breaking with consequent depression of $T_c$ does not occur; all of the formable members of the LnBCO family superconduct with nominal 90-100 K superconducting transition temperatures. While this is perhaps due to the layered nature of the LnBCO structure, pair-breaking is inescapable in the Ba$_2$LnRu$_{1-x}$Cu$_x$O$_6$ series, particularly with $s$-state Gd. Gd is the only of the magnetic lanthanides with $l$=0 and $j$>0, and its propensity to break pairs is not mitigated by crystal-field effects. In the crystal structure there are only two distinct chemical layers, the LnRuO$_4$ and the BaO; wherever the superconductivity resides, it is always only a small fraction of the lattice parameter from a magnetic ion. A similar study [23] to the study described above where fully-formed Ba$_2$GdRuO$_6$ was doped with ~5% by weight amounts of superconducting GdBa$_2$Cu$_3$O$_7$ had interesting results. As no superconductivity was expected from the bulk material, any observed superconducting behavior would have to come from GdBa$_2$Cu$_3$O$_7$ that had survived the heat treatment at 1380 °C. Following the high temperature treatment, no superconductivity was observed
by SQUID magnetization or electron spin resonance measurements, implying that the GdBa$_2$Cu$_3$O$_7$ was completely destroyed in the processing, and that the Ba$_2$GdRu$_{1-x}$Cu$_x$O$_6$ phase is the stable phase at high temperatures. The electron spin resonance data (Figure 3.6) on the high temperature processed mixture also fails to show paramagnetic Gd that would be characteristic of GdBa$_2$Cu$_3$O$_7$. In the O$_7$ phase, the Ln site orders antiferromagnetically at ~2K [114]; it is paramagnetic for temperatures above this. In the Ba$_2$LnRuO$_6$ series, the Ln site orders at ~12 K [23], but due to strong spin-spin coupling with magnetically ordered Ru, the paramagnetic Gd resonance vanishes [111] below the Ru ordering temperature, ~48 K. As a result, paramagnetic Gd$^{3+}$ resonance below ~48 K can be used as a fingerprint to demonstrate the existence of any GdBa$_2$Cu$_3$O$_7$ phase surviving in a sample post heat treatment. None is observed, again confirming that GdBa$_2$Cu$_3$O$_7$ does not survive high temperature processing, and suggesting that the chemically very similar YBa$_2$Cu$_3$O$_7$ does not survive high temperature processing. These studies have refuted the idea that observation of superconductivity in Ba$_2$YRu$_{1-x}$Cu$_x$O$_6$ is due to accidental synthesis of YBa$_2$Cu$_3$O$_7$. 
Additional members of the $\text{Ba}_2\text{LnRuO}_6$ series have been studied. The most effort has been applied to $\text{Ln}=$Dy. The material is classified as face centered cubic, space group $Fm\overline{3}m$, with lattice parameter $a=8.35$ Å. An investigation was carried out to determine the optimal sintering temperature for successful doping of the system with $\text{Cu}$.

Figure 3.6: Magnetic resonance at 20.3 GHz in $\text{Ba}_2\text{GdRuO}_6$ with 5% by weight of $\text{GdBa}_2\text{Cu}_3\text{O}_7$ sintered for 12 h at 1380 °C. No paramagnetic Gd resonance is observed below $T_{\text{N,Ru}}=48$ K.
Stoichiometric amounts of dried out precursors were weighed out as per the formula

\[ 2 \text{BaCO}_3 + 0.5 \text{Dy}_2\text{O}_3 + (1-x)\text{RuO}_2 + x\text{CuO} \rightarrow \text{Ba}_2\text{DyRu}_{1-x}\text{Cu}_x\text{O}_6 \]

and thoroughly mixed with a clean agate mortar and pestle, adhering to the previously mentioned 30 minutes per 4 grams rule. Following grinding, the material was placed in a clean alumina crucible, put in a box furnace, and rapidly heated to 970 °C in air for 48 hours, and allowed to cool to room temperature. After cooling, the material was thoroughly reground, then pressed into 1 g pellets at 10000 PSI with a 1 mm diameter stainless steel die. These pellets were then stacked and placed in a clean alumina boat atop small piles of unpressed (but calcined) powder of the same material. The boat was then sealed in a standard tube furnace with a flowing gas atmosphere of 70% Ar and 30% O, replicating atmosphere without the water vapor or N\textsubscript{2} gas (as N\textsubscript{2} chemistry occurs at sufficiently high temperatures). Four different sintering temperatures were studied: 1100 °C, 1200 °C, 1300 °C, and 1400 °C, where 1400 °C is the optimal processing temperature of high-quality (undoped) Ba\textsubscript{2}DyRuO\textsubscript{6}. In each case, the temperature was ramped up from and down to 500 °C over the course of 4 hours, and the high temperature was held for 12 hours. The oven was rapidly ramped up to 500 °C, and cooled to room temperature at the end of the thermal cycle. The tube furnace was not opened and thus the samples were not exposed to air until cooled to room temperature. Samples were typically cut from the center of the middle pellet in a stack for characterization. Powder x-ray diffraction measurements (Figure 3.7) indicate single-phase cubic material with lattice parameters comparable to that found in the literature.
The material Ba$_2$DyRuO$_6$, as is typical for the Ba$_2$LnRuO$_6$ family of materials, has interesting magnetic behavior; this could be anticipated as the Dy$^{3+}$ ion has the largest magnetic moment among all stable elements. SQUID magnetization data collected at 10 Oe (Figure 3.8) demonstrate that the magnetic structure of the material is nontrivial. The zero field-cooled and field-cooled measurements are essentially identical, and the field-cooled warming or remnant magnetization measurement is essentially zero. Any observed signal in the field-cooled warming data likely is due to the superconducting magnet not being at exactly 0.0 Oe, and thus eliciting a response from the very large moment of the Dy$^{3+}$ ions. In the data, there is a magnetic transition at ~48 K; this is
slightly higher in temperature than the Ru$^{5+}$ magnetic transition in the Y homologue, and in fact the Ru$^{5+}$ ordering temperature is known to vary slightly across the Ln series, peaking with Ln=Dy [42,83]. The magnetization increases substantially below this temperature; with exception of a change in slope at ~27 K, the material behaves like a paramagnet below 48 K. The transition at 48 K can thus be assigned to Ru antiferromagnetic order, but from susceptibility measurements alone it is not clear what the state of magnetic order of the Dy is. For the data of Figure 3.8, the magnetic moment of the sample over the temperature range 50-300 K may be fit by the Curie-Weiss formula as discussed in Appendix C resulting in an effective magnetic moment of 11.08 $\mu_B$ and a Weiss $\theta$ of +21.5 K, indicating antiferromagnetic exchange is the predominant magnetic interaction. The magnetic moment of the free Dy$^{3+}$ ion is 10.6 $\mu_B$, and that of the Ru$^{5+}$ is 3.87 $\mu_B$; the net moment given by $\mu_{\text{net}} = (\mu_{\text{Dy}}^2 + \mu_{\text{Ru}}^2)^{1/2}$ is then 11.28 $\mu_B$, in close agreement with the observed result; the Dy moment is clearly paramagnetic above 50 K. At lowest temperatures, the magnetization of the material is too small to caused by paramagnetic Dy$^{3+}$; the Dy$^{3+}$ ions must be experiencing magnetic interactions. This is already clear from studies of the Gd-homologue, where the Gd$^{3+}$ paramagnetic resonance vanishes below the Ru$^{5+}$ ordering temperature, even though the Gd$^{3+}$ ions do not magnetically order until 12 K. In a similar study of this material, Kumar et al. [83] observed no jumps in the heat capacity of Ba$_2$DyRuO$_6$ below 48 K, indicating that there are no magnetic transitions below this temperature. It is likely that both ion species order at 48 K, and a spin-reordering occurs at a lower temperature with zero latent heat. The molar susceptibility of Kumar's sample is comparable to the sample discussed here. AC
SQUID magnetometry measurements on the same samples that the DC measurements were performed on show identical susceptibility as a function of temperature, and show no frequency dependence, suggesting no spin-glass behavior.

Additionally, SQUID magnetization measurements were performed at constant field on a sample of Ba$_2$DyRuO$_6$ at 2 K (Figure 3.9). The magnetization never saturates in fields up to 7 T, and no metamagnetism is visible; there is only a very slight deviation from linear behavior, with second and third power terms in the fit being essentially zero, suggesting paramagnetic behavior (which is ruled out by the temperature dependence of the susceptibility) or antiferromagnetic behavior.

![Figure 3.8: Temperature dependence of magnetic susceptibility of Ba$_2$DyRuO$_6$ with H=10 Oe](image)
Structural characterization via neutron diffraction measurements and Rietveld refinement performed by J. Lamsal at the University of Missouri indicates the material is face-centered cubic with space group $Fm\bar{3}m$ at all temperatures, and lattice parameter $a=8.35\text{ Å}$ at room temperature and $a=8.34\text{ Å}$ at 12 K, the difference due to simple lattice contraction. No secondary phases were detectable to the limit of sensitivity of the instrument ($\sim 1\%$). Refinement shows good spatial arrangement of the Dy and Ru ions, but also that the oxygen site is not fully occupied. Neutron diffraction data at various temperatures show a transition at 48 K, and show an additional, very weak peak at 25 K. The additional peak intensity is so small that it is possible this peak was not visible at

![Graph](image.png)

Figure 3.9: Field dependence of magnetic susceptibility with $T = 2\text{ K}$ of Ba$_2$DyRuO$_6$.
higher temperatures due to noise, and there is no clear evidence for any additional magnetic orderings below 48 K.

Electron spin resonance measurements carried out on several samples of Ba$_2$DyRuO$_6$ do not reveal substantial information about the magnetic structure of the material. Measurements performed at both 12.885 GHz (Figure 3.10, Figure 3.11) and 20.3 GHz (Figure 3.12, Figure 3.13) in fields up to ~2 T show essentially no resonant response besides that of the paramagnetic DPPH sample used as a calibration marker. At each frequency, samples were placed on the bottom of a rectangular TE$_{101}$ resonant cavity, and measurements were performed with both $H_{rf}$ perpendicular to $H_{dc}$, and with $H_{rf}$ parallel to $H_{dc}$, which would allow for characterization of any type of observed magnetic resonance. There is a small paramagnetic impurity visible in Figure 3.12 that also was visible in an empty cavity; there was a contaminant somewhere in the system during the measurement. An additional set of measurements was performed to more closely examine the temperature window surrounding the magnetic transition at 48 K; this data shows no magnetic resonance whatsoever (Figure 3.14). This is to be expected as Ru$^{5+}$ is known to be ESR silent, and in this crystal symmetry, crystal field effects are evidently too large such that the excited states of the paramagnetic Dy ion are well above the microwave energies in question.
Figure 3.10: Magnetic resonance at 12.885 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in $\text{Ba}_2\text{DyRuO}_6$
Figure 3.11: Magnetic resonance at 12.885 GHz with $H_{\text{rf}}$ parallel to $H_{\text{dc}}$ in Ba$_2$DyRuO$_6$
Figure 3.12: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in $Ba_2DyRuO_6$. A small paramagnetic impurity is observed that was also seen in an empty cavity.
Figure 3.13: Magnetic resonance at 20.3 GHz with $H_{rf}$ parallel to $H_{dc}$ in Ba$_2$DyRuO$_6$
The doping of Ba$_2$DyRuO$_6$ with Cu has interesting results; a 10% doping level was chosen due to the uncertainty of the solubility limit of Cu in the host material. Powder x-ray diffraction on the samples sintered at four different temperatures show very little minority phase to the limit of x-ray diffraction sensitivity (~5%), and show that the materials are structurally identical to the undoped material with lattice parameter ~8.360 Å. In Figure 3.15, the principle peaks can all be identified easily, and a small shift in peak location as sintering temperature is increased is observable, indicating a slight decrease in lattice parameter as the optimal sintering temperature is approached. The

Figure 3.14: Magnetic resonance at 20.3 GHz near $T_N$ with $H_{rf}$ perpendicular to $H_{dc}$ in Ba$_2$DyRuO$_6$. No resonance is observed.
magnitude of the peaks increases steadily with sintering temperature: this indicates a change in the structure factor due to increased spatial ordering of the two transition metal ion sites in the lattice.

The magnetization of samples sintered at different temperatures shows distinct differences. SQUID magnetization data as a function of temperature in an applied field of 10 Oe was collected on samples sintered at each temperature. In the sample sintered at 1100 °C, there is a divergence in the zero field-cooled and field-cooled magnetizations (Figure 3.16) at 49 K, the ordering temperature attributed to the Ru sublattice. This does

Figure 3.15: Powder x-ray diffraction on Ba$_2$DyRu$_{0.9}$Cu$_{0.1}$O$_6$ at different sintering temperatures. The indexed peaks are all O$_6$-phase. The red stars indicate very small impurity peaks not observed in the undoped material.
not occur in the undoped material. At 31.5 K, there is an antiferromagnetic transition, and at 12 K, there is an abrupt decrease in the magnetization in both the zero field-cooled and field-cooled measurements. The nature of this transition suggests an onset of diamagnetism. Thus, it is possible that there is superconductivity in this material below 12 K, but the diamagnetism is ineffective in screening the very large magnetic moment of the Dy$^{3+}$ ion, preventing the observation of net negative magnetization; from temperature dependent susceptibility measurements alone this is not clear. In the field-cooled warming or remnant magnetization measurement, substantial flux is trapped in the material below 48 K, with small changes in the slope of the curve evident at both 31.5 K and 12 K, implying a change in ability to trap flux at these temperatures. As an antiferromagnet cannot trap flux, this flux trapping must be due to either canted ferromagnetism or diamagnetism.
In the sample sintered at 1200 °C, there is again a divergence between the zero field-cooled measurement and the field-cooled measurement (Figure 3.17) at the temperature associated with the Ru sublattice ordering, ~49 K, and there is no longer an antiferromagnetic transition observable near 31.5 K. The divergence at 49 K is much smaller than in the sample sintered at 1100 °C. The transition at ~11 K is still visible and has shifted down 1 K, and is also much more abrupt. The magnitude of the change in magnetization starting at 11 K is comparable to that observed in the sample sintered at 1100 °C. Paramagnetic Dy is still observed at lowest temperatures, just as in the undoped material. In the field-cooled warming measurement, substantially less trapped flux is
observed, but it still persists to 49 K and the signal is noise-level of the machine above this temperature. There is a clear change in the trapped flux at ~11 K. Noise in the field-cooled warming data above 80 K due to the sample slipping in the instrument is omitted. This data is again consistent with a diamagnetic transition at ~11 K.

![Figure 3.17: Temperature dependence of magnetic susceptibility with H = 10 Oe for Ba$_2$DyRu$_{0.9}$Cu$_{0.1}$O$_6$ sintered at 1200 °C.](image)

In the sample sintered at 1300 °C, the divergence between the zero field-cooled and the field-cooled measurements (Figure 3.18) still occurs starting at ~49 K but is very small. Once again there is no evidence for a sharp transition near ~31.5 K, and the magnetization is approaching that of the undoped material. There is a very small but quite distinct transition at 11 K in both the zero field-cooled and field-cooled
measurements; this is dramatically different when compared to the sample sintered at 1200 °C. In the field-cooled warming or remnant magnetization measurement, there is essentially noise-level only signal above ~20 K, which rises sharply at ~11 K. Again, this data could be consistent with a diamagnetic transition. If it is an antiferromagnetic transition or a spin-reordering between antiferromagnetic modes, additional flux trapping would not occur below the transition as antiferromagnets trap no flux.

Figure 3.18: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1300 °C. Inset: Expansion detailing transition at 11 K.
In the sample sintered at 1400 °C, the optimal sintering temperature for undoped Ba$_2$DyRuO$_6$, the divergence starting at ~49K between zero field-cooled and field-cooled magnetization (Figure 3.19) is still present but even smaller. As there was some noise in the field-cooled warming measurement, it is possible that the transition observed in the zero field-cooled measurement at ~7 K is simply noise, as it does not fit the trend of the three previous graphs; however, the measurement cycle is such that the zero field measurement is performed first, the field-cooled second, and the field-cooled warming third, which implies that the noise did not start occurring until well after the zero field-cooled data was acquired. It would be quite a coincidence as well if the two noisy points of data in the zero field-cooled measurement happened to occur right near an anticipated transition temperature. In the field-cooled warming measurement, the same trend of flux trapping to ~10 K is observed, implying a magnetic ordering of some sort that can trap flux. This again suggests superconductivity.
Magnetization measurements (Figure 3.20) performed at constant temperature as a function of field on a sample do not show evidence of diamagnetic behavior, but do show interesting metamagnetism. In the material sintered at 1400 °C, the slope of the susceptibility versus temperature is constant at low fields, and then changes to a new constant value at about 1 T, indicating a change in the magnetic ordering of the system induced by the field.

Figure 3.19: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1400 °C.
Electron spin resonance measurements add evidence to the existence of superconductivity in this compound. Measurements were performed at 20.3 GHz on a sample sintered at 1200 °C, and as well on a sample sintered at 1400 °C. The differences in resonance data between the two samples are quite striking. In both cases, the samples were mounted on the bottom of a TE\textsubscript{101} resonant cavity, and a piece of DPPH was used for calibration. In the sample sintered at 1200 °C, with $H_{rf}$ perpendicular to $H_{dc}$ (Figure 3.21), no magnetic resonance is observable up to room temperature for any temperatures above 17.5 K. Two features appear at low temperature: a broad resonance centered at low field starts to appear at 17.5 K, and at 10 K, a feature appears that may vary as $\sim H^{1/2}$,
as is the case for superconducting dissipation. The same two features are observed when
the fields are rotated such that $H_{rf}$ and $H_{dc}$ are parallel (Figure 3.22), at approximately the
same temperatures. This indicates that the low-field resonance is either antiferromagnetic
or weakly ferromagnetic in origin, and supports the suggestion that the high-field feature
actually is superconducting dissipation. It is not clear that the low-field resonance
persists above 20 K. The low-field resonance starts too high in temperature to be
associated with the large transition in the magnetization data at 11 K; the possible
superconducting dissipation starts at just the right temperature, suggesting these two
features share a common cause. In all cases, the very sharp resonance response is due to
the DPPH sample.
Figure 3.21: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in $\text{Ba}_2\text{DyRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1200 °C as a function of temperature.
Careful resonance data collected at 20.3 GHz on the sample sintered at 1400 °C is very different from that on the sample sintered at 1200 °C. With \( H_{rf} \) perpendicular to \( H_{dc} \) (Figure 3.23), no magnetic resonance is observed for temperatures above 30 K, whereas below 30 K, a magnetic resonance peaking at \( \sim 2400 \) Oe is observable. No high-field behavior is observed whatsoever. With \( H_{rf} \) parallel to \( H_{dc} \) (Figure 3.24), the same magnetic resonance is observed, and may persist until at least 60 K, but does not get large until below 20 K. Observation of resonance in both angular configurations suggests that there is either antiferromagnetic or weakly ferromagnetic order, with no diamagnetism.
Figure 3.23: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in $Ba_2DyRu_{0.9}Cu_{0.1}O_6$ sintered at 1400 °C as a function of temperature.
There are several conclusions that may tentatively be reached on the basis of this data. The Dy magnetic ordering is complex and the correct magnetic structure is still not clear. Doping the system with 10% Cu for Ru shows possible evidence of superconductivity. No resistive transitions were visible, but the samples were of extremely high resistance at and below room temperature, so it is possible that the sample quality and superconducting content is simply not high enough to percolate. The phase responsible for superconductivity is not an impurity, at least to a 95% accuracy; neutron diffraction measurements could lower this uncertainty. The superconducting-like phase is
only stable through a narrow range of temperatures, with an optimal processing temperature near 1200 °C; this is evidenced by the largest and sharpest transition occurring in the sample sintered at 1200 °C. The electron spin resonance measurements show that the Cu moments are antiferromagnetically ordered with an onset temperature equal to the onset temperature of superconductivity, just as was the case in Ba$_2$YRu$_{1-x}$Cu$_x$O$_6$. The divergence in magnetization below ~49 K between zero field-cooled and field-cooled magnetization measurements is likely due to Ru canting or weak ferromagnetism originating in poor Y-Ru spatial ordering due to processing at lower temperatures; higher temperature processing does not show this feature. A more detailed study of this system, which would include smaller increments in processing temperatures and extensive neutron diffraction measurements, would shed light on the situation. The notion that Ba$_2$DyRu$_{0.9}$Cu$_{0.1}$O$_6$ is a low temperature superconductor certainly is suggested by these data.

A set of experiments, similar to the published experiments on studying the breakdown of YBa$_2$Cu$_3$O$_7$ and GdBa$_2$Cu$_3$O$_7$ in Ba$_2$YRuO$_6$ and Ba$_2$GdRuO$_6$, respectively, was carried out with a prepared sample of DyBa$_2$Cu$_3$O$_7$ and prepared Ba$_2$DyRuO$_6$. DyBa$_2$Cu$_3$O$_7$ orders antiferromagnetically at ~1 K [64]. The sample of DyBa$_2$Cu$_3$O$_7$ was prepared by weighing out dried precursor compounds as per the chemical formula

$$0.5 \text{Dy}_2\text{O}_3 + 2 \text{BaCO}_3 + 3 \text{CuO} \rightarrow \text{DyBa}_2\text{Cu}_3\text{O}_7$$

and thoroughly grinding in a clean agate mortar and pestle. The mixed powder was then put into an alumina crucible and rapidly heated in a box furnace to 925 °C, and held at that temperature for 67 hours. After cooling to room temperature, the powder was again
thoroughly ground, pressed at 10000 PSI into 1g pellets with a clean 1mm die. The pellets were then stacked on a pile of unpressed powder of the same material in an alumina boat, and placed in a tube furnace with a flowing gas mixture of 90% Ar, 10% O₂. The furnace was rapidly heated to 945 °C and held at that temperature for 24 hours before being allowed to cool to room temperature. Following this, the gas was switched to 100% O₂, and the samples were allowed to anneal for 4 days at 400 °C before returning to room temperature. Pieces were then cut, and the material was ground up for mixture into prepared Ba₂DyRuO₆. Bars of the DyBa₂Cu₃O₇ showed a sharp diamagnetic transition at 93 K, typical of the material. DyBa₂Cu₃O₇ undergoes a well-known peritectic breakdown at 1005 °C [81], and the resulting compounds break down into a mixture of Dy₂O₃, BaCuOₓ, and CuO at 1335 °C, so it is unlikely that the DyBCO phase survives the high temperature processing necessary for synthesis of high-quality Ba₂DyRuO₆. Doping the host material with CuO did not demonstrate an ~85 K superconductor, so it was expected that with the DyBa₂Cu₃O₇ destroyed by the heat treatment, the behavior of the Cu-doped materials would result, which would again reinforce that Ba₂YRu₀.₈₅Cu₀.₁₅O₆ cannot contain any YBCO that would account for the observed superconductivity.

By weight, 6% of ground, superconducting DyBa₂Cu₃O₇ was mixed into ground Ba₂DyRuO₆ as prepared above, with the resultant material processed as if it were the precursor compounds for synthesis of Ba₂DyRuO₆; the synthesis procedure follows that described for synthesis of the undoped compound. Separate pellets of the mixed material were fired at 970 °C and at 1400 °C, and samples were cut out for characterization.
SQUID magnetometer characterization of the mixed material, prior to heat treatment (Figure 3.25), shows behavior characteristic of both DyBa$_2$Cu$_3$O$_7$ and Ba$_2$DyRuO$_6$. The 93 K superconducting transition is very sharp. The magnetic transition at ~49 K is evident in both the zero field-cooled and field-cooled measurements, and the deviation from paramagnetism characteristic of the Ba$_2$DyRuO$_6$ is observed at low temperatures. The large difference between the zero field-cooled and field-cooled magnetization is due to flux trapping in the superconducting phase. The field-cooled warming measurement shows no features aside from flux trapping in the superconducting phase, and above 93 K the magnetization is essentially zero.

Figure 3.25: Susceptibility as a function of temperature of mixed Ba$_2$DyRuO$_6$ + 6% DyBa$_2$Cu$_3$O$_7$ with $H = 10$ Oe
The magnetization of the material taken to 970 °C (Figure 3.26) shows signs of breakdown of the DyBa$_2$Cu$_3$O$_7$ phase. The susceptibility scales of Figure 3.25 and Figure 3.26 are the same. The superconducting transition still occurs at ~93 K, but there is not enough superconducting phase remaining to generate net diamagnetism; this is likely due to the oxygen content of the DyBa$_2$Cu$_3$O$_7$ changing as 970 °C is below the peritectic decomposition temperature. It is not clear if the transition has broadened, or if that apparent broadening is simply a consequence of less diamagnetism to offset the paramagnetism of Dy$^{3+}$. The magnetic transition at ~49 K is still clear, and an additional feature at 11 K appears in both the zero field-cooled and field-cooled measurements. The field-cooled warming measurement is again featureless aside from flux trapping in the superconducting phase. There is a tail in the field-cooled warming data; this suggests that there are two diamagnetic transitions in the material, one at 93K and another at ~85 K; this would explain the broadening of the transition as observed in the zero field and field-cooled measurements.
The magnetization of the material taken to 1400 °C (Figure 3.27) much more resembles the magnetization of the undoped material. The vertical scales of Figure 3.25 and Figure 3.27 are identical. There is no transition visible at either 85 K or 93 K, indicating that the DyBa$_2$Cu$_3$O$_7$ phase has been destroyed. The existence of paramagnetic BaCuO$_x$ cannot be inferred due to the large magnetic moment of the Dy$^{3+}$ ions. The transition at ~49 K still is visible, and there is no difference between the zero field and field-cooled magnetization below this value. At 11 K there is a clear transition, and below this temperature there is a slight separation between zero field and field-cooled magnetization; this is the same feature found via Cu-doping of Ba$_2$DyRuO$_6$. The field-
cooled warming measurement is essentially zero, with only a very small upturn at lowest temperatures not visible at this scale. This may be due to either flux trapping by the possibly superconducting low temperature magnetic phase, or by Dy$^{3+}$ paramagnetism due to the superconducting magnet not being at exactly 0.0 Oe.

![Graph](image)

**Figure 3.27: Susceptibility as a function of temperature of Ba$_2$DyRuO$_6$ + 6% DyBa$_2$Cu$_3$O$_7$ after 1400 °C heat treatment, with H = 10 Oe**

This sequence of experiments supports the argument that the DyBa$_2$Cu$_3$O$_7$ phase is chemically not stable at elevated temperatures, and it is consistent with the superconductivity observed in Ba$_2$YRu$_{0.85}$Cu$_{0.15}$O$_6$ being intrinsic to the material and not due to YBa$_2$Cu$_3$O$_7$ impurity phase. The experiment was repeated again, with fresh batches of Ba$_2$DyRuO$_6$ and DyBa$_2$Cu$_3$O$_7$, prepared identically as mentioned above, in
order to investigate the results of processing at 1070 °C, just above the peritectic breakdown temperature (1005 °C); the results were similar but not identical (Figure 3.28). The zero field-cooled magnetization curves all show the magnetic transition at 49 K attributed to the Ru sublattice, and only the mixed material fails to show a transition at ~11 K. The material heated to 970 °C, just below the peritectic breakdown temperature, still shows net diamagnetism, unlike the previous processing round; it also still has a sharp diamagnetic transition. The material processed at 1070 °C shows the same type of diamagnetic transition observed in Figure 3.26; at this temperature, all of the DyBa$_2$Cu$_3$O$_7$ should be decomposed. The material processed at 1400 °C still shows a broad diamagnetic transition, now starting at ~86 K, the characteristic temperature for superconductivity in the Ba$_2$YRuO$_6$ system; the shape of the transition is also strikingly similar to that in Ba$_2$YRu$_{0.85}$Cu$_{0.15}$O$_6$. It is not clear what caused the differences between these two sets of experiments, as great care was taken to repeat the procedures exactly. The two batches were processed by two different people, so it is possible that sufficient technical expertise was not applied in one case. These measurements suggest that Ba$_2$DyRu$_{1-x}$Cu$_x$O$_6$ does not only have a diamagnetic transition at ~11K, it may also be superconducting at ~86 K as in the Y homologue. It is not clear if there are two different minority phases that account for the observed diamagnetism, or if one or both are inherent to the bulk phase.
Powder x-ray diffraction measurements performed on the materials from this second experiment indicate the survival of DyBa$_2$Cu$_3$O$_7$ above the high processing temperature. In Figure 3.29, the indexed peaks are those of the DyBa$_2$Cu$_3$O$_7$ phase; when the mixed batch is compared to the diffraction profile of pure Ba$_2$DyRuO$_6$, the additional lines indicating the DyBa$_2$Cu$_3$O$_7$ phase are obvious. These lines still appear, although diminished, following the heat treatment at 1400 °C. The lines belonging to the main phase are substantially larger and are not indexed. It is not clear what caused the difference between the two experiments; a detailed study carried out at a variety of synthesis temperatures would further explain this.
Cu doping of Ln=Nd was also examined. There has been some disagreement about the crystal structure of the undoped material in published accounts [12,67]; the most recent report [48] characterizes the material as face centered cubic with space group $Fm\bar{3}m$, consistent with the rest of the $Ba_2LnRuO_6$ family, and with lattice parameter $a=8.4706\ \text{Å}$. A similar investigation into the optimal sintering temperature for successful
Cu doping of the system was carried out. Stoichiometric amounts of dried out precursors were weighed out as per the formula

\[ 2 \text{BaCO}_3 + 0.5 \text{Nd}_2\text{O}_3 + (1-x) \text{RuO}_2 + x \text{CuO} \rightarrow \text{Ba}_2\text{NdRu}_{1-x}\text{Cu}_x\text{O}_6 \]

and were processed in an identical manner to the Ln=Dy samples. Four different sintering temperatures for \( x=0.1 \) were studied: 1100 °C, 1200 °C, 1300 °C, and 1400 °C; 1400 °C is believed to be the optimal processing temperature of high-quality \( x=0 \) \( \text{Ba}_2\text{NdRuO}_6 \). Analysis of x-ray diffraction data (Figure 3.30) show the \( x=0 \) \( \text{Ba}_2\text{NdRuO}_6 \) is single-phase and has a lattice parameter in close agreement with the published values.

![Figure 3.30: Powder x-ray diffraction on undoped Ba2NdRuO6 sintered at 1400 °C. All peaks belong to the O6-phase, and no impurity phases are detectable.](image)
The x=0 material Ba$_2$NdRuO$_6$ has a complex magnetic structure, markedly different from the Ln=Gd, Dy homologues; SQUID magnetization data collected at 10 Oe (Figure 3.31) demonstrate this. There is an antiferromagnetic transition at 56 K, and the zero field-cooled and field-cooled magnetization plots are identical above 52 K. Below this temperature there is a sharp increase in the magnetization, peaking at 33 K in the zero field-cooled measurement and 31 K in the field-cooled measurement, then rapidly decreasing until a new magnetic state occurs at ~24 K; the increase in magnetization is different in the two different measurements. Below 10 K a slight divergence occurs between the the zero field-cooled and the field-cooled measurement, and there is little evidence of paramagnetism at lowest temperatures. The field-cooled warming or remnant magnetization measurement is the most interesting. Below 10 K, a small amount of trapped flux is observed corresponding with the divergence in the zero field and field-cooled measurements; above 10 K, there is essentially no trapped flux until ~24 K, where the anomalous magnetic transition occurs. This material shows a spontaneous, substantial increase in its magnetization in the absence of an applied field as the temperature is increased, implying a transition from antiferromagnetic state to a ferromagnetic or weakly ferromagnetic state; there is no other way to account for the increase in magnetization. The material must have a antiferromagnetic Ru$^{5+}$ transition at 56 K, a ferromagnetic Nd$^{3+}$ ordering at 52 K, and an antiferromagnetic realignment of the Nd$^{3+}$ spin system at 24 K, possibly canting below 10 K to create a small net ferromagnetic moment that accounts for the trapped flux observed below 10 K.
SQUID magnetization measurements (Figure 3.32) in an applied field of 1000 Oe were performed to room temperature to allow calculation of the effective magnetic moment of the material in the paramagnetic regime above 58 K. The fit to the Curie-Weiss law as discussed in Appendix C yields an effective magnetic moment of 4.2099 $\mu_B$, which is slightly smaller than the value (4.96 $\mu_B$) reported in the literature, and a Weiss $\theta$ of +11.2 K, suggesting that antiferromagnetic interactions are predominant. There are no transitions visible above the antiferromagnetic ordering at ~56 K, and the abrupt increase in magnetization still occurs at 52 K, again peaking at ~32 K. In this higher field measurement, the zero field and field-cooled magnetizations are almost identical. At
lowest temperatures, a slight deviation is again observable, which also manifests itself in the field-cooled warming measurement. Above 52 K, the field-cooled warming signal is essentially zero, and the measurement was halted above 80 K in the interest of conservation of instrument time. It is not that the zero field-cooled susceptibility is proportionally larger, but rather that the field-cooled susceptibility is proportionally lower in 1000 Oe as compared to 10 Oe. This suggests a suppression of the ferromagnetic transition in increased fields; the field-cooled warming magnetization is also substantially reduced. Izumiyama et al. [67] report a maximum molar susceptibility in a field of 1000 Oe of ~0.0475 emu mol\(^{-1}\); this sample has a maximum molar susceptibility measured in the same field of more than twice this value. Their sample also indicates substantial paramagnetism at low temperatures, a feature not observed in this material; also, the peak magnetization occurs at a suppressed temperature ~27 K in their material; magnetically at least, this sample is superior. This is most likely due to Izumiayama's poor choice of processing parameters causing poor Dy-Ru spatial ordering, especially the 60 hour sintering time.
Several SQUID magnetization measurements were performed in high fields to observe the suppression of the ferromagnetic component, and are shown in Figure 3.33. The magnetic ordering at ~56 K is clearly visible and unaffected by field, and the paramagnetic susceptibility above this temperature is field-independent. Fitting the paramagnetic region of this data to the Curie-Weiss law yields comparable values to those listed above. Field-cooled warming measurements are not shown as it is difficult to return the superconducting magnet to exactly zero field immediately following fields above ~1 T due to persisting supercurrents. The suppression of the ferromagnetic response eventually saturates, and the low-temperature antiferromagnetism starts to

Figure 3.32: Temperature dependence of magnetic susceptibility for \( \text{Ba}_2\text{NdRuO}_6 \) with \( H=1000 \text{ Oe} \)
disappear; the latter of these is expected as the antiferromagnetic lattice begins to cant yielding a net ferromagnetic moment. The suppression of the ferromagnetic susceptibility is easily understood as the magnetization of a saturated ferromagnet is constant; the susceptibility of a saturated ferromagnet decreases with applied field, and the susceptibility of a nearly saturated ferromagnet will decrease as well. As applied field is increased, the ferromagnetic transition width $\Delta T$ becomes increasingly narrow, such that dividing the magnetization by the field to yield the susceptibility should yield a saturation as the transition becomes more like a step function.

Figure 3.33: Temperature dependence of magnetic susceptibility for $\text{Ba}_2\text{NdRuO}_6$ in various high fields. Closed circles are zero field-cooled measurements; open circles, field-cooled.
To further illustrate the effect, SQUID magnetization measurements (Figure 3.34) were performed at a variety of fixed temperatures in fields up to 7 T. No saturation is observed at 2 K, indicating very little if any paramagnetic behavior, matching the observations of Figure 3.33. Linear behavior is observed at 50 K and 70 K, but measurements at all other temperatures show field-induced metamagnetism. At 2 K, the metamagnetism is observed above 1000 Oe; this is possibly attributable to the small ferromagnetic component observed at low fields below 10 K in Figure 3.31 and Figure 3.32. The metamagnetism apparent at 10 K, 20 K, and 37 K likely has a different origin, and the onset field of the metamagnetism decreases as the temperature is increased; at 50 K and above, metamagnetic response is no longer observed. The data suggest a field-induced spin-reordering from antiferromagnetic to ferromagnetic, consistent with a collapse or canting of the antiferromagnetic spin system.
Izumiyma's [67] neutron diffraction measurements observed peaks of magnetic origin at 35 K that were not present at 100 K, and their refinements suggest *ab*-planar ferromagnetism, stacked antiferromagnetically along the *c*-axis. Diffraction measurements at 7 K only varied from that at 35 K by intensities of magnetic peaks, indicating that the two magnetic ion types are both ordered below 35 K; Izumiyma assumes this means that both are ordered starting at the highest transition temperature, but this is not justified. Izumiyma also performed heat capacity measurements as a function of temperature and found a discontinuity at ~58 K, but none below this; the spin-reordering at ~32 K has no latent heat, just as in the case of Ba$_2$DyRuO$_6$. It is possible
that spin-reorderings involving ferromagnetic planes beginning to couple antiferromagnetically have no latent heat [129].

The doping of Ba$_2$NdRuO$_6$ with Cu does not have as dynamic of an effect as was the case observed in Ba$_2$DyRuO$_6$. This was somewhat unexpected as the Nd$^{3+}$ magnetic moment is substantially smaller than the Dy$^{3+}$ magnetic moment. A 10% doping level was again chosen due to uncertainty of the solubility limit of Cu in the host material. Powder x-ray diffraction (Figure 3.35) on the samples sintered at four different temperatures shows bulk Ba$_2$NdRuO$_6$ phase with lattice parameters in agreement with published values, but there is an obvious impurity phase visible that cannot be indexed as any of the precursor compounds or BaCuO$_x$, the most likely impurity formed as a result of Cu doping. Additionally, a peak at ~32° appears in only the sample sintered at 1400 °C; it is not clear if this is due to an additional impurity phase. The magnitude of the main peaks steadily increases with sintering temperature, indicating increased spatial ordering of Nd and Ru in the rock-salt structure. There is little deviation in the peaks belonging to the Ba$_2$NdRuO$_6$ phase or the impurity peaks as a function of sintering temperature, implying the impurity peaks are not due to a crystallographic change from cubic to another symmetry as the Cu replaces Ru. It is not known what this impurity phase is, but it clearly will only be a small percentage (5-10%) of the bulk sample.
The magnetization of samples sintered at different temperatures gives information about the impurity phase(s). SQUID magnetization data as a function of temperature in an applied field of 10 Oe was collected on samples sintered at each temperature. In the sample sintered at 1100 °C, magnetic behavior (Figure 3.36) very different than the undoped material is observed. The zero field and field-cooled magnetizations still diverge at ~52 K, and there is still flux trapping observed associated with the spin-reordering at ~32 K, but the dominant feature is the appearance of a new transition at 15 K that shows “apparent ferromagnetism”, seeming antiferromagnetic in the zero field-

Figure 3.35: Powder x-ray diffraction on Ba$_{2}$NdRu$_{0.9}$Cu$_{0.1}$O$_{6}$ at different sintering temperatures. The indexed peaks are all O$_{6}$-phase. Impurity peaks are marked with red stars, and are not found in the undoped material.

The magnetization of samples sintered at different temperatures gives information about the impurity phase(s). SQUID magnetization data as a function of temperature in an applied field of 10 Oe was collected on samples sintered at each temperature. In the sample sintered at 1100 °C, magnetic behavior (Figure 3.36) very different than the undoped material is observed. The zero field and field-cooled magnetizations still diverge at ~52 K, and there is still flux trapping observed associated with the spin-reordering at ~32 K, but the dominant feature is the appearance of a new transition at 15 K that shows “apparent ferromagnetism”, seeming antiferromagnetic in the zero field-
cooled measurement but ferromagnetic in the other two measurements. As the magnitude of this transition dwarfs that of the nominal phase at ~32 K, it is unlikely that this belongs to the impurity phase; it is probably due to poor Nd-Ru spatial order causing Ru and/or Nd weak ferromagnetism, or poor Cu integration. The impurity phase cannot be ruled out as the source of this magnetization, however. There is no evidence for a diamagnetic transition.

Figure 3.36: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{NdRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1100 °C
In the sample sintered at 1200 °C, the magnetic behavior is very similar (Figure 3.37). The magnetic transitions of the bulk material are observable, but the magnetization is dominated even more strongly by “apparent ferromagnetism” at 15 K, which likely again originates in poor spatial ordering of Nd and Ru, or poor Cu integration. Impurity phase magnetism cannot be ruled out as the cause of this anomalous magnetization. There is once again no real evidence for a diamagnetic transition.

Figure 3.37: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $Ba_2NdRu_{0.9}Cu_{0.1}O_6$ sintered at 1200 °C.
In the sample sintered at 1300 °C, the magnetic behavior (Figure 3.38) begins to resemble the undoped material, but the low-temperature magnetic phase still dominates the response. The spin-reordering at now peaks at ~36 K, and the slight deviation between zero field and field-cooled magnetization measurements begins at ~58 K; no transition was observed between 58 K and 150 K. A change in the field-cooled warming characteristic of the spin-reordering is also larger. The large “apparent ferromagnetism” still has an onset temperature of ~15 K, but the transitions are decreased in magnitude. A slight paramagnetic upturn is visible at lowest temperatures. Again, impurity phase magnetization, poor Nd-Ru spatial ordering, or poor Cu inclusion is the cause of the low-temperature magnetism. No suggestion of a diamagnetic transition is visible.

Figure 3.38: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{NdRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1300 °C
The sample sintered at 1400 °C shows striking differences from the rest. It may be that there is a very narrow range of sintering that allows for good inclusion of the Cu that still preserves good Nd-Ru spatial ordering. When plotted at the same scale as Figure 3.38, the magnetization measurement data (Figure 3.39) shows the spin-reordering transition to be of comparable magnitude, and most importantly, no low-temperature ferromagnetism or antiferromagnetism is observed. A slight paramagnetic upturn is still visible at lowest temperatures. Interestingly, the zero field-cooled and field-cooled magnetization measurements are not equal below the spin-reordering, unlike in the doped material, and there appears to be flux trapping in the field-cooled warming magnetization measurement, persisting up until the highest magnetic transition. No transitions were observed between 60-150 K.
Scale expansion of the same data (Figure 3.40) shows some interesting features not seen in the other samples. The very slight divergence between zero field-cooled and field-cooled magnetization measurements starts above 70 K, with the antiferromagnetic transition peaking at ~62 K, which is higher than in the undoped material. In the undoped material, the two magnetization measurements were identical until 52 K, the onset temperature of the spin-reordering transition; here, the spin-reordering transition has an onset temperature of ~47 K, but the two magnetization measurements start to strongly diverge at temperature ~12 K higher than this. Below the spin-reordering transition, the two magnetization measurements are no longer identical due to the
divergence at ~60 K. At low temperatures, a paramagnetic upturn is obvious. The field-cooled warming measurement is particularly interesting; not only is there flux trapping due to the spin-reordering transition, as was the case in the undoped material, but there is also substantial flux trapping persisting up to ~60 K, which does not occur in the undoped material. It is possible that the decrease in magnetization observed at ~60 K is due to a diamagnetic transition; this would be consistent with the data, and it is unlikely that canting of the Ru antiferromagnetic lattice would account for the observed substantial decrease in magnetization.

Figure 3.40: Expansion of temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{Ba}_2\text{NdRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1400 °C.
To further characterize the sample sintered at 1400 °C, SQUID magnetization measurements at constant temperature in fields up to 7 T were also performed (Figure 3.41). At 2 K, the paramagnetic phase observable in the constant-field measurement dominates the response below 6 T, above which the metamagnetism observed in the undoped material is visible. The trend is still the same, that increasing the temperature lowers the field necessary to induce metamagnetism below the spin-reordering transition; above the transition, the response is entirely linear as expected of an antiferromagnet or paramagnet. No decrease in magnetization characteristic of diamagnetism was observed at any temperatures.

![Figure 3.41: Field dependence of magnetic susceptibility at various temperatures for Ba$_2$NdRu$_{0.9}$Cu$_{0.1}$O$_6$ sintered at 1400 °C.](image)
Electron spin resonance measurements were performed on the sample sintered at 1400 °C to look for possible signs of superconductivity in the material. Measurements were performed at 20.3 GHz on a sample placed at the bottom of a TE\(_{101}\) resonant cavity, and a piece of DPPH was used for calibration. With H\(_{rf}\) perpendicular to H\(_{dc}\) (Figure 3.42), a small magnetic resonance is observed, increasing as the temperature is decreased. The resonance peaks at a field of \(~6550\) Oe, typical of the well-characterized [29] paramagnet BaCuO\(_x\) at this frequency; however, this impurity was not evident in the x-ray diffraction results. With H\(_{rf}\) parallel to H\(_{dc}\) (Figure 3.43), no magnetic resonance is observed, indicating that the resonance observed in the other angular configuration is indeed a paramagnetic impurity. No sign of superconducting dissipation was observable in either angular orientation, casting doubt on the existence of a diamagnetic transition at \(~60\) K in the material.
Figure 3.42: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in $\text{Ba}_2\text{NdRu}_{0.9}\text{Cu}_{0.1}\text{O}_6$ sintered at 1400 °C as a function of temperature.
To further investigate the possibility of a diamagnetic transition in the material, an additional sample was prepared in an identical manner at 1400 °C with 20% Cu doping, intending to increase the carrier concentration and thus allow observation of a larger diamagnetic transition. SQUID magnetization data (Figure 3.44) collected at 10 Oe is similar to that of the x=0.1 samples sintered at lower temperatures, with the low-temperature magnetization dominated by the “apparent ferromagnetism” in the unknown magnetic phase. Paramagnetism is observed at lowest temperatures, and no change due to Cu doping in the magnetization is observable near the onset of the spin-reordering.
transition; the suggestion may be made that x=0.2 is above the solubility limit of Cu for this material.

The magnetic structure of Ba$_2$NdRuO$_6$ is very rich and warrants a more detailed study. The magnetic structure most consistent with the data is the following: the Ru$^{5+}$ order ferromagnetic sheets in the $ab$-plane and then stack antiferromagnetically about the $c$-axis at ~58 K and the Nd$^{3+}$ order in ferromagnetic sheets in the $ab$-plane at ~52 K, which stack antiferromagnetically at ~32 K. Smaller sintering temperature windows and thorough neutron diffraction measurements would help more thoroughly characterize the magnetic structure of the material. Doping with Cu does not explicitly show

Figure 3.44: Temperature dependence of magnetic susceptibility with H = 10 Oe for Ba$_2$NdRu$_{0.8}$Cu$_{0.2}$O$_6$ sintered at 1400 °C

The magnetic structure of Ba$_2$NdRuO$_6$ is very rich and warrants a more detailed study. The magnetic structure most consistent with the data is the following: the Ru$^{5+}$ order ferromagnetic sheets in the $ab$-plane and then stack antiferromagnetically about the $c$-axis at ~58 K and the Nd$^{3+}$ order in ferromagnetic sheets in the $ab$-plane at ~52 K, which stack antiferromagnetically at ~32 K. Smaller sintering temperature windows and thorough neutron diffraction measurements would help more thoroughly characterize the magnetic structure of the material. Doping with Cu does not explicitly show
superconducting behavior at any of the sintering temperatures tried, different from the case of the Ln=Dy system.

3.5 \( \text{Ba}_2\text{SmRu}_{1-x}\text{Cu}_x\text{O}_6 \)

Cu doping of Ln=Sm was also examined. Sm was chosen for study as it has the smallest magnetic moment of all the lanthanides, and with an ionic size very close to that of Nd\(^{3+}\), behavior common to both the Y-homologue and the Nd-homologue was expected with Cu doping of the system. The material is face-centered cubic [83] with space group \( Fm3m \), with lattice parameter \( a=8.4259 \text{ Å} \). Samples were prepared in an identical manner to the Ln=Dy samples, as per the formula

\[
2 \text{BaCO}_3 + 0.5 \text{Nd}_2 \text{O}_3 + (1-x) \text{RuO}_2 + x \text{CuO} \rightarrow \text{Ba}_2\text{SmRu}_{1-x}\text{Cu}_x\text{O}_6
\]

Two different sintering temperatures for \( x=0.1 \) were studied: 1300 °C and 1400 °C; 1400 °C was believed to be the optimal processing temperature of high-quality \( x=0 \) \( \text{Ba}_2\text{SmRuO}_6 \) based on experience with other members of the \( \text{Ba}_2\text{LnRuO}_6 \) family, and lower sintering temperatures were not tried due to the experience learned processing the Ln=Nd homologue. Powder x-ray diffraction data (Figure 3.45) indicates single phase material; all peaks could be sequenced as belonging to the cubic structure.
As anticipated from the small moment of the Sm$^{3+}$ ion, SQUID magnetization data at 10 Oe (Figure 3.46) on the x=0 material Ba$_2$SmRuO$_6$ is not as dramatic as that in the Ln=(Dy,Nd) homologues. The data is noisy, but in the inset an antiferromagnetic transition at ~60 K is clear, with a divergence between the zero field-cooled and field-cooled measurements below this temperature. At lowest temperatures, there is suggestion of a small paramagnetic component. The field-cooled warming measurement indicates very slight flux trapping up to the ~60 K transition, but it should be noted that this data is near the limit of sensitivity of the instrument. Kumar [83] reports comparable molar susceptibilities, but finds a ferromagnetic transition at ~42 K not observed in this sample;
in fact, Kumar's data is reminiscent of the Ln=Nd homologue when sintered at too low a temperature. Kumar's sintering temperature was 1140 °C so his observation of a transition at ~42 K is likely due to a magnetic impurity phase not observed in his x-ray diffraction measurements.

Doping at x=0.1 produces similar results to the Ln=Nd material. A 10% doping level was again chosen due to uncertainty of the solubility limit of Cu in the host material. Powder x-ray diffraction (Figure 3.47) performed on the samples sintered at two different temperatures shows bulk Ba$_2$SmRuO$_6$ phase with lattice parameters in agreement with published values, but there is an obvious impurity phase whose peaks
cannot be indexed as a precursor compound or as BaCuO$_x$. The magnitude of the main peaks steadily increases with sintering temperature, matching the expectation of better Sm-Ru spatial ordering in the material resulting from high temperature sintering. Little deviation in the peaks occur as a function of sintering temperature, implying the impurity peaks are a secondary phase and not a result of symmetry changing as the dopant Cu is included in the lattice. The peak locations and intensities loosely match those observed in the Ln=Nd homologue, but all appear at slightly larger angles, implying this impurity phase has a slightly smaller unit cell than that in the Ln=Nd homologue. This suggests that the impurity phase includes Sm as the Sm$^{3+}$ ion is only slightly smaller than the Nd$^{3+}$ ion. It is not known what this impurity phase is, but it clearly will only be a small percentage (5-10%) of the bulk sample.
The magnetization of doped samples sintered at two different temperatures shows features different from the undoped material. SQUID magnetization data as a function of temperature in an applied field of 10 Oe was collected on each sample. In the sample sintered at 1300 °C, the magnetic behavior (Figure 3.48) shows features not evident in the undoped material. In Figure 3.48 the scales are the same as in Figure 3.46. The data show a large difference between the zero field and field-cooled measurements starting above 50 K, and the inset indicates the antiferromagnetic transition temperature is ~49 K. Substantial paramagnetism is observed at low temperatures, and additionally, there is

![Figure 3.47: Powder x-ray diffraction on Ba$_2$SmRu$_{0.9}$Cu$_{0.1}$O$_6$ at different sintering temperatures. The indexed peaks are all O$_6$-phase. Impurity peaks are marked with red stars, and are not seen in the undoped material.](image)
significant trapped flux in the field-cooled warming measurement, persisting until ~55 K. The data show no evidence of a diamagnetic transition.

In the sample sintered at 1400 °C, the magnetic behavior (Figure 3.49) is similar. There is now evidence for a second magnetic transition at a temperature, at least in the field-cooled and field-cooled warming measurements, near the 42 K reported by Kumar [83]. This transition is much more clearly ferromagnetic than that in Figure 3.48. The inset shows the antiferromagnetic transition at 49 K much more clearly. Once again, there is no evidence of a diamagnetic transition.

![Diagram](image)

*Figure 3.48: Temperature dependence of magnetic susceptibility with \( H = 10 \, \text{Oe} \) for \( \text{Ba}_2\text{SmRu}_{0.9}\text{Cu}_{0.1}\text{O}_6 \) sintered at 1300 °C. The inset shows an enlargement of the ZFC and FC susceptibility near the magnetic transition.*
To further examine the behavior of this material, SQUID magnetization measurements on the sample sintered at 1400 °C at higher fields were also performed. In an applied field of 1000 Oe, the magnetic behavior (Figure 3.5) no longer includes the ferromagnetic-like response in the field-cooled warming. This is similar to the suppression of the ferromagnetic transition observed in the Ln=Nd response. The inset shows the antiferromagnetic transition clearly at 54 K, and a second transition near 40 K is still evident, but the magnitude of the transition is significantly smaller. The field-cooled warming response is smaller as well, again suggesting suppression of the ferromagnetic phase. Additionally, a magnetization measurement was carried out with an
applied field of 100 Oe up to 300 K; fitting the paramagnetic portion of this data over the range 52-300 K yields an effective magnetic moment of 4.251(2) μ\textsubscript{B}, comparable to published values on the material. It is not clear if this ferromagnetic-like magnetism is due to the bulk material or to an impurity phase.

The magnetic structure of Ba\textsubscript{2}SmRu\textsubscript{6} is complicated by the well-known mixing of the ground state of the Sm\textsuperscript{3+} ion with its low-lying excited states, and this as well as the spin-reordering transitions observed in other members of the Ba\textsubscript{2}LnRu\textsubscript{6} family may account for the magnetism in this material. Cu doping of this material failed to reproduce any of the behavior observed in other members of the series. There is no reported

![Figure 3.50: Temperature dependence of magnetic susceptibility with H = 1000 Oe for Ba\textsubscript{2}SmRu\textsubscript{0.9}Cu\textsubscript{0.1}O\textsubscript{6} sintered at 1400 °C. The inset shows a blowup of the ZFC and FC susceptibility near the magnetic transition.](image)
neutron diffraction on this material, and further characterization would help explain why Cu doping fails to generate superconductivity in the member of the Ba$_2$LnRuO$_6$ family formed with the Ln with the smallest magnetic moment.

3.6 O$_6$ Family Conclusions

There is clearly rich magnetic behavior across the family of Ba$_2$MnRuO$_6$ (M=Y, Ln), and high temperature (above 1300 °C) processing is essential to formation of high-quality samples to ensure M-Ru site order, a fact generally not reported in the literature. The observation of superconductivity in Ba$_2$YRu$_{1-x}$Cu$_x$O$_6$ may remain controversial, but the evidence for is quite clear, and the evidence against [12,51] falls apart under scrutiny; the LnBCO and YBCO compounds do not survive high temperature processing. No superconductivity is observed for the Ln=Gd homologue, which is expected due to magnetic scattering from the $l=0$ Gd$^{3+}$ ion. Superconductivity is suggested for the Ln=Dy homologue, which is interesting as this has the largest magnetic moment in the lanthanides, and the Ln shares a chemical layer with the Ru/Cu ions, which begs the question of how magnetic scattering does not explicitly prohibit superconductivity in this material. For the other members of the Ln series thus far examined, no evidence of superconductivity has been found; this may in part be due to the complicated magnetic structures found in the class of materials. There are reports [116] of superconductivity for Ln=Pr. The lack of superconductivity in the Ln=Sm compound was surprising as it
has the smallest magnetic moment of the trivalent lanthanides; this suggests that magnetic scattering in these materials (with the exception of Gd) may be of little consequence. It is possible that the trivalent ion size is critical, as Dy$^{3+}$ is close to Y$^{3+}$; this suggests further investigation into the Ln=(Ho,Er) would be of merit, as these are the two closest in size to Y$^{3+}$, although two data points are not a trend line. The magnetic ordering of the Y-homologue does not interfere with the superconductivity, despite the isotropic nature of the crystal; the data show this is the case as well for the Ln=Dy compound, where bulk magnetic ordering of Dy$^{3+}$, Cu$^{3+}$, and Ru$^{5+}$ occurs at the same temperatures as superconductivity. This is a rare case of a material without CuO$_2$ planes that simultaneously shows bulk superconductivity and magnetic order, and may even show superconductivity in the members with magnetically ordered lanthanides. These materials are distinctly different in character from YBCO and its derivatives in this regard and as such should receive much more attention in discussions of theoretical models of high-temperature superconductivity.
CHAPTER 4:
MAGNETISM AND SUPERCONDUCTIVITY IN La$_2$CuRuO$_6$

4.1 La$_2$CuRuO$_6$

Based on extensive experience with the processing of ruthenate double perovskites, and observation of superconductivity in several of these materials, it is natural to explore connections between materials of the form A$_2$BB'O$_6$ and the superconducting grandparent LnCuO$_4$; there are similarities as well as differences. Instead of distinct chemical metal ion layers as found in the O$_4$ and the rest of the high-$T_c$ cuprates, the O$_6$ materials have rock salt arrangement of metal ions; similar antiferromagnetism is observed though where ferromagnetic sheets are stacked antiferromagnetically. A variation of the ruthenate double perovskite that more closely resembles the O$_4$ is La$_2$CuRuO$_6$, and it was hoped that hole doping this system would result in superconductivity as was the case in La$_2$CuO$_4$ and is the case with Ba$_2$YRuO$_6$.

The undoped material is monoclinic with space group $P2_1/n$ and has unit cell parameters $a=5.5897$ Å, $b=5.7550$ Å, $c=7.7584$ Å and $\beta=90.15^\circ$. The Ru and Cu order spatially in a rock salt manner, forming a CuRuO$_4$ layer, and the structure is shown in Figure 4.1. There is little reporting on this material in the literature beyond the work of Battle et al.
Successfully generating superconducting material requires optimally formed undoped material, as well as a working knowledge of the structural and magnetic behavior of the undoped material. The optimal synthesis temperature of this material was not known; Battle reports sintering at 1150 °C for several days results in single-phase material, but also claims of 22% Ru occupancy on the Cu sites in the material. From experience with processing other ruthenates where B-B' site order is essential, it was obvious that Battle's synthesis procedure would yield this. An investigation into the synthesis of this material was carried out in an effort to generate and characterize optimal material.
Figure 4.1: One quarter of the unit cell of La$_2$CuRuO$_6$. Optimally formed material has the Cu and Ru occupying adjacent sites of a rock salt lattice; poor quality samples will have some Ru/Cu site mixing.
The material $\text{La}_2\text{CuRuO}_6$ is formed by a standard solid-state chemical reaction. Stoichiometric amounts of dried out precursors were weighed out as per the formula

$$\text{La}_2\text{O}_3 + \text{CuO} + \text{RuO}_2 \rightarrow \text{La}_2\text{CuRuO}_6$$

and thoroughly mixed with a clean agate mortar and pestle, adhering to the 30 minutes of grinding per 4 grams of powder rule. As $\text{La}_2\text{O}_3$ is very hygroscopic, it was dried at 900 °C immediately prior to usage; weighing out amounts of $\text{La}_2\text{O}_3$ still above 100 °C was found to produce better materials. As there are no carbonates in this synthesis route, it was thought that the intermediate heat treatment step in the ruthenate processing methods used for $\text{Ba}_2\text{LnRuO}_6$ would not be necessary. Ground sample powder was pressed into 1 g pellets using a 1 cm die in a hydraulic press at 10000 PSI; these pellets were then stacked on a pile of ground powder in an alumina boat, which was then sealed in a tube furnace under a mixture of 70% Ar, 30% O$_2$ flowing gas. The tube was rapidly heated to 500 °C, then ramped up to 1400 °C over a 4 hour period, and held at that temperature for 12 hours. The oven was then ramped down to 500 °C over a 4 hour period, and then allowed to cool to room temperature. The characterization of these materials showed that skipping the intermediate heat treatment produced poor quality material, and no data are shown.

Additional samples were prepared identical to the above method except that prior to sintering, a 24 hour heat treatment at 970 °C in a box furnace under atmosphere was performed. Following this heat treatment, the samples were again thoroughly ground, pressed into pellets, and sintered as above, at several different temperatures. Six different sintering temperatures were studied: 1100 °C, 1200 °C, 1300 °C, 1350 °C, 1400 °C, and
1450 °C. The processing of all samples was identical except for the variation in final sintering temperature, and sintered samples were not exposed to air until cooled to room temperature inside the tube furnace under gas control. Samples were typically cut from the center of the middle pellet in a stack for characterization.

Powder x-ray diffraction was performed on each sample, and all show the same crystal structure. Rietveld refinement on the sample sintered at 1300 °C yields a monoclinic structure with lattice parameters $a=b=5.6$ Å, $c=7.6$ Å, comparable to Battle's published results. A few very small peaks that could not be indexed by the monoclinic bulk phase appear in the samples sintered at 1200 °C and 1300 °C; it is not clear what these impurity phases are. Neither La$_2$CuO$_4$ or La$_2$RuO$_5$ could at all be indexed in any of the materials; both are magnetic compounds [133]. Literature searches indicate that there are no other reported magnetic phases consisting of La, Cu and Ru. Thus, any magnetic behavior observed in the material is due to the La$_2$CuRuO$_6$ phase, to the limit of x-ray diffraction sensitivity (~2-3%). A limited range of the powder x-ray diffraction on all samples is shown in Figure 4.2. Increased sintering temperature has the effect of sharpening all diffraction peaks, and at highest temperatures, a slight shift towards smaller angle implying a slight stretching of the lattice. Peak intensity and width at low sintering temperatures is poor; the peak widths are mostly constant for samples sintered at or above 1300 °C. Rietveld refinement shows the slight variation in peak heights in the higher temperature materials coming from increased Cu-Ru spatial order, with the best occupancies found in the samples sintered at 1350 °C and 1400 °C.
To confirm that any possible magnetic (or superconducting) behavior was not due to accidental formation of \( \text{La}_2\text{CuO}_4 \), good quality samples of \( \text{La}_2\text{CuO}_4 \) were synthesized at 900 °C following the method of Grant et al. [54]. In parallel to this, stoichiometric amounts of dried \( \text{La}_2\text{O}_3 \) and \( \text{CuO} \) were thoroughly mixed and then subjected to the same synthesis conditions as the \( \text{La}_2\text{CuRuO}_6 \) samples. The \( \text{La}_2\text{CuO}_4 \) pellets did not survive high temperature processing; in fact, the alumina boat did not either. The pellets almost entirely melted in the furnace, and the boat had to be shattered to isolate a lump of surviving material. Powder x-ray diffraction performed on both optimal \( \text{La}_2\text{CuO}_4 \) and the

\[ \text{La}_2\text{CuRuO}_6 \]
melted material clearly show that the leftover compound is *not* La$_2$CuO$_4$. This was anticipated as reports suggest that La$_2$CuO$_4$ undergoes a peritectic breakdown at 1367 °C [18]; it is very unlikely that any magnetic or superconducting behavior observed in this class of materials is due to accidental synthesis of minority-phase La$_2$CuO$_4$.

*Figure 4.3:* Powder x-ray diffraction on single-phase La$_2$CuO$_4$ optimally processed at 900 °C and La$_2$CuO$_4$ sintered at 1400 °C. Clearly no La$_2$CuO$_4$ survived high temperature processing.
The magnetization of samples sintered at different temperatures show consistent antiferromagnetic behavior with published data [14], with the exception that there is substantially more “apparent ferromagnetism” observed in all samples; the published data do not show bulk ferromagnetism. SQUID magnetization measurements were performed on all samples with a field of 10 Oe. It was technically challenging to perform these measurements, as samples of this material are quite surprisingly sensitive to cooling in a background field smaller than 0.5 Oe; great care was given to attempt to minimize the residual field in the superconducting magnet. The reason for this extreme sensitivity to background fields is not clear. In the sample sintered at 1100 °C, SQUID magnetization data (Figure 4.4) show a divergence in the zero field-cooled and field-cooled measurements starting at ~20 K, with an antiferromagnetic transition evident in both measurements at 12.5 K. In the field-cooled warming or remnant magnetization measurement, there is substantial trapped flux persisting to 20 K or higher. This is once again an observation of “apparent ferromagnetism”; the magnetization appears antiferromagnetic in a zero field-cooled measurement, and ferromagnetic in a field-cooled measurement. The vertical scale is intentionally set to be consistent among the next several susceptibility figures in order to highlight the change in the magnetic properties as a function of sample processing temperature; the inset in Figure 4.4 shows an expansion of the vertical scale illustrating the magnetic behavior more clearly.
In the sample sintered at 1200 °C, similar magnetic behavior is observed in SQUID magnetization data (Figure 4.5), but with a susceptibility approximately 2.5 times larger. Again there is a divergence in the zero field and field-cooled measurements, and again the zero field-cooled measurement indicates antiferromagnetism whereas the field-cooled measurement indicates ferromagnetism. The antiferromagnetic transition has been pushed higher, to ~13.5 K. The field-cooled warming data again show flux trapping up to ~20 K.

Figure 4.4: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_2CuRuO_6$ sintered at 1100 °C. The inset shows an expansion of the vertical scale, highlighting the transitions.
In the sample sintered at 1300 °C, the magnetic behavior is similar, but there are subtle changes in the SQUID magnetization data (Figure 4.6). The antiferromagnetic transition in the zero field-cooled magnetization measurement still occurs at 13.5 K, but the transition magnitude is much narrower and is approximately twice as high. Interestingly, the ferromagnetic response in the field-cooled measurement is larger, but did not increase by this factor of two. The divergence between the two measurements now happens closer to the antiferromagnetic transition temperature. In the field-cooled warming measurement, the trapped flux persists to a somewhat lower temperature.

Figure 4.5: Temperature dependence of magnetic susceptibility with \( H = 10 \text{ Oe} \) for \( \text{La}_2\text{CuRuO}_6 \) sintered at 1200 °C

In the sample sintered at 1300 °C, the magnetic behavior is similar, but there are subtle changes in the SQUID magnetization data (Figure 4.6). The antiferromagnetic transition in the zero field-cooled magnetization measurement still occurs at 13.5 K, but the transition magnitude is much narrower and is approximately twice as high. Interestingly, the ferromagnetic response in the field-cooled measurement is larger, but did not increase by this factor of two. The divergence between the two measurements now happens closer to the antiferromagnetic transition temperature. In the field-cooled warming measurement, the trapped flux persists to a somewhat lower temperature.
In the material sintered at 1350 °C, more dramatic changes have occurred in the magnetic behavior (Figure 4.7). The magnetic behavior is similar, but the transition temperature has been increased to 18.5 K. The antiferromagnetic transition visible in the zero field-cooled measurement is slightly larger, and the ferromagnetic response in the field-cooled measurement is substantially larger. This is likely a direct result of better Cu-Ru spatial ordering. The field-cooled warming measurement shows flux trapping to nearly 25 K, and almost co-linear with the ferromagnetism; an anticipated response from a good ferromagnet.
In the sample sintered at 1400 °C, the SQUID magnetization data (Figure 4.8) again show increased magnetic behavior. The antiferromagnetic transition evident in the zero field-cooled measurement now peaks at 19 K, and is slightly sharper. The ferromagnetic response evident in the field-cooled measurement is also larger; once again, this is evidence for increased Cu-Ru spatial ordering. The field-cooled warming measurement is essentially identical to the field-cooled measurement at low temperatures, and only deviates near the transition temperature, trapping flux until ~22.5 K; this is clearly a ferromagnetic response.

Figure 4.7: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_2CuRuO_6$ sintered at 1350 °C

In the sample sintered at 1400 °C, the SQUID magnetization data (Figure 4.8) again show increased magnetic behavior. The antiferromagnetic transition evident in the zero field-cooled measurement now peaks at 19 K, and is slightly sharper. The ferromagnetic response evident in the field-cooled measurement is also larger; once again, this is evidence for increased Cu-Ru spatial ordering. The field-cooled warming measurement is essentially identical to the field-cooled measurement at low temperatures, and only deviates near the transition temperature, trapping flux until ~22.5 K; this is clearly a ferromagnetic response.

163
In the final sample sintered at 1450 °C, a decrease in sample quality in terms of magnetic transitions is evident. The SQUID magnetization data (Figure 4.9) show a decrease in the antiferromagnetic transition temperature visible in the zero field-cooled measurement to ~17 K, and the magnitude of the transition is diminished considerably. The ferromagnetic response observed in the field-cooled measurement is also diminished substantially. The field-cooled warming measurement still shows flux trapping, but not persisting to the temperature observed in the sample sintered at 1400 °C.

*Figure 4.8: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_2CuRuO_6$ sintered at 1400 °C*
The magnetic behavior of these materials suggest that the optimal sintering conditions are close to 1400 °C, with clear limits put at 1350 °C and 1450 °C; this temperature window produces samples that are the most magnetic at the highest temperatures. It should be pointed out that in the published data on this material, a molar magnetic susceptibility at the cusp of the antiferromagnetic transition of ~0.8 emu/mol is reported, with the transition occurring at 12 K; here, the sample sintered at 1400 °C shows a molar magnetic susceptibility at the cusp of the antiferromagnetic transition of ~8.37 emu/mol at a temperature of 19 K, both indicating substantial improvement in material quality and Cu-Ru spatial ordering. A comparison of the zero field-cooled
magnetization measurements on the six samples summarizes the progression of quality as a function of sintering temperature in Figure 4.10.

![Figure 4.10: Temperature dependence of ZFC magnetic susceptibility with H = 10 Oe in all samples of La$_2$CuRuO$_6$](image)

To further understand the magnetic behavior of La$_2$CuRuO$_6$, several additional SQUID magnetization measurements were performed on the sample sintered at 1400 °C. This sample was chosen as it showed the largest and highest temperature transitions. Magnetization measurements at 7 T (Figure 4.11) show no additional transitions up to 300 K, and fail to show any antiferromagnetism; the zero field-cooled and field-cooled magnetization measurements are almost identical. Remnant magnetization measurements were not performed as it is difficult to reset the superconducting magnet to exactly zero
field immediately following a field strength above 1 T. A fit to the Curie-Weiss law (as described in Appendix C) in the paramagnetic regime over the temperature range $40 \, \text{K} < T < 300 \, \text{K}$ yields an average effective magnetic moment of $2.57 \, \mu_B$ per transition metal ion, and a Weiss $\theta$ of -5.89 K, indicating ferromagnetic exchange dominates at high fields; this could be expected as the high field has likely collapsed the antiferromagnetic spin system.

Figure 4.11: Temperature dependence of magnetic susceptibility with $H = 7 \, \text{T}$ for $\text{La}_2\text{CuRuO}_6$ sintered at $1400 \, ^\circ\text{C}$. No transitions are evident at higher temperatures.
Additional temperature-dependent SQUID magnetization measurements were performed on the same sample at 100 Oe, 1000 Oe, and 1 T. In the measurements performed at 100 Oe, the data (Figure 4.12) show no substantial difference in the magnetic behavior. The susceptibility is smaller by nearly a factor of two, but the overall response is similar. The field-cooled warming measurement indicates flux trapping persists to a temperature lower than that in the measurement at 10 Oe.

Figure 4.12: Temperature dependence of magnetic susceptibility with $H = 100$ Oe for $La_2CuRuO_6$ sintered at 1400 °C
In the measurements performed at 1000 Oe, the data (Figure 4.13) show the susceptibility is reduced by a factor of about seven, and the antiferromagnetic response in the zero field-cooled measurement has been suppressed. This is likely due to the field inducing severe canting of the antiferromagnetic lattice. In the field-cooled warming measurement, the flux trapping now persists to the same temperature as in lower fields, but is also reduced by a factor of nearly eight.

Figure 4.13: Temperature dependence of magnetic susceptibility with $H = 1000$ Oe for $La_2CuRuO_6$ sintered at 1400 °C
In the SQUID magnetization measurement performed at 1 T, the data (Figure 4.14) no longer show the antiferromagnetic behavior in the zero field-cooled measurement, and the zero field and field-cooled measurements are essentially identical, suggesting a complete collapse of the antiferromagnetic state. The susceptibility is again severely diminished in scale, and the field-cooled warming data are much smaller than the field-cooled data. This may indicate that the field induced ferromagnetism is not stable, and that the antiferromagnetism is reestablished upon removal of the field, such that all that can contribute to flux trapping is the ferromagnetic phase.

Figure 4.14: Temperature dependence of magnetic susceptibility with $H = 1 \, T$ for $La_2CuRuO_6$ sintered at 1400 °C
Further SQUID magnetization measurements as a function of field at fixed temperature were also performed on this sample; the results are shown in Figure 4.15. At 2 K, the response is linear, indicating antiferromagnetism, up until ~5000 Oe, where the antiferromagnetism collapses quickly. At 15 K, closer to the transition temperature, the antiferromagnetic lattice is not as stiff, and as such is collapsed at a much lower field. In neither case is saturation reached; it is not clear why. It is possible that there are two distinct magnetic sublattices, both ordering antiferromagnetically, of which one remains antiferromagnetic in a field and the other collapses into ferromagnetism; that would explain why saturation is never reached. However, this is not consistent with the high-field temperature dependency; at 7 T, the system is a ferromagnet.

Figure 4.15: Field dependence of magnetic susceptibility for La$_2$CuRuO$_6$ sintered at 1400 °C. In both measurements there is a trend towards ferromagnetic saturation.
Electron spin resonance measurements were also performed to characterize the magnetic behavior of this material. Samples sintered at 1350 °C and 1400 °C were both studied at a frequency of 20.3 GHz. In both cases, the samples were mounted on the bottom of a TE$_{101}$ resonant cavity, and a piece of DPPH was used for field calibration. In both samples, microwave resonance was observed for $H_{rf}$ perpendicular to $H_{dc}$ (Figure 4.16, Figure 4.18) as well as $H_{rf}$ parallel to $H_{dc}$ (Figure 4.17, Figure 4.19), indicating antiferromagnetic or at least weakly ferromagnetic resonance [132]. The observed microwave resonances peak at low field and begin at about 36 K, peaking at ~18 K, the magnetic transition temperature. There is no resonance observed at temperatures above 36 K through room temperature. As the Ru is known to be ESR silent when in octahedral coordination with oxygen [20], this must be magnetic resonance due to ordered Cu.
Figure 4.16: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in $\text{La}_2\text{CuRuO}_6$ sintered at 1300 °C as a function of temperature. No high temperature resonance is observed.
Figure 4.17: Magnetic resonance at 20.3 GHz with $H_n$ parallel to $H_{dc}$ in La$_2$CuRuO$_6$ sintered at 1300 °C as a function of temperature. No high temperature resonance is observed.
Figure 4.18: Magnetic resonance at 20.3 GHz with $H_{rf}$ perpendicular to $H_{dc}$ in $La_2CuRuO_6$ sintered at 1400 °C as a function of temperature
The material La$_2$CuRuO$_6$, when made properly, is an ordered antiferromagnet with transition temperature $T_N = 19$ K. High processing temperatures for short durations is essential to formation of well-ordered material, a lesson learned from experience with Ba$_2$YRuO$_6$. The type of antiferromagnetic ordering in this material is not clear; however, it is clear that both Cu$^{2+}$ and Ru$^{4+}$ order at the same temperature. Field-dependent susceptibility measurements at constant temperature suggest the possibility that the two sublattices act independently of each other; however, the temperature dependence of the susceptibility in high fields rules this out. In the layered O$_8$/O$_{10}$ materials, the “apparent

Figure 4.19: Magnetic resonance at 20.3 GHz with $H_{rf}$ parallel to $H_{dc}$ in La$_2$CuRuO$_6$ sintered at 1400 °C as a function of temperature
ferromagnetism” observable in magnetization data is caused by rotation of the direction of magnetization of ferromagnetic CuO₂ planes; here, it is not clear if the magnetism is caused by canting away from an antiferromagnetic axis, or from rotation of ferromagnetic planes, although the magnitude of the magnetizations observed suggest the latter. The microwave resonance suggests antiferromagnetic Cu ordering, and is evidence against a spin-glass system as the relaxation times are characteristic of conventional magnetic order.

The material La₂CuRuO₆ is, with ideal oxygen content, a charge-balanced insulator, and as such, should not superconduct as it has no free carriers that can pair up. Hole-doping on the La site generates superconductivity in the homologue La₂CuO₄, and electron-doping on the Nd site in Nd₂CuO₄ has the same effect [134]; it is possible that in this material, doping will also induce superconductivity as the system a hybrid between several superconducting families: the O₄, the O₈/O₁₀, and Ba₂YRuO₆.

4.2 Hole Doped: La₂₋ₓ(Sr,Ba)ₓCuRuO₆

Hole doping results in superconductivity in the La₂CuO₄ system, and as such, this doping was the charge type first examined in the La₂CuRuO₆ system. Holes were introduced by partial substitution of lower-valence Sr²⁺ or Ba²⁺ for La³⁺. The processing temperature for ideal formation of the undoped material was shown to be ~1400 °C; however, as the ideal processing temperature for good inclusion of the dopant was not
known, samples were synthesized with processing temperatures in the temperature range 1300-1450 °C.

For Sr doping, x=0.1 was chosen. The doping was provided by SrCO$_3$ in the doped variation of the undoped chemical formula,

$$0.95La_2O_3 + 0.1SrCO_3 + CuO + RuO_2 \rightarrow La_{1.9}Sr_{0.1}CuRuO_6$$

following the exact same synthesis parameters as the undoped material. Samples were sintered at the following temperatures: 1300 °C, 1350 °C, 1400 °C, and 1450 °C. Following synthesis, powder x-ray diffraction was performed on each sample, and all (Figure 4.20) are similar to the monoclinic structure of the undoped material. No peaks could be indexed with SrCO$_3$, indicating that the Sr substituted for La. Interestingly, at the highest sintering temperature some of the diffraction peaks begin to split, indicating a slight change in the symmetry; the cause of this is not clear, as it does not occur in the undoped material. If it were due to Sr inclusion in the lattice, it would be evident at all temperatures, as no impurity phases are seen.
SQUID magnetization measurements at 10 Oe on the samples (Figure 4.21, Figure 4.22, Figure 4.33, Figure 4.34) all show a sharpened antiferromagnetic transition, with severely diminished susceptibility as compared to the undoped material. The data resemble that of the low-quality published susceptibility [14] data; it is possible that introducing the Sr generated enough Cu-Ru site disorder to affect the magnetism. No evidence for any superconductivity was observed.

Figure 4.20: Powder x-ray diffraction on \( \text{La}_{1.9}\text{Sr}_{0.1}\text{CuRuO}_6 \) at different sintering temperatures. No \( \text{SrCO}_3 \) is observable.
Figure 4.21: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.9}Sr_{0.1}CuRuO_6$ sintered at 1300 °C

Figure 4.22: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.9}Sr_{0.1}CuRuO_6$ sintered at 1350 °C
Figure 4.23: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.9}Sr_{0.1}CuRuO_6$ sintered at 1400 °C

Figure 4.24: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.9}Sr_{0.1}CuRuO_6$ sintered at 1450 °C
For Ba doping, in light of the failure of observation of any diamagnetism with Sr doping, x=0.2 was chosen. The doping was provided by BaCO$_3$ in the doped variation of the undoped chemical formula,

$$0.9 \text{La}_2O_3 + 0.2 \text{BaCO}_3 + \text{CuO} + \text{RuO}_2 \rightarrow \text{La}_{1.8} \text{Ba}_{0.2} \text{CuRuO}_6 + 0.3O$$

following the exact same synthesis parameters as the undoped material. Samples were sintered at the following temperatures: 1300 °C, 1350 °C, 1400 °C, and 1450 °C. Following synthesis, powder x-ray diffraction was performed on each sample, and all (Figure 4.25) are similar to the monoclinic structure of the undoped material. No peaks could be indexed with BaCO$_3$, indicating that the doping was successful. There is a slight peak location shift indicating stretching of the lattice to accommodate the large Ba$^{2+}$ ion.

\[\text{Figure 4.25: Powder x-ray diffraction on } \text{La}_{1.8} \text{Sr}_{0.2} \text{CuRuO}_6 \text{ at different sintering temperatures. No BaCO}_3 \text{ is observable.}\]
SQUID magnetization measurements at 10 Oe on the samples (Figure 4.26, Figure 4.27, Figure 4.28, Figure 4.29) all show a sharpening of the antiferromagnetic transition, and a lowering of the transition temperature. The data resemble that of the Sr-doped material, again suggesting that introducing the Ba generated enough Cu-Ru site disorder to affect the magnetism. The susceptibility is orders of magnitude smaller in the Ba doped material than in the undoped material; this again suggests poor Cu-Ru site order. There is again no evidence of diamagnetism or superconductivity; hole doping has only made the material more disordered, and thus, less magnetic.

![Figure 4.26: Temperature dependence of magnetic susceptibility with H = 10 Oe for La$_{1.8}$Ba$_{0.2}$CuRuO$_6$ sintered at 1300 °C](image)
Figure 4.27: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.8}Ba_{0.2}CuRuO_6$ sintered at 1350 °C

Figure 4.28: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $La_{1.8}Ba_{0.2}CuRuO_6$ sintered at 1400 °C
4.3 Electron Doped: $\text{La}_{2-x}(\text{Ce, Th})_x\text{CuRuO}_6$

Following the hole doping experiments, electron doping was attempted. Electrons were introduced by partial substitution of higher-valence Ce or Th for La. As the ideal processing temperature for inclusion of the dopant was not known, synthesis parameters in the temperature range 1300-1450 °C were tried. Extra care had to be taken in the processing of the Th containing sample due to the health hazard of this α emitter.

For Ce doping, $x=0.2$ was chosen. The doping was provided by CeO$_2$ in the doped variation of the undoped chemical formula,
following the exact same synthesis parameters as the undoped material. Samples were sintered at the following temperatures: 1300 °C, 1350 °C, 1400 °C, and 1450 °C. Due to an accidental furnace failure, the samples sintered at 1350 °C and 1450 °C were never brought to high temperature; as a result, samples sintered at 1300 °C and 1400 °C were the only samples characterized. Following synthesis, powder x-ray diffraction was performed on each sample, and both (Figure 4.30) are similar to the monoclinic structure of the undoped material. No peaks could be indexed with CeO$_2$, indicating that the dopant was substituted for La. However, diffraction peaks appear that are not in the undoped material; it is most likely that the peak at ~28° is due to a changing in the symmetry of the lattice and not due to an impurity phase, as few additional new peaks appear. The [220] peak at ~45.5° is split in the sample sintered at 1300 °C, but not in the sample sintered at 1400 °C; the same is true of the [111] peak at ~25°. The unknown peak at ~28° also shifts angle in each sample, and the peak at ~35° shifts angle as well. There is a clear processing temperature dependence to the crystal structure of the material, and it is not evident from x-ray diffraction alone what, if either, processing temperature results in the best inclusion of Ce in the lattice and thus the best doping.
SQUID magnetization measurements at 10 Oe on the two samples (Figure 4.31, Figure 4.32) are similar to that of the undoped material, not showing the sharpening of the antiferromagnetic transition observed in the hole-doped materials. The susceptibility is comparable to that in the undoped material. This suggests that the introduction of Ce did not generate the Cu-Ru site disorder apparent in the hole-doped materials. Interestingly, the sample sintered at 1300 °C (Figure 4.31) shows a transition temperature slightly above that of the undoped material processed at the same temperature; it is not clear if this is due to enhancement resulting from doping, or from superior processing of

Figure 4.30: Powder x-ray diffraction on La$_{1.8}$Ce$_{0.2}$CuRuO$_6$ at different sintering temperatures. The indexed peaks are those distinctly belonging to the monoclinic phase O$_6$. No CeO$_2$ is observable.
the doped sample. In the sample sintered at 1400 °C (Figure 4.32), the nominal processing temperature for the undoped material, the transition temperature is slightly depressed and the transition is widened compared to the undoped material processed at that temperature. The magnitude of the magnetization is also smaller by nearly a factor of three. When the field is increased to 1000 Oe (Figure 4.33), the same collapse of the antiferromagnetism into ferromagnetism is observed that was seen in the undoped material. No evidence of diamagnetism or superconductivity is observed. Electron doping with Ce has not substantially changed the magnetic behavior of the material.

Figure 4.31: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for La$_{1.8}$Ce$_{0.2}$CuRuO$_6$ sintered at 1300 °C
Figure 4.32: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for La$_{1.8}$Ce$_{0.2}$CuRuO$_6$ sintered at 1400 °C

Figure 4.33: Temperature dependence of magnetic susceptibility with $H = 1000$ Oe for La$_{1.8}$Ce$_{0.2}$CuRuO$_6$ sintered at 1400 °C
For Th doping, x=0.2 was again chosen. The doping was provided by ThO$_2$ in the doped variation of the undoped chemical formula,

$$0.9 \text{La}_2\text{O}_3 + 0.2 \text{ThO}_2 + \text{CuO} + \text{RuO}_2 \rightarrow \text{La}_{1.8} \text{Th}_{0.2} \text{CuRuO}_6$$

following the exact same synthesis parameters as the undoped material. Due to the health hazards involved in processing materials containing α-emitting Th, precautions were taken. All grinding was done in a clean agate mortar and pestle while wearing latex gloves extending over long sleeves, a laboratory jacket, dust mask, and safety goggles to prevent exposure of bare skin to Th. It was felt that grinding inside a glove box was an unnecessary precaution. Samples were sintered at the following temperatures: 1300 °C, 1350 °C, 1400 °C, and 1450 °C. Following synthesis, powder x-ray diffraction was performed on each sample, and all (Figure 4.34) are similar to the monoclinic structure of the undoped material. Several peaks that could be indexed by ThO$_2$ and not by La$_{1.8}$Th$_{0.2}$CuRuO$_6$ are visible, indicating the substitution was not very successful if at all. The [111] and [220] lines again show splitting as a function of temperature, indicating a changing of the symmetry of the crystalline lattice; however, in light of the presence of significant ThO$_2$ peaks, this splitting of peaks cannot be directly attributed to the dopant entering and thus stretching the lattice. The failure of doping is likely due to ThO$_2$ having the highest melting temperature of all oxides (~3300 °C) [59]; with this extremely tight binding, the anticipated solid-state chemical reaction simply does not occur.
SQUID magnetization measurements at 10 Oe on the samples (Figure 4.35, Figure 4.36, Figure 4.37) all show behavior similar to that of the undoped material. These samples were found to be extremely sensitive to background fields; cooling the samples in a field of ~0.1 Oe would change the magnetic behavior. To give this number some scale, it should be pointed out that the magnetic field of the earth is ~0.5 Oe. Interestingly, the sample sintered at 1300 °C was once again magnetically far superior to the undoped material processed at the same temperature; again, it is not clear if the doping enhanced the magnetism, or if the doped material was simply more carefully handled than the undoped material. No unique magnetic behavior was observed in these
samples that was not seen in the undoped materials; the scale of the susceptibility and the value of the transition temperatures are comparable between doped and undoped, with the exception of the sample sintered at 1400 °C.

Figure 4.35: Temperature dependence of magnetic susceptibility with $H = 10 \text{ Oe}$ for $La_{1.8}Th_{0.2}CuRuO_6$ sintered at 1300 °C
Figure 4.36: Temperature dependence of magnetic susceptibility with $H = 10 \text{ Oe}$ for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at $1350^\circ \text{C}$

Figure 4.37: Temperature dependence of magnetic susceptibility with $H = 10 \text{ Oe}$ for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at $1450^\circ \text{C}$
Collecting SQUID magnetization data on the sample sintered at 1400 °C proved to be quite challenging due to the surprising sensitivity of the material to background fields. Several measurements indicated the presence of net negative magnetization (Figure 4.38), implying superconductivity. Careful measurements with a negative applied field also resulted in positive magnetization, as would be expected of a superconductor. Ultimately however zero field-cooled measurements (Figure 4.39) cooled from 300 K with very carefully calibrated minimized background fields failed to demonstrate the net negative magnetization initially seen, suggesting the net negative magnetization was actually due to trapped flux in the ferromagnetic state of the material, induced in a background field of ~0.1 Oe or less. It is not clear how such a minimal field can affect the magnetic state of the material; this behavior was observed throughout the doped and undoped series of materials, but was most prevalent in the Th-doped material. No additional transitions were observed in the material in low or high fields up to 300 K, indicating that the flux trapping is caused by the low temperature transition only. In a field of 7 T (Figure 4.40), the antiferromagnetic state visible in the zero field-cooled measurements has collapsed into ferromagnetism, just as in the case of the undoped material; the susceptibility is of comparable value at lowest temperatures. Aside from the anomalously high sensitivity to background fields, no additional magnetic behavior was observed in the material due to doping. The net negative magnetization is not due to superconductivity in the sample, and no other evidence for superconductivity in the sample was observed; as such, no further study of the material was performed.
Figure 4.38: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at $1400$ °C. No transitions are observable above $\sim 19$ K. The inset shows an expansion of the low-temperature region, showing the net negative magnetization.
Figure 4.39: Temperature dependence of zero field-cooled magnetic susceptibility with $H = 10$ Oe for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at 1400 °C with very careful calibration of the background field to less than 0.1 Oe. The net negative magnetization no longer occurs.
Figure 4.40: Temperature dependence of magnetic susceptibility with $H = 7$ T for $\text{La}_{1.8}\text{Th}_{0.2}\text{CuRuO}_6$ sintered at 1400 $^\circ$C. The antiferromagnetic state has collapsed into ferromagnetism, and no additional transitions are visible.

4.4 $\text{La}_2\text{CuRuO}_6$ Family Conclusions

Optimization of the synthesis of the material $\text{La}_2\text{CuRuO}_6$ was evident in both the magnetization and diffraction data collected on a variety of samples. There is very interesting magnetic behavior in this class of materials that to date has not been reported on in the literature, and extensive neutron diffraction measurements would help explain
the antiferromagnetic order of the Ru$^{4+}$ and Cu$^{2+}$ ions in this material, and hopefully would help explain why these materials are *extremely* sensitive to background fields, a trait not shared among the other perovskite ruthenates. The origin of the “apparent ferromagnetism” in this material is likely due to Cu planar magnetism, but without neutron diffraction, this is not clear. This class of materials is a hybrid of sorts between the superconducting O$_8$/O$_{10}$ systems and the superconducting Ba$_2$YRuO$_6$ system; however, the doping study carried out showed no evidence for superconductivity whatsoever. The doping study has illustrated the importance of Cu-Ru disorder, a point recognized but not studied in the literature [14]. There is rich behavior in these materials, but no superconductivity with these doping attempts; it is not clear that changing the dopant concentrations would generate superconductivity.
CHAPTER 5:

MAGNETISM AND SUPERCONDUCTIVITY IN La$_2$CuMO$_6$

5.1 La$_2$CuMO$_6$

In an effort to further understand the origins of the “apparent ferromagnetism” in the La$_2$CuRuO$_6$ system, and to provide another test case for superconductivity, a logical followup is to remove the issue of Ru magnetism. There are at least eleven known metal ions that can occupy the M spot in La$_2$CuMO$_6$ [4,11,123,124], but not all form a rock salt structure with alternating Cu-M ions; in most, the distribution of ions is random, resulting in uninteresting magnetic behavior. It was proposed that the experience gained in synthesizing high-quality La$_2$CuRuO$_6$ would be beneficial in starting an expanded survey into similar materials. Four different metal ions were examined: Ti, Ir, Nb, Sn; all are nonmagnetic, and the goal was to isolate the Cu magnetic behavior by removing the issue of the magnetism of Ru as well as to improve the magnetic properties of other materials in the family La$_2$CuMO$_6$ as was possible in the M=Ru system.
5.2 La$_2$CuNbO$_6$

For M=Nb, synthesis of the compound La$_2$CuNbO$_6$ was attempted. M=Nb is an obvious choice given the experience with the O$_8$/O$_{10}$ families of materials, but there are no published reports on the compound. Samples were prepared in a manner identical to the processing of the Ru homologue, as per the formula

$$La_2O_3 + CuO + Nb_2O_5 \rightarrow La_2CuNbO_6$$

A sintering temperature of 1450 °C was tried as a guess based on experience with the Ru homologue. Nb does have a 4+ valence, but the 3+ and 5+ states are far more common, so this chemical formula does not necessarily represent the actual reaction that takes place at high temperatures. Samples sintered at 1450 °C were very porous and showed significant signs of melting at high temperature. Powder x-ray diffraction measurements performed on samples showed no peaks that could be indexed by either precursor chemicals or the monoclinic or orthorhombic structures found in most La$_2$CuMO$_6$ materials; the data suggest multiple phases, none of which were anticipated. It is likely that the reaction is impossible as the Nb ion never becomes 4+, and thus the compound is not formable.
5.3 \( \text{La}_2\text{CuTiO}_6 \)

For \( M=\text{Ti} \), synthesis of the compound \( \text{La}_2\text{CuTiO}_6 \) was attempted. The existence of \( \text{La}_2\text{CuTiO}_6 \) was first reported in 1977 [112], predating the discovery of high-\( T_c \) superconductors by nearly a decade, and before the realization of the interesting magnetic properties of mixed-metal double perovskites. A more recent study by Anderson et al. [3] indicates that the material is orthorhombic with space group \( Pbnm \), with lattice parameters \( a=5.587 \, \text{Å}, b=5.616 \, \text{Å}, \) and \( c=7.842 \, \text{Å} \). Samples were prepared in a manner identical to the Ru homologues, as per the formula

\[
\text{La}_2\text{O}_3+\text{CuO}+\text{TiO}_2 \rightarrow \text{La}_2\text{CuTiO}_6
\]

Reports in the literature have sintering temperatures of \( \sim 1000 \, ^\circ\text{C} \), from 2 to 56 days; it was anticipated that synthesis at a higher temperature could substantially lower this time while yielding superior material. Samples were sintered at \( 1400 \, ^\circ\text{C} \) to investigate this.

Powder x-ray diffraction (Figure 5.1) measurements were performed on the sample, indicating an orthorhombic crystal structure with parameters comparable to published data. No impurity peaks were observed, suggesting single phase product to the limit of x-ray diffraction, \( \sim 3\% \). There is no evidence for \( \text{La}_2\text{CuO}_4 \), a magnetic impurity reported by Anderson. This result was anticipated due to the peritectic breakdown of \( \text{La}_2\text{CuO}_4 \) at \( 1367 \, ^\circ\text{C} \) [18]. Spatial ordering of the Cu and Ti could not be determined from x-ray diffraction.
SQUID magnetization measurements at 10 Oe on the sample (Figure 5.2) show uninteresting magnetic behavior. The material is paramagnetic with a very small susceptibility, and the zero field-cooled and field-cooled magnetization measurements are essentially identical. The field-cooled warming measurement indicates no trapped flux, and is essentially noise-level for the instrument. There is no evidence of any antiferromagnetic order or “apparent ferromagnetism”; the Cu does not magnetically order. Again there is no evidence for the magnetic La$_2$CuO$_4$ impurity reported by Anderson. This is consistent with the report by Anderson et al. [4] that the compound La$_2$CuTiO$_6$ has a random arrangement of Cu and Ti instead of the rock salt arrangement;

Figure 5.1: Powder x-ray diffraction on La$_2$CuTiO$_6$ sintered at 1400 °C. The indexed peaks are all orthorhombic O$_{c}$-phase. No impurity peaks are observed.
high-temperature treatment did not force this system to take on the rock salt structure found in the M=Ru homologue.

Figure 5.2: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_2\text{CuTiO}_6$ sintered at 1400 °C, showing the paramagnetic character of the material. The FCW data is noise-level for the instrument.
5.4 \text{La}_2\text{CuIrO}_6

For M=Ir, synthesis of the compound \text{La}_2\text{CuIrO}_6 was attempted. The material was first reported on by Blasse [28] in 1965, who found long range spatial ordering between Cu and Ir, but no reports on the magnetization of the material were published until Powell \textit{et al.} [110] in 1993 and Ramos \textit{et al.} [113] in 1994, who were both studying the properties of iridium in a handful of mixed-metal oxides. In neither case was high temperature sintering attempted. Powell includes susceptibility data that is quite reminiscent of the \text{La}_2\text{CuRuO}_6 homologue; the data contained in Powell's paper instigated the investigation into the M=Ir system. Ramos indicates the material is monoclinic with lattice parameters $a=5.795$ Å, $b=5.600$ Å, $c=7.730$ Å, $\beta=87.33^\circ$. Samples of \text{La}_2\text{CuIrO}_6 were prepared in a manner identical to the Ru homologues, as per the formula

$$\text{La}_2\text{O}_3 + \text{CuO} + \text{IrO}_2 \rightarrow \text{La}_2\text{CuIrO}_6$$

Synthesis temperatures of $\sim 1100$ °C were reported in the literature; experience with the Ru homologue suggested processing at a higher temperature, and sintering temperatures of 1100 °C, 1300 °C, and 1400 °C were studied. In the case of the sample sintered at 1400 °C, the Ar gas cylinder ran out during the heat treatment, and as a result the sample was discarded following processing.

Powder x-ray diffraction (Figure 5.3) was performed on both samples, with both showing similar crystal structures. Peaks could easily be sequenced by a monoclinic structure similar to that in published reports. The two diffraction patterns show clear differences; primarily the main peaks have decreased in intensity, and additionally several of the smaller peaks have split substantially. The peak splitting indicates a change in
symmetry of the crystal lattice; the [111] peak splits into two peaks, and the [220] peak vanishes; it is not clear if in the sample sintered at 1100 °C, the peaks surrounding the [220] peak are due to some stretching of the lattice even at the lower sintering temperature. The immediate suggestion from the x-ray diffraction profile is that the spatial ordering of Cu and Ir in the two different samples is quite different; the decrease in peak intensities suggests that the sample sintered at higher temperatures is less spatially ordered.

Figure 5.3: Powder x-ray diffraction on La$_2$CuIrO$_6$ sintered at different temperatures. The indexed peaks are all monoclinic $O_\beta$-phase. No impurity peaks are observed.
SQUID magnetization data measurements at 10 Oe on each sample show no antiferromagnetism. Each sample shows substantial low-temperature ferromagnetism; as published reports claim an antiferromagnetic transition with $T_N = 77$ K, this low-temperature ferromagnetism likely belongs to a magnetic impurity phase or to spatially disordered Cu and Ir. As the data fails to show any antiferromagnetism, and in particular, fails to show any “apparent ferromagnetism”, it is not reproduced here. Due to the prohibitive cost of high-quality IrO$_2$ and the lack of interesting results, further experiments on this material were not carried out.

5.5 La$_2$CuSnO$_6$

For M=Sn, synthesis of the compound La$_2$CuSnO$_6$ was attempted. The existence and characterization of La$_2$CuSnO$_6$ was first reported in 1991 [5] in an investigation into layered oxides sharing structural symmetries with the superconducting family La$_2$CuO$_4$. Through Rietveld analysis of neutron diffraction studies, it was observed that this material has an atypical structure; instead of random ordering or rock salt ordering of the two metal ion sites, the Cu and Sn form separate planes of CuO$_2$ and SnO$_2$ (Figure 5.4). The structure is monoclinic [11] with space group $P21/m$, with lattice parameters $a=8.5032$ Å, $b=7.8109$ Å, $c=7.8131$ Å, $\beta=91.143^\circ$. The structure of this material is of a layered form, similar to all of the high-$T_C$ superconductors derived from the La$_2$CuO$_4$ structure; the immediate implication is that this material is an excellent candidate for
superconductivity. Most interestingly, this material displays “apparent ferromagnetism” with a transition temperature of ~215 K. It was hoped that, based on experience in raising the transition temperature of La$_2$CuRuO$_6$ by nearly a factor of two over published values, it would be possible to improve the magnetic properties of La$_2$CuSnO$_6$ via high-temperature processing. Samples were prepared in an identical manner to the Ru homologue, as per the formula

$$La_2O_3 + CuO + SnO_2 \rightarrow La_2CuSnO_6$$

Reports in the literature have sintering temperatures of 980 °C from 7 to 48 days; it was anticipated that synthesis at a higher temperature could substantially lower this time while yielding superior material. Samples were sintered at a range of temperatures to investigate this. The temperatures 1100 °C, 1150 °C, 1200 °C, 1250 °C, 1300 °C, and 1400 °C were chosen as sintering temperatures for separate samples, with the only differences in sample processing being the sintering temperature. Substantial damage to the alumina boats used during sintering was observed as the sintering temperature was increased; significant sublimation of material may have occurred.
Figure 5.4: The unit cell of $La_2CuSnO_6$. Optimally formed material has the Cu and Sn forming separate planes; poor quality samples will have some Sn/Cu site mixing. This cell has one quarter of the atoms of the unit cell of $La_2CuRuO_6$. 
Powder x-ray diffraction (Figure 5.5) was performed on each sample, and a disturbing trend is immediately evident as the sintering temperature is raised. Peaks that can be indexed as a monoclinic structure with lattice parameters comparable to those in the literature vanish as the sintering temperature is raised, and peaks that can be indexed as belonging to the pyrochlore-type La$_2$Sn$_2$O$_7$ appear as the sintering temperature is raised. The implication is that the O$_6$-phase is not stable at higher sintering temperatures, whereas the O$_7$-phase is. The peak locations and relative intensities for the O$_7$ match neatly with published accounts of the material [72]. This trend was not observed in the Ru homologue, and no literature reports on the existence of a homologous impurity compound La$_2$Ru$_2$O$_7$. The blowup in Figure 5.6 clearly shows the destruction of the O$_6$-phase and the creation of the O$_7$-phase at high temperatures. A sample was also processed with a sintering temperature of 1300 °C for 48 hours instead of the typical 12 hours; powder x-ray diffraction on the sample shows significant degradation, and is not reproduced here. The conclusion is that high temperature processing does not work for La$_2$CuSnO$_6$, and that increasing the sintering time at higher temperatures is detrimental. This is unfortunate as 48 day sintering times do not allow for expediency of alternating processing sequences to discover better and faster processing parameters.
Figure 5.5: Powder x-ray diffraction on $La_2CuSnO_6$ sintered at different temperatures, showing the destruction of $La_2CuSnO_6$ and synthesis of $La_2Sn_2O_7$ as sintering temperatures are raised. The red stars indicate peaks belonging to $O_7$-phase; this includes all of the largest peaks in the sample sintered at 1400 °C.
SQUID magnetization data (Figure 5.7, Figure 5.8, Figure 5.9, Figure 5.10, Figure 5.11) on several of the La$_2$CuSnO$_6$ samples also show a change in behavior as the sintering temperature is increased. The only sample that shows the “apparent ferromagnetism” reported on in the literature is the sample sintered at 1300 °C (Figure 5.10); all other samples show either some antiferromagnetism with low temperature ferromagnetism, or are entirely ferromagnetic. The transition temperature is constant in all samples, and is comparable to published values. The sharpness of the antiferromagnetic peak seen in the literature is never observed, nor is the magnitude of

Figure 5.6: Blowup of powder x-ray diffraction on La$_2$CuSnO$_6$ sintered at different temperatures, clearly indicating the destruction of La$_2$CuSnO$_6$ peaks and creation of La$_2$Sn$_2$O$_7$ peaks at higher sintering temperatures. The indexed peaks all belong to monoclinic O$_6$-phase, whereas the red stars indicate peaks belonging to O$_7$-phase.
the antiferromagnetic transition; this is likely due to poor phase formation, as discussed. The behavior is consistent though with Cu moments ordered ferromagnetically in-plane, stacked antiferromagnetically, but extensive neutron diffraction would have to be performed to validate this. No evidence for any diamagnetism was observed, and the extreme sensitivity to background fields observed in the Ru homologue was conspicuously absent.

Figure 5.7: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for La$_2$CuSnO$_6$ sintered at 1100 °C
Figure 5.8: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for La$_2$CuSnO$_6$ sintered at 1200 °C

Figure 5.9: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for La$_2$CuSnO$_6$ sintered at 1250 °C
Figure 5.10: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_2\text{CuSnO}_6$ sintered at 1300 $^\circ$C

Figure 5.11: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for $\text{La}_2\text{CuSnO}_6$ sintered at 1400 $^\circ$C
Published reports of doping studies [3] where several different dopants were tried, failed to yield a superconductor in the La$_2$CuSnO$_6$ family. In Anderson's study, hole doping with Al and electron doping with Sb were tried on the Sn site, and hole doping with Sr and electron doping with Ce were tried on the La site; isoelectric doping of Ti on the Sn site was also tried. None yielded superconductivity. This is surprising given the structural similarities between the material and several other known high-$T_c$ families. High temperature processing does not solve this, as high temperature processing does not form higher quality material in this system.

To examine the effect of hole doping on the Sn site, a sample was synthesized with 10% of the Sn replaced with In. The sample was prepared in an identical manner as the undoped materials as per the formula

$$La_2O_3 + CuO + 0.9SnO_2 + 0.1In_2O_3 \rightarrow La_2CuSn_{0.9}In_{0.1}O_6$$

As the only undoped sample that shows the expected magnetic behavior was sintered at 1300 °C, this sample was processed at 1350 °C thinking that a slightly higher sintering would increase the sample quality and the inclusion of the dopant in the lattice. SQUID magnetization measurements at 10 Oe on this sample (Figure 5.12) show uninteresting magnetic behavior. The magnetic transition is lowered in temperature substantially, and there is no evidence for any diamagnetism; hole doping on the Sn site did not succeed.
5.6 La$_2$CuMO$_6$ Family Conclusions

High temperature processing of several materials in the family La$_2$CuMO$_6$ is not the same as the synthesis of La$_2$CuRuO$_6$. Several compounds were investigated in order to remove the magnetism of the Ru$^{4+}$ ion, without substantially altering the electronic environment of the Cu$^{2+}$ ion; this investigation had mixed results. High temperature processing did not form the compound La$_2$CuNbO$_6$ as Nb would not readily go to $4^+$.

Figure 5.12: Temperature dependence of magnetic susceptibility with $H = 10$ Oe for La$_2$CuSn$_{0.9}$In$_{0.1}$O$_6$ sintered at 1350 °C. No diamagnetism is visible.
ionization. There are several examples of stable compounds where Nb$^{5+}$ is substituted for Ru$^{5+}$; this does not seem to happen for the Nb$^{4+}$ and Ru$^{4+}$ ions, and the Nb homologue does not form. It was not possible to generate the rock salt arrangement of B and B' ions in the La$_2$CuTiO$_6$ system, and as such, there was no magnetic ordering in the material.

The most interesting material, La$_2$CuSnO$_6$, does not benefit at all from high temperature processing; this is due to the stability of compounds of the form La$_2$M$_2$O$_7$. The compound La$_2$RuO$_7$ does not form, which is why the high temperature processing of the La$_2$CuRuO$_6$ material was successful and the Sn homologue did not. Preliminary doping studies in the La$_2$CuSnO$_6$ system were ineffective, as high temperature processing destroys the desired phase; the failure of observation of superconductivity in the La$_2$CuSnO$_6$ system, even when processed under ideal conditions [3], is interesting as it contains CuO$_2$ planes separated by nonmagnetic layers, just as in the case of YBCO; conventional wisdom would suggest that this should superconduct with the right dopant.
The materials discussed in this work all share structural similarities with La$_2$CuO$_4$, (the first of all high-temperature superconductors) and its derivative cuprates, but differ strongly in their magnetism; this may suggest an entirely different pairing mechanism is necessary to describe these materials.

The magnetic order in the Ln$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ series of materials has CuO$_2$ planes ordered ferromagnetically in the $ab$-plane, stacked antiferromagnetically along the $c$-axis, with Ru ordered antiferromagnetically along the $c$-axis. This is the only interpretation of the magnetic structure that fits with all experiments. The superconductivity coexists with magnetically ordered CuO$_2$ planes, and the proof is the diffraction, magnetization and electron spin resonance data on Y$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$; the "apparent ferromagnetism" observed in these materials is due to magnetically ordered CuO$_2$ planes rotating the direction of their magnetization in the $ab$-plane.

In the LnSr$_2$Cu$_2$RuO$_8$ series of materials, the situation is the same. There are CuO$_2$ planes that are ordered ferromagnetically in the $ab$-plane, stacked
antiferromagnetically. The Ru is aligned antiferromagnetically along the $c$-axis. This is the only interpretation of the magnetic structure that fits with all experiments. Although the mechanism for doping is not clear, superconductivity does occur and coexists with the ordered CuO$_2$ planes. The near-room temperature magnetic ordering in the superconducting compound YSr$_2$Cu$_2$NbO$_8$ is the strongest evidence for CuO$_2$ magnetic order coexisting with superconductivity, along with diffraction and electron spin resonance measurements. The "apparent ferromagnetism" observable in the entire family of materials is due to rotation of the direction of magnetization of the CuO$_2$ planes in the $ab$-plane; weak ferromagnetism or canting of Ru moments has been ruled out.

Removing the Ln layer and thus reducing from two to one CuO$_2$ layer per unit cell results in the Ba$_2$YRuO$_6$ structure, with Y and Ru in alternate sites distributed over the former CuO$_2$ and RuO$_2$ layers. In this cubic material, there are only two distinct chemical layers due to the rock salt arrangement of Y and Ru: a layer of YRuO$_4$ and a layer of BaO. This is in contrast to the four distinct layers in the LnSr$_2$Cu$_2$RuO$_8$ structure, with four distinct layers, or the Ln$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$, with five distinct chemical layers and a glide plane. This system, when lightly doped with Cu, is superconducting, and shows bulk magnetic order of both the Ru and the Cu, with both ordering ferromagnetic in the $ab$-plane, stacking antiferromagnetically. Spatial ordering of the Y$^{3+}$ and Ru$^{5+}$ is vital for superconductivity in this material, and is greatly enhanced by high temperature synthesis; poor spatial arrangement of the Y$^{3+}$ and Ru$^{5+}$ leads to failure of observation of superconductivity, suggesting magnetic interactions are very important to the pairing mechanism. The dopant Cu orders antiferromagnetically at the same temperature as the
onset of superconductivity, which is above the antiferromagnetic ordering temperature of the Ru. Multiple experiments have shown that this material is a superconductor and that it is not simply a matter of a superconducting impurity phase, and that the magnetism and the superconductivity coexist.

In the series Ba$_2$LnRuO$_6$, interesting magnetic behavior is found. The dynamics of the spin reordering transitions in Ln=(Dy,Gd,Sm,Nd) is not yet fully understood. Light doping of Cu in the material with Ln=Dy results in superconductivity below 13 K; the diamagnetism is insufficient to screen the magnetism of Dy, and net negative magnetization was never observed. Cu antiferromagnetism coexisting with the superconductivity is observable in electron spin resonance measurements, and this system warrants further investigation. Light doping of Cu in the material with Ln=Gd does not superconduct, and was not expected to; light doping of Cu in the materials with Ln=(Nd,Sm) also fails to show superconductivity. The effect of the Cu doping on the magnetic order in these two materials is novel and not entirely clear, but does not suggest diamagnetism in either magnetization measurements or in electron spin resonance measurements. This suggests that the Ln$^{3+}$ ion size may be critical in the observation of superconductivity in the Ba$_2$LnRuO$_6$ system.

An alternative double perovskite that is very similar to the Ba$_2$YRuO$_6$ system, La$_2$CuRuO$_6$, shows several interesting features. This compound replaces Y with Cu and Ba with La, still preserving two distinct chemical layers, as the Cu$^{2+}$ and Ru$^{4+}$ are arranged in a rock salt arrangement. The quality of samples is greatly enhanced by high temperature processing, a lesson learned in the study of the Ba$_2$YRuO$_6$ system. This
system shows the same type of "apparent ferromagnetism" that was found in the Ln$_{1-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ and LnSr$_2$Cu$_2$RuO$_8$ families; experiments suggest that canting of ferromagnetically ordered Cu, stacked antiferromagnetically, is responsible for this as in Ln$_{1-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ and LnSr$_2$Cu$_2$RuO$_8$. These materials show extreme sensitivity to background fields, changing the magnetic order when cooled in fields of less than 0.5 Oe; this is smaller than the magnetic field of the Earth. It is not yet clear why these materials are so sensitive, and there may be uses of such an effect. Several attempts to dope the material with both holes and electrons did not result in superconductivity, despite good inclusion of the dopant in the lattice, suggesting perhaps that Ru$^{5+}$ and not Ru$^{4+}$ is vital to superconductivity. The magnetic behavior was strongly affected by hole doping, but not electron doping; the reason for the asymmetry is not understood.

High-temperature synthesis of several other members of the La$_2$CuMO$_6$ family was also performed, with varying degrees of success. The compound with M=Nb does not form; the compounds with M=Ti formed, but the Cu and Ti were randomly arranged across the B and B' sites, and the material showed no magnetic order. The compound with M=Ir formed poorly, and did not show magnetic behavior reported in the literature. The most promising compound, with M=Sn, did not form well with high-temperature processing. In the compound La$_2$CuSnO$_6$, there are three separate chemical layers, as the Cu$^{2+}$ and Sn$^{4+}$ form separate planes as opposed to a rock salt arrangement; this quite closely resembles the YSr$_2$Cu$_2$NbO$_8$ structure, where CuO$_2$ planes are separated across a two SrO layers surrounding a (nonmagnetic) NbO$_2$ layer. The high-temperature synthesis of La$_2$CuSnO$_6$ was a failure due to the stability of La$_2$Sn$_2$O$_7$ at high temperatures; no
homologous compound La$_2$Ru$_2$O$_7$ is known to form. Preliminary doping studies failed to generate superconductivity in the material, and the magnetic behavior of samples was never as good as published reports due to large amounts of impurity phase, especially after processing at the highest temperatures.

New facts about high-temperature superconductors have been uncovered, and perhaps one new superconducting compound (Ba$_2$DyRu$_{1-x}$Cu$_x$O$_6$) has been discovered. Magnetically ordered CuO$_2$ planes exist in the superconducting state of both the O$_{10}$ and O$_8$ materials, and the "apparent ferromagnetism" observable in these materials is not due to Ru canting or ferromagnetism. Magnetically ordered Cu and Ru exists in the superconducting state of Ba$_2$LnRu$_{1-x}$Cu$_x$O$_6$. Attempts to discover superconductivity in the La$_2$CuMO$_6$ family failed, but the magnetic properties of La$_2$CuRuO$_6$ were greatly enhanced by high-temperature synthesis, and it is likely the "apparent ferromagnetism" in this material has the same origin as in the O$_8$ and O$_{10}$ materials. The same high-temperature synthesis procedure was found to be detrimental to an interesting homologue, La$_2$CuSnO$_6$, due to stability of La$_2$Sn$_2$O$_7$ at high temperatures; this was also found to be the case for several other members of the La$_2$CuMO$_6$ series. No superconductivity was observed in the La$_2$CuSnO$_6$ material, despite its similarities to several other superconducting systems. A tentative conclusion is that the presence of CuO$_2$ planes is neither necessary nor in some cases sufficient to produce high-temperature superconductivity. The magnetic behavior observed is inconsistent with popular models of high-temperature superconductivity featuring the CuO$_2$ planes. These studies on unconventional superconductors add to the body of knowledge on high-$T_c$
materials, and hopefully will open new avenues of investigation that will further explain
the mystery behind high-temperature superconductivity.
Polycrystalline ruthenate perovskites and ruthenocuprate oxides are synthesized by a solid state chemical reaction at elevated temperatures. Precursor powders of basic metal oxides (LnO$_2$, Ln$_2$O$_3$, etc.) and carbonates (BaCO$_3$, SrCO$_3$, Li$_2$CO$_3$, etc.) are first heated to 300 °C in a dry furnace to remove moisture, then weighed out in stoichiometric ratios and mixed. Some very hygroscopic materials such as La$_2$O$_3$ and Nd$_2$O$_3$ must be heated to 900 °C immediately prior to use in order to remove moisture. Moisture trapped in the oxide powders will make the stoichiometry of the final product incorrect by underestimating the mass of any given precursor compound. As several of the precursors are hygroscopic, it is occasionally a race to weigh out the right amounts of powder before the materials cool enough to absorb any significant amount of moisture from the ambient atmosphere. The precursor powders are mixed in an agate mortar with an agate pestle by hand until thoroughly ground. Prior to usage, the agate is cleaned with aqua regia, a mixture of hydrochloric and nitric acids, then rinsed with water and acetone. These steps are necessary to prevent cross-contamination of samples.
Experience has shown that thorough grinding is *vital* to preparing high-quality samples. All grinding is done by hand as samples mixed using a zirconia ball mill have always had inferior crystalline and magnetic properties. A high-energy milling machine was tried at Missouri University of Science and Technology, but this also produced inferior quality samples for unknown reasons. There is a remote chance that the zirconia contaminates the material. As a result, all grinding continues to be done by hand. Grinding duration is essential. The longer the materials are ground, the smaller the particles become, the more homogenous the mixture becomes, and the more complete the solid state reaction can be. Technique is also very important—it seems a trivial task, but thirty minutes of grinding by an expert is usually equivalent to two or more hours by a novice. A regimen of 30 minutes per 4 grams of powder was adopted as this consistently shows acceptable results. It is possible that longer could be better, but as batches of sample are usually 16 grams, the 30 minute/4 gram rule was adopted in the interest of expediency. In the literature there are reports of people grinding powders by hand for ten to twelve hours.

Once the precursor powders are thoroughly ground, the powder is placed into a dry alumina crucible or boat for heat treatment. The alumina vessels are also cleaned with the aqua regia acid mixture described above, then rinsed with water, thoroughly dried and rinsed with acetone immediately prior to usage. There are usually several steps to the heat treatment process. Typically the first step is a calcination at 1000 °C or less in air in a box furnace for 24 to 48 hours, with the temperature driven to the desired value as quickly as possible. This step is intended to burn out all carbon and start generating
product phases. The duration of the calcination depends on the chemical makeup of the sample; many of the elements in question are quite volatile at elevated temperatures and sublimation of metal ions is a significant problem as it depletes the amount of final product that can be formed. Thus, for some materials, longer calcination helps remove impurities but can ruin the stoichiometry of the batch. It has been seen that the calcination step is still important for materials without any carbonate precursors. Skipping this lower temperature step altogether has always had detrimental results on the final material, regardless of which material it is. Calcination in a controlled gas environment instead of air has been tried several times without any clear benefit. Vacuum calcination was also attempted, with disastrous results. Lowering the vapor pressure without mechanical agitation of the powder while in the furnace results in different redox reactions going on at different depths in the powder.

Following calcination, the vessel containing the powder is allowed to cool to room temperature, then the powder is removed and ground again by hand in a mortar and pestle, cleaned as above. This intermediate grinding also is done according to the 30 minute/4 gram rule and is important to ensure homogeneity in the material prior to high temperature processing. After grinding, the powder is then densified into 1 gram pellets with a hydraulic press with 10,000 lbs of force. The die is stainless steel and has a 1 cm diameter, and is thoroughly scrubbed with acetone prior to use. Paraffin wax is used to lubricate the die piston. There is little risk of contaminating the material with wax, as the wax is a simple organic that vaporizes at temperatures well below the material processing temperatures [65]. Densification is performed, as the denser the sample, the closer all of
the microcrystallites are to each other, and thus the chemical reaction is much more likely to occur. Also the mechanical toughness of a densified pellet makes many experiments, such as measuring resistivity, much easier. After pressing, the pellets are typically put into stacks of three and placed in an alumina boat for high temperature processing in a controlled gas environment. Care is taken to thoroughly clean the boat to prevent cross-contamination of samples from dirty boats; occasionally, some boats are single-use and disposed of, or become used only for one family of materials to prevent contamination from sample residue that cannot be cleaned off. To prevent the pellets from reacting with the alumina boat, the stack of pellets is placed on a small pile of calcined powder of the same material (simply excess material that was not pressed into pellets). Pt foil has also been used to serve the same purpose; however, there are some instances where high-temperature reactions involving Pt have occurred, leading to having 1 cm holes eaten into the platinum foil—this is not cost effective. Pt was chosen due to its inertness. Alumina is regularly used for crucibles and vessels as it has an extremely high melting temperature, is mechanically very sturdy, can withstand repeated thermal cycling, and is chemically nearly inert. However, at temperatures of 1500 °C, it always is a good idea to be cautious and have some sort of buffer layer between the crucible or vessel and sample pellets.

The pellets and boat are then placed at the center of a high-temperature tube furnace under a controlled gas environment. Generally the gas environment mimics atmospheric conditions minus the water vapor and N\textsubscript{2}; usually, 70% Ar and 30% O\textsubscript{2} gas. Ar is chosen instead of N\textsubscript{2}, as at elevated temperatures, there are many possible chemical
reactions involving the otherwise inert N\textsubscript{2} gas, whereas Ar is always inert. Trial and error have shown this gas ratio to produce high quality samples. The uptake of oxygen ions by the sample from the gas can be very important. This ratio is not used for synthesis of every material, however; materials like YBCO need a significantly lower oxygen content because in YBCO oxygen is the dopant and its concentration must be carefully controlled. The gas ratios are controlled by a custom-built mass flow controller, and the gas is blown through the tube constantly throughout the heat treatment. The exhaust of the gas at the far end of the tube goes into a cup of oil to prevent any entry of air into the tube as the gas in the tube cools. Expanded alumina inserts are also put inside each end of the tube to act as heat reflectors. This prevents the end caps from melting as well as making the temperature of the hot zone more homogenous. The exact temperature that the pellets are raised to, and the duration that the temperature is maintained for, depends on the particulars of the sample. In order to get the best single phase materials, trial and error has determined the optimal processing parameters. This can be due to the existence of several possible phases at several different temperatures: too cool, and the right phase is never formed; too hot, and the right phase may not be stable. Sometimes the temperature window that makes one phase stable versus another is only 50 °C wide. With Ru-containing materials, this problem is compounded by the volatility of the Ru ion at high temperatures; with Ir it is even worse. Experience has shown for several ruthenates and iridates that the hotter and the shorter the processing, the better—but this is not true for all materials, even for direct homologues of the ruthenate systems. A typical heat treatment would involve rapidly heating the pellets to 500 °C, then ramping
up to 1400 °C over the course of 4 hours, holding at that temperature for 12 hours, cooling back to 500 °C over the course of 4 hours, then cooling to room temperature. At all times the gas environment is controlled as mentioned above, and the samples are never exposed to air until completely cooled. The sequencing is controlled by an Athena-brand programmable temperature process controller. If volatility of ions is not a concern in a particular sample, then it can be beneficial to take the finished pellets, grind them again with a clean agate mortar and pestle, press the reground powder into new pellets, and repeat the heat treatment. The problem has occurred that 1500 °C, which is the maximum operating temperature of the furnaces, appears to be insufficient to force certain dopants into some crystal structures; unfortunately more exotic equipment is needed to go above 1500 °C as there are several engineering challenges to work at such extremely high temperatures, and it is not known if the chemical phases of interest even would survive even higher temperatures. This has occasionally limited the selection of dopants to work with while investigating superconducting behavior in ruthenates and similar materials.

Doping a system is accomplished by adding stoichiometric amounts of alternative compounds at the beginning of processing, then handling the material identically to an undoped sample. The solid-state chemical reaction will still occur, and the dopant will enter the lattice at the site most suited for its charge and size; with correct choice of dopant, it is possible to guarantee that the dopant will be on a particular lattice site. There are cases of doping failing where secondary phases are produced, or the precursor dopant compound is never broken down, but the list of these can be kept short by correct choice
of dopants; not all dopants can be expected to work in every system due to ion size and charge mismatch.

The high temperature processing, known as sintering, has a chemical purpose as well as a mechanical purpose. The solid state chemical reaction occurs at a substantially slower rate, if at all, at lower temperatures. Additionally, it has repeatedly been seen that high temperature processing generates better site ordering in many materials, evidenced by superior crystallographic as well as magnetic and superconducting properties. The mechanical advantage is in the partial melting of microcrystallites. Tiny adjacent microcrystallites will not melt, but will get soft, essentially sticking together at high temperatures, and becoming one piece as the material cools. With \( \sim 10^{20} \) microcrystallites in a pellet, this substantially increases the density of the material as air pockets are squeezed out, and greatly increases the grain size, which can enhance the magnetic and superconducting properties.

Following the high-temperature heat treatment(s), the pellets should be nominally single-phase polycrystalline pieces of finished product, and can be ground up into powder or cut into rods for analysis of structural, electrical and magnetic properties. Samples are stored in airtight jars and many have been observed to not have degraded over a span of several years on the shelf.
B.1 Introduction

Diffraction allows quantitative measurement of phase purity in a sample as well as quantitative measurement of lattice parameters, crystal and magnetic structure, magnetic moment, and site occupancy. Immediate access to an x-ray diffractometer is available at Notre Dame, whereas collaborators at the University of Missouri Research Reactor, a tank-type nuclear research reactor, have performed neutron diffraction measurements.

B.2 Crystal Structure

There are only 230 distinct ways [57] of periodically arranging atoms to form a crystalline solid. The smallest arrangement of atoms that, when translated, recreates the original pattern is called the primitive unit cell, and the shortest set of vectors that span this are known as the primitive unit vectors, which yield the unit cell of smallest volume. Multiple sets of unit vectors exist; it is possible and common for a set of orthogonal unit
vectors to best demonstrate the symmetry of the structure, but not be the shortest set of unit vectors. The cell that most clearly graphically demonstrates the symmetry is called the conventional unit cell, and the vectors that span it are the lattice parameters. The 230 different space groups can be categorized by their common symmetries into 7 distinct lattice systems. In decreasing order of symmetry, these are: cubic, hexagonal, rhombohedral, tetragonal, orthorhombic, monoclinic, and triclinic. Representations [145] are shown in Figure B.1 through Figure B.14. A cubic system is the most symmetric and is a cube where all vertices are right angles and all edge lengths, or 'lattice parameters', are equal. Hexagonal has only two lattice parameters and resembles a hexagonal prism. Rhombohedral has faces with equal edge lengths and all vertices of equal angle but not right angled. Tetragonal is a rectangular prism with two edges of equal length, and one edge different. Orthorhombic is a rectangular prism where no edges have equal length. Monoclinic has unequal edge lengths and only two vertices that are right angles. Finally, triclinic has unequal edge lengths and has no right angled vertices nor vertices of the equal angle. These lattice systems can be subdivided into the 14 different Bravais lattices, which reflects the location of lattice points on the unit cell. Simple type lattices have lattice positions on the corners of the unit cell only. Face centered lattices have lattice positions on the corners as well as on the face of the unit cell, and a variation of this has single-face centering with an additional lattice point only occurring on two of six faces of the unit cell. Body centered lattices have lattice positions on the corners as well as at the center of the cell. It should be noted that more than one atom can be associated with one lattice point; a simple cubic unit cell has only 8 lattice points, one at each corner.
of the unit cell, but this does not restrict the cell from describing crystals only containing 8 atomic positions—the 'basis' may be greater than one, meaning that more than one atom is associated with a given lattice point; the structure of the crystal is then described by the combination of the lattice type and the basis. Thus very complicated seeming crystals can be identified as having very simple symmetries.

Figure B.1: Simple cubic

Figure B.2: Body-centered cubic

Figure B.3: Face-centered cubic
Figure B.4: Hexagonal

Figure B.5: Simple tetragonal

Figure B.6: Body-centered tetragonal

Figure B.7: Rhombohedral
Figure B.8: Simple orthorhombic

Figure B.9: Base-centered orthorhombic

Figure B.10: Body-centered orthorhombic
Figure B.11: Face-centered orthorhombic

\[ \alpha \neq 90^\circ \]
\[ \beta, \gamma = 90^\circ \]

Figure B.12: Simple monoclinic

\[ \alpha \neq 90^\circ \]
\[ \beta, \gamma = 90^\circ \]

Figure B.13: Base-centered monoclinic

\[ \alpha, \beta, \gamma \neq 90^\circ \]

Figure B.14: Triclinic
Crystalline lattices are a discrete space; multiplying unit vectors by any combinations of integers will yield a point elsewhere in the lattice:

\[ \mathbf{T} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \]

where \( n_i \) are any integer and \( \mathbf{a}_i \) are the unit vectors that span the unit cell. The primitive unit vectors that describe a primitive unit cell are not always trivial; for the simple cubic system, the primitive unit vectors are simply

\[ \mathbf{a}_1 = a \hat{x} \]
\[ \mathbf{a}_2 = a \hat{y} \]
\[ \mathbf{a}_3 = a \hat{z} \]

but for a face-centered simple cubic unit cell, the primitive unit vectors are

\[ \mathbf{a}_1 = \frac{a(\hat{x} + \hat{y})}{2} \]
\[ \mathbf{a}_2 = \frac{a(\hat{y} + \hat{z})}{2} \]
\[ \mathbf{a}_3 = \frac{a(\hat{z} + \hat{x})}{2} \]

This choice of vectors \( \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \) to represent the unit cell is not orthogonal and does not graphically demonstrate the symmetry as clearly, but it has the smallest volume, contains the fewest number of atoms, and is thus the set of primitive unit vectors. Translations between identical spots in different cells of the lattice are still described by the translation vector \( \mathbf{T} \), and points within the unit cell are described in terms of fractions of the unit vector lengths \( a_i \). Thus the center of the face-centered cubic cell would be located at \( (n_1, n_2, n_3) = (.25, .25, .25) \), or at a location \( (.5a \hat{x}, .5a \hat{y}, .5a \hat{z}/2) \) from one corner of the
orthogonally drawn unit cell. Likewise for the body-centered simple cubic unit cell, the primitive vectors are

\[ \vec{a}_1 = \frac{a(-\hat{x} + \hat{y} + \hat{z})}{2} \]
\[ \vec{a}_2 = \frac{a(\hat{x} - \hat{y} + \hat{z})}{2} \]
\[ \vec{a}_3 = \frac{a(\hat{x} + \hat{y} - \hat{z})}{2} \]
as this choice of vectors defines the unit cell with the smallest volume. For all three of these systems, the conventional unit cell is a cube with edge length \( a \). Having unequal edge lengths generates the orthorhombic and rhombohedral structures. Similar relations can be enumerated for the remaining four Bravais lattices.

Planes in a crystalline lattice are indexed by their intercepts with axes defined by the lattice parameters of the unit cell. The reciprocals of the coefficients of these intercepts in terms of the lattice parameters are then taken and reduced to the smallest three integers with the same ratio. These three integers are written as \((hkl)\) and are known as the index of the plane. There are an infinite number of planes parallel to a plane with a given index—the spacing between two parallel planes in a crystal is responsible for the diffraction of incident x-rays from a crystal, which is essential to quantifying the purity of a synthesized sample as every material will diffract x-rays differently.
B.3 Diffraction

A discussion of crystal lattices is essential to an understanding of diffraction of x-rays by a crystalline solid. Bragg diffraction occurs for x-rays just as it does all other wavelengths of light; a grating with spacing on the order of the wavelength of the incident light is the only requirement. W.L. Bragg's lasting contribution to physics was the realization that x-ray wavelengths are on the order of atomic spacings in crystalline solids, and that diffraction of x-rays should occur in a solid. In a crystal, incident x-rays are scattered from planes of atoms in the lattice separated by some interplanar distance. The scattering occurs due to the interaction of the incident x-rays with atomic electron clouds. Constructive interference occurs in the scattering of x-rays when the x-ray path length difference between two crystallographic planes is equal to an integer multiple of wavelengths. Thus, knowing the wavelength of the x-ray source means measuring the interplanar spacing of the crystalline lattice as per Bragg's law,

\[ n \lambda = 2d \sin(\theta) \]

By applying Fourier analysis to a periodic lattice structure, one can easily calculate what angles will satisfy the Bragg condition. As the lattice is periodic, the electron number density \( n(\vec{r}) \) is also periodic; the electron number density will determine the amplitude of scattered waves in any given direction. Expanding the electron number density into a Fourier series,

\[ n(\vec{r}) = \sum n_G e^{i\vec{G} \cdot \vec{r}} \]

indicates that there are a discrete set of vectors \( \vec{G} \) that represent the crystalline lattice in momentum space, just as there are a discrete set of vectors \( \vec{T} \) that represent the
crystalline lattice in real space. The smallest set of vectors that span this 'reciprocal space' are known as the primitive unit vectors of the reciprocal lattice, and can be calculated directly from the primitive unit vectors of the crystal lattice:

\[
\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\
\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\
\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}
\]

and thus points in reciprocal space are defined by

\[
\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3
\]

By this definition of the vectors \( \vec{b}_i \)

\[
\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}
\]

must be valid. These reciprocal lattice vectors are then each perpendicular to two of the real space primitive unit vectors, and thus share a nomenclature with lattice planes: the reciprocal lattice vector \( \vec{G}(hkl) \) is perpendicular to the plane \((hkl)\). Given this knowledge about the vectors \( \vec{G} \), it is clear that these reciprocal lattice vectors satisfy the periodicity of the crystal lattice, as

\[
\vec{T} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3 \\
n(\vec{r} + \vec{T}) = \sum G n_G e^{i\vec{G} \cdot (\vec{r} + \vec{T})} = \sum G e^{i\vec{G} \cdot \vec{r}} e^{i\vec{G} \cdot \vec{T}}
\]

and by orthogonality

\[
e^{i\vec{G} \cdot \vec{T}} = e^{i(\vec{h}\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3) \cdot (n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3)} = e^{i2\pi (n_1 h + n_2 k + n_3 l)} = 2\pi \delta_{ij}
\]
An x-ray beam incident on a material with momentum $\mathbf{k}$ and phase $e^{i\mathbf{k} \cdot \mathbf{r}}$ will diffract with new momentum $\mathbf{k}'$ and phase $e^{i\mathbf{k}' \cdot \mathbf{r}}$; the path difference between two parallel incident x-rays is proportional to the separation $\mathbf{r}$ between the two beams at the point of scattering. The difference in phase is the projection of the vector $\mathbf{r}$ onto the momentum $\mathbf{k}$; thus for the incident beam there is a phase shift of $\mathbf{k} \cdot \mathbf{r}$ and for the outgoing beam there is a phase shift of $-\mathbf{k}' \cdot \mathbf{r}$, for a total phase shift of $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}$.

Thus, the phase factor for the x-ray beam scattered at coordinate $\mathbf{r}$ is $e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}}$ relative to the x-ray beam scattered at the origin. As the amplitude of scattered waves must be proportional to the local electron density $n(\mathbf{r})$, the total amplitude of the scattered wave in the direction of $\mathbf{k}'$ is proportional to integrating the electron density multiplied by the phase factor over the volume of the crystal:

$$I_{\text{scattering}} = \int n(\mathbf{r}) e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} dV$$

Inserting the Fourier expansion of the electron density into the scattering amplitude results in

$$I_{\text{scattering}} = \sum \int n_G e^{i\mathbf{G} \cdot \mathbf{r}} e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} dV$$

$$I_{\text{scattering}} = \sum \int n_G e^{i\mathbf{G} \cdot (\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}} dV$$

which suggests that whenever the change in the momentum $\Delta \mathbf{k} = \mathbf{k}' - \mathbf{k}$ is equal to a particular value of $\mathbf{G}$, the argument of the exponent is zero and the scattering amplitude is at a maximum. For any value of $\Delta \mathbf{k}$ that significantly differs from any possible reciprocal lattice vector $\mathbf{G}$, the scattering amplitude is negligibly small for macroscopic crystals [76]. Thus, enumerating the reciprocal lattice vectors is the same
thing as listing all directions of scattering that will constructively interfere, and this vector diffraction condition can be reduced to Bragg's law. As the photon is elastically scattered, the magnitudes of the incident momentum and outgoing momentum are equal, 

\[ \vec{k} = \vec{k}' \]. Thus, as the diffraction condition is \( \Delta \vec{k} = \vec{G} \) or \( \vec{k} + \vec{G} = \vec{k}' \) and squaring this relation yields

\[
(\vec{k} + \vec{G}) \cdot (\vec{k} + \vec{G}) = k^2
\]

\[
k^2 + 2 \vec{k} \cdot \vec{G} + G^2
\]

\[
2 \vec{k} \cdot \vec{G} + G^2 = 0
\]

As \( \vec{G} \) and \(-\vec{G}\) both are valid vectors of reciprocal space, the diffraction condition can be most succinctly written as

\[
2 \vec{k} \cdot \vec{G} = G^2
\]

The spacing between adjacent parallel planes is given by the magnitude of the reciprocal lattice vector by

\[
d(hkl) = \frac{2\pi}{|\vec{G}|}
\]

Thus, the diffraction condition can be rewritten as

\[
2 \left(\frac{2\pi}{\lambda}\right) \sin \theta = \frac{2\pi}{d(hkl)}
\]

which reduces to the Bragg result of

\[
2d \sin (\theta) = n\lambda
\]

where \( d \) is the spacing between adjacent parallel planes with indices \( h/n, k/n, l/n \). The intensity of higher order diffraction is essentially negligible, so \( n = 1 \) for all relevant cases. Knowing the reciprocal lattice vectors and the wavelength of incident x-rays then
allows calculation of the angles which will generate constructive interference, and thus a
diffraction peak in a plot of intensity versus angle in an x-ray diffraction experiment.

The calculation required then is to enumerate all $\vec{G}$ magnitudes, and determine
which angles satisfy the Bragg condition. The Bragg condition can be manipulated to
read:

$$\theta = \arcsin \left( \frac{\lambda |\vec{G}|}{4\pi} \right)$$

When the argument of the inverse sine is less than one, there will be a diffraction peak.
This is most easily tested by a short computer code to loop through values of $h$, $k$, and $l$
and calculate the corresponding $\vec{G}$ vectors and magnitudes. For a simple cubic system,
the calculation is trivial as the vectors of reciprocal space are easily obtained:

$$\vec{a}_1 = a \hat{x}$$

$$\vec{a}_2 = a \hat{y}$$

$$\vec{a}_3 = a \hat{z}$$

$$\vec{a}_1 \times (\vec{a}_2 \times \vec{a}_3) = a^3$$

$$\vec{a}_2 \times \vec{a}_3 = a^2 \hat{x}$$

$$\vec{a}_3 \times \vec{a}_1 = a^2 \hat{y}$$

$$\vec{a}_1 \times \vec{a}_2 = a^2 \hat{z}$$

so the reciprocal lattice basis vectors are

$$\vec{b}_1 = \frac{2\pi}{a} \hat{x}$$

$$\vec{b}_2 = \frac{2\pi}{a} \hat{y}$$

243
\[ \vec{b}_3 = \frac{2\pi}{a} \hat{z} \]

and points in reciprocal space are mapped by the vectors

\[ \vec{G}(hkl) = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 = \frac{2\pi}{a} (h\hat{x} + k\hat{y} + l\hat{z}) \]

with magnitudes

\[ |\vec{G}(hkl)| = \frac{2\pi}{a} \sqrt{h^2 + k^2 + l^2} \]

For body-centered cubic, it is not as trivial:

\[ \vec{a}_1 = \frac{a}{2} (-\hat{x} + \hat{y} + \hat{z}) \]

\[ \vec{a}_2 = \frac{a}{2} (\hat{x} - \hat{y} + \hat{z}) \]

\[ \vec{a}_3 = \frac{a}{2} (\hat{x} + \hat{y} - \hat{z}) \]

\[ \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \frac{a^3}{2} \]

\[ \vec{a}_2 \times \vec{a}_3 = \frac{a^2}{2} (\hat{y} + \hat{z}) \]

\[ \vec{a}_3 \times \vec{a}_1 = \frac{a^2}{2} (\hat{x} + \hat{z}) \]

\[ \vec{a}_1 \times \vec{a}_2 = \frac{a^2}{2} (\hat{x} + \hat{y}) \]

so the reciprocal lattice basis vectors are

\[ \vec{b}_1 = \frac{2\pi}{a} (\hat{y} + \hat{z}) \]

\[ \vec{b}_2 = \frac{2\pi}{a} (\hat{x} + \hat{z}) \]
\[ \vec{b}_3 = \frac{2\pi}{a} (\hat{x} + \hat{y}) \]

and points in reciprocal space are mapped by the vectors

\[ \vec{G}(hkl) = h \vec{b}_1 + k \vec{b}_2 + l \vec{b}_3 = \frac{2\pi}{a} [h(\hat{y} + \hat{z}) + k(\hat{x} + \hat{z}) + l(\hat{x} + \hat{y})] \]

\[ \vec{G}(hkl) = \frac{2\pi}{a} [(k + l)\hat{x} + (h + l)\hat{y} + (h + k)\hat{z}] \]

with magnitudes

\[ |\vec{G}(hkl)| = \frac{2\pi}{a} \sqrt{(k + l)^2 + (h + l)^2 + (h + k)^2} \]

This mixing of indices comes despite both systems being cubic; adding an additional lattice site at the center of the cube significantly changes the allowed diffraction peaks.

For a monoclinic system, the angle of deviation away from 90° must be taken into account, and the basis vectors are

\[ \vec{a}_1 = a \hat{x} \]

\[ \vec{a}_2 = b \cos \phi \hat{x} + b \sin \phi \hat{y} \]

\[ \vec{a}_3 = \frac{1}{c} \hat{z} \]

\[ \vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3 = a b c \sin \phi \]

\[ \vec{a}_2 \times \vec{a}_3 = b c \sin \phi \hat{x} - b c \cos \phi \hat{y} \]

\[ \vec{a}_3 \times \vec{a}_1 = a c \hat{y} \]

\[ \vec{a}_1 \times \vec{a}_2 = a b \sin \phi \hat{z} \]

so the reciprocal lattice basis vectors are

\[ \vec{b}_1 = \frac{2\pi}{a} \hat{x} - \frac{2\pi \cos \phi}{a \sin \phi} \hat{y} \]

245
\[ \vec{b}_2 = \frac{2\pi}{b \sin \phi} \hat{y} \]
\[ \vec{b}_3 = \frac{2\pi}{c} \hat{z} \]

and points in reciprocal space are mapped by the vectors

\[ \vec{G}(hkl) = h \vec{b}_1 + k \vec{b}_2 + l \vec{b}_3 = \frac{2\pi}{a} h \hat{x} - \frac{2\pi \cos \phi}{a \sin \phi} h \hat{y} + \frac{2\pi}{b \sin \phi} k \hat{y} + \frac{2\pi}{c} l \hat{z} \]

\[ \vec{G}(hkl) = \frac{2\pi}{a} h \hat{x} + \frac{2\pi}{b \sin \phi} k \hat{y} + \frac{2\pi}{c} l \hat{z} \]

with magnitudes

\[ |\vec{G}(hkl)| = 2\pi \sqrt{\frac{h^2}{a^2} + \frac{h^2 \cos^2 \phi}{a^2 \sin^2 \phi} + \frac{k^2}{b^2 \sin^2 \phi} + \frac{l^2}{c^2}} \]

The methodology extends to any lattice; all that is needed to calculate the vectors \( \vec{G} \) is knowledge of the lattice parameters and of the primitive unit vectors of the lattice. The contribution of a basis larger than 1 is to cause destructive interference if the electron number densities for the two (or more) atoms associated with that basis are comparable. Also of relevance is the ability of the electron cloud to scatter the x-rays; for most cases, this 'atomic form factor' is fairly close to that of a free atom, such that the x-ray reflection intensities in a solid are comparable the values of free atoms; this is linearly proportional to \( Z \), such that the locations of low-\( Z \) atoms in a lattice can be difficult to determine, and distinguishing atoms with similar \( Z \) is difficult as well. It is possible via Fourier analysis and a least squares fitting method due to H. Rietveld to determine what the lattice parameters and space group of a particular crystal are given only the incident x-ray wavelength and the resulting diffraction pattern (and likewise what the long range magnetic ordering of a particular material is given the incident neutron wavelength and
resulting diffraction pattern). The biggest usage of x-ray diffractometry is as a method for qualitatively and quantitatively analyzing a sample during and after synthesis to identify the phase purity of the material, and to judge the progress of the synthesis. It is usually easy to identify impurity phases or at least the existence of impurity phases in a processed sample via x-ray diffraction.

Long-range magnetic order in a material also represents a periodic structure that will reflect an incident beam of particles that have magnetic moments. The neutron is such a particle; it has no electric charge and a magnetic moment of \(-1.913 \mu_N\) where \(\mu_N\) is the nuclear magneton, approximately \(-9.662 \times 10^{-27}\) J/T. As such, a neutron beam will not be disturbed by electric charges, but will be scattered by magnetic dipoles, perfectly suiting neutrons for diffraction experiments. Slow neutron beams with wavelengths on the order of Angstroms are also used to perform diffraction measurements. The neutrons scatter off of the periodic arrangement of nuclei, just as the x-rays scatter off the periodic arrangement of atoms' electron clouds. In addition, the neutrons interact with the magnetic moment of the electron clouds, causing additional scattering. Scattering off of the nucleus is very different between different atoms or even isotopes; this is due to strong resonances associated with the scattering process and the spin (if any) of the nucleus [36]. For these reasons, scattering intensity does not vary linearly with \(Z\), as it does with x-rays; this can be extremely useful, as two atoms with close \(Z\) can be difficult to distinguish with x-ray diffraction, and light-\(Z\) atoms can be easily identified. This introduces a different problem, however, that some isotopes of elements of interest have very large neutron cross-sections, and as such, readily absorb any incident neutrons,
making diffraction experiments impossible without very expensive isotopically-selected compounds. A benefit is that the neutron scattering is isotropic with scattering angle, as the nucleus is essentially a point particle when interacting with a neutron of wavelength orders of magnitude larger than the nuclear diameter. The diffraction pattern generated by x-rays and neutrons of the same wavelength should generate peaks at all of the same angles. However, there is additional information discernible with neutrons; magnetic order is a periodic arrangement of atomic dipole moments, and a magnetically ordered material will diffract neutrons coherently due to the magnetic structure as well as the crystalline structure, and the size of the magnetic unit cell is not necessarily that of the crystalline unit cell: this will cause additional diffraction peaks to appear. For neutron scattering, the magnetic scattering from paramagnetic ions is described by the differential scattering cross section into a unit solid angle [58],

\[
\frac{\partial \sigma}{\partial \Omega} = \frac{2}{3} S(S+1) \left( \frac{\mu_0^2 e^2 \mu^2}{m} \right)^2 f^2 + C^2
\]

where \( S \) is the total spin of the paramagnetic ion, \( \mu \) the neutron's magnetic moment in nuclear magnetons, \( C \) the constant nuclear scattering amplitude, and \( f \) the form factor of the ion, which describes the ability of the dipole moment to scatter the nucleus much as the form factor of the ion describes the interaction between the x-ray and the electron cloud. In a paramagnetic material, the magnetic scattering would simply enhance the intensity of the peaks originating from scattering off of the crystalline lattice. For a magnetically ordered material, the differential scattering cross section per unit solid angle may be written as
\[ \frac{\partial \sigma}{\partial \Omega} = S^2 \left( \frac{\mu^2 e^2 \mu^2}{m} \right) f^2 q^2 + C^2 \]

where \( q \) is the magnitude of the vector given by

\[ \vec{q} = (\vec{e} \cdot \vec{x}) \vec{e} - \vec{x} \]

where the unit scattering vector \( \vec{e} \) replaces the reciprocal lattice vector \( \vec{G} \)

\[ \vec{e} = \frac{\vec{k} - \vec{k}'}{|\vec{k} - \vec{k}'|} \]

and the vector \( \vec{x} \) is a unit vector parallel to the magnetic moment of the scattering atom.

The reciprocal-space math is then identical for neutron diffraction. Thus by performing neutron diffraction measurements, the crystal and magnetic structure as well as the dipole moment values can be determined. As the intensities of the crystalline and magnetic scattering are sometimes comparable, making magnetic order difficult to establish, it is common to perform neutron diffraction measurements both above and below an anticipated magnetic ordering temperature, or to measure neutron diffraction intensity at a given angle as a function of temperature or applied magnetic field.

B.4 Apparatus

Examining a polycrystalline sample has the distinct advantage that essentially all crystal orientations are visible at all times due to the random orientation of microcrystallites. Thus, the detector must only be swept through one angular coordinate to detect diffracted x-rays. A typical x-ray diffractometer has a compact x-ray source and
an x-ray detector each mounted on the arms of a gonimeter, and moved in tandem such
that the angle between the source and vertical and the angle between the detector and
vertical is equal. The gonimeter measures the angle between the x-ray source and the
detector; this is twice the angle in the Bragg diffraction equation. The source and arm are
rastered through some range of angle, resting for a controlled time at some incrementally
increasing angle. The detector counts x-rays during this holding time, then the arms of
the gonimeter are moved, and the measurement repeats. Counting rates of 0.125°/minute
over a 20 window of 10°-110° are employed unless specified otherwise; these parameters
usually generate data with excellent signal-to-noise. The instrument can go lower in
angle, but diffuse scattering of x-rays generates noise at lowest angles. The instrument
can also go higher in angle, but there is a risk that loosely packed sample powder will
spill inside the instrument at higher angles; also, the peak intensities at high angles
generally are small and thus contain less useful information than those at lower angles.
Measured intensities and angles are fed directly into a PC running Rigaku-brand control
and acquisition software via RS-232 communication, and is output into an ASCII data
file.

Access to the departmental Rigaku Miniflex II benchtop powder diffractometer
has enabled the characterization of numerous samples prior to, during and post
processing. The Miniflex II works slightly differently than a conventional powder
diffractometer in that the x-ray generating tube is kept stationary (Figure B.15), and the
sample holder and x-ray detector are moved in tandem to maintain the same net angular
orientation as the traditional design. This is done simply to make the machine smaller.
The x-rays are generated by bombarding a Cu target with high speed electrons: this has the effect of knocking out Kα shell electrons from the Cu, which then emits a characteristic x-ray line as higher state electrons drop down to fill the vacancy. By this method of x-ray generation, there is a standard x-ray wavelength used in instruments around the world. Co, Mo, and Fe targets are also popularly used to generate x-rays, but the Cu 1.540 Å line is the most common. The Cu target must be water cooled to prevent from overheating and melting under constant irradiation from the 30 keV electrons. The Kβ line is suppressed by a Ni filter. Soller slits take the line source of the x-ray beam, and split it into smaller, parallel beams; this is done to reduce the axial divergence of the beam. A monochromator is used to select the wavelength, and the detector is a NaI scintillator with a Be window.

![Block diagram of x-ray diffractometer](image)

*Figure B.15: Block diagram of x-ray diffractometer*
APPENDIX C:  
MAGNETIZATION

C.1 Introduction

Understanding magnetic structure is essential to explaining many macroscopically observable effects in solids. Superconductivity is a magnetic effect that has resistive consequences. Magnetic ordering of layered materials may prove to be the key to a final theoretical understanding of high-temperature superconductivity. The ability to measure and characterize different types of ordered magnetic ions plays a major part in understanding the behavior of many materials.

C.2 Paramagnetism and Diamagnetism

All atoms with unpaired electrons have an intrinsic atomic magnetic dipole moment due to electrons' orbital and spin angular momenta. Of course, atoms with paired spin up and spin down electrons (such as the ground state He atom) may have no magnetic moment. The magnetic moment of nuclei are three orders of magnitude smaller
than that of the electron; as a result, the magnetic moment of the nucleus plays little effect in the magnetism of solids. Magnetization is defined as the net magnetic moment per unit volume. In a bulk material, the effect on the atomic magnetic dipoles by an applied magnetic field is characterized by the dimensionless quantity called the magnetic susceptibility $\chi$:

$$\chi = \frac{M}{B}$$

In a material with no long-range magnetic ordering, the magnetization is relatively easy to describe. At any finite temperature, the vector direction of any atom's magnetic dipole moment is random; thus, the net magnetic moment of the bulk solid averages to zero. Application of a field changes this, and in all materials will generate some magnetization. If the susceptibility is positive, the material is 'paramagnetic'; if the susceptibility is negative, the material is 'diamagnetic'. The term 'paramagnetic' arises from the fact that when a paramagnetic material is placed in a magnetic field, it becomes magnetized; when the field is removed, the dipole moments become randomly oriented again and the material is no longer magnetized. Diamagnetism finds its origin in the same effect that drives Lenz's law in electrostatics. Just as changing the magnetic flux through a loop of wire induces a current in the wire that acts to cancel the change in flux, changing the magnetic field on an atom causes the electron(s), acting like little current loops, to move in a way such that the change in the flux is opposed: thus, applying a field causes a net magnetization opposite the direction of the applied field.

In a classical picture, application of a magnetic field on an atom causes, to first order in $B$, a precession of the electron with frequency
So long as this frequency is much lower than the frequency of the electron's motion in the absence of the field, this Larmor precession generates an electric current,

\[ I = -\frac{e}{2\pi} \frac{eB}{2m} \]

simply the charge multiplied by the number of revolutions per unit time. This current loop acts as a magnetic dipole moment. If the radius of this loop is \( R \), the magnetic moment of \( Z \) electrons can be written

\[ \mu = -\frac{Ze^2B}{4m} \langle R^2 \rangle \]

where \( \langle R^2 \rangle \) is the mean square of the distance of the electron from the nucleus in the plane perpendicular to the direction of the applied field, \( \langle R^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle \). For radially symmetric s-state orbits, the average distance of the electron from the nucleus along all three axes must be equal; thus, the average distance of the electron in three dimensions will be \( \langle r^2 \rangle = 1.5 \langle R^2 \rangle \) [137]. The quantity \( \langle r^2 \rangle \) can be directly calculated for atoms by integrating over the exact wavefunction of the state in question. Thus the expression for the diamagnetic susceptibility of a material with \( N \) atoms per unit volume can be written classically as

\[ \chi = \mu \frac{N}{B} = -\frac{N Ze^2}{6m} \langle r^2 \rangle \]

Perturbation theory yields the same formula for hydrogen-like systems. This magnetic behavior results in very small but measurable diamagnetic susceptibilities; in most measurements involving small applied fields, this contribution to the susceptibility of a
material can usually be ignored. Conduction band electrons in a solid as well as superconducting Cooper pairs also contribute diamagnetically to the susceptibility.

Paramagnetism is easily understood in terms of statistical mechanics. The magnetic dipole moments of a paramagnetic solid are randomly oriented at any finite temperature; application of a magnetic field creates distinct energy levels proportional to the angular momentum of the electron. The populations of these levels are determined by statistical mechanics, and the net magnetization can be calculated from the expectation value of the magnetic dipole moment. The energy levels of a system in a magnetic field are given by

\[ U = -\vec{\mu} \cdot \vec{B} \]

and the magnetic moment of a free atom or ion is given by

\[ \vec{\mu} = \gamma \hbar \vec{J} \]

where \( \hbar \vec{J} \) is the total angular momentum. The gyromagnetic ratio \( \gamma \) is defined as

\[ g \mu_B = -\gamma \hbar \]

where \( \mu_B \) is the Bohr magneton and the \( g \)-factor is given by the Landé equation,

\[ g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \]

where \( S \) and \( L \) are the spin and orbital angular momenta, respectively. This allows the energy levels to be written in terms of the azimuthal quantum number of the system,

\[ U = g m_J \mu_B B \]

where \( m_J \) is limited in integer increments from \( J \) to \(-J\). Calculating the magnetization then requires calculation of the expectation value of the azimuthal quantum number \( m_J \). The magnetization of a paramagnet of arbitrary angular momentum \( J \) can be obtained by
calculating the expectation value of the magnetic moment $\mu$ and multiplying by the number of atoms or ions per unit volume $N$. The expectation value can be found by summing over each possible value of $\mu$, multiplied by the probability of occupancy of that value. The probability of occupancy is found by dividing the Boltzmann factor for the energy level corresponding to a particular value of $\mu$ by the partition function $Z$ of the system. As the energy $U$ of a given value of $\mu$ is

$$U = \mu B = g m_J \mu_B B$$

the partition function $Z$ is

$$Z = \sum_{m_J = -J}^{J} e^{-g m_J \mu_B B/kT}$$

Thus, the expectation value $\langle \mu \rangle$ is

$$\langle \mu \rangle = \sum_{m_J = -J}^{J} \frac{g m_J \mu_B e^{-g m_J \mu_B B/kT}}{Z}$$

and $M = N \langle \mu \rangle$ so

$$M = N \sum_{m_J = -J}^{J} \frac{g m_J \mu_B e^{-g m_J \mu_B B/kT}}{Z} = N \sum_{m_J = -J}^{J} \frac{g m_J \mu_B e^{-U_m/kT}}{Z}$$

substituting in the value of the $m_J$-th energy level. Set

$$x = -\frac{g \mu_B B}{kT}$$

such that the sums may be written as
\[ M = N \sum_{m_j = -J}^{J} g m_j \mu_B e^{m_j x} \frac{\sum_{m_j = -J}^{J} m_j e^{m_j x}}{\sum_{m_j = -J}^{J} e^{m_j x}} = N g_\mu_B \frac{\sum_{m_j = -J}^{J} m_j e^{m_j x}}{\sum_{m_j = -J}^{J} e^{m_j x}} \]

but

\[ \sum_{m_j = -J}^{J} m_j e^{m_j x} = \frac{d}{dx} \sum_{m_j = -J}^{J} e^{m_j x} = \frac{d}{dx} \left[ \ln \left( \sum_{m_j = -J}^{J} e^{m_j x} \right) \right] \]

so then

\[ M = N g_\mu_B \frac{d}{dx} \left[ \ln \left( \sum_{m_j = -J}^{J} e^{m_j x} \right) \right] \]

Using the identity

\[ \sum_{m_j = -J}^{J} e^{m_j x} = e^{-Jx} e^{x} \left( \frac{e^{(J+1)x}}{e^x} - 1 \right) \]

the sum in the expression can be replaced, so

\[ M = N g_\mu_B \frac{d}{dx} \left[ \ln \left( e^{(J+1)x} - e^{-Jx} \right) \right] = N g_\mu_B \frac{d}{dx} \left[ \ln \left( e^{Jx} e^{x} - e^{-Jx} \right) \right] \]

\[ M = N g_\mu_B \frac{d}{dx} \left[ \ln \frac{e^{x} e^{Jx} - e^{-x} e^{-Jx}}{e^{x} - e^{-x}} \right] = N g_\mu_B \frac{d}{dx} \left[ \ln \frac{(J+1)x - Jx}{2} \right] \]

but by definition,

\[ \sinh x = \frac{e^{x} - e^{-x}}{2} \]

so then
\[ M = N g \mu_B \frac{d}{dx} \left[ \ln \frac{\sinh(J + \frac{1}{2})x}{\sinh \frac{x}{2}} \right] \]

and, differentiating by chain rule,

\[ \frac{d}{dx} \left[ \ln \frac{\sinh(J + \frac{1}{2})x}{\sinh \frac{x}{2}} \right] = \frac{(2J + 1)}{2} \coth \frac{2J + 1}{2} \frac{x}{2} - \frac{1}{2} \coth \frac{x}{2} \]

shows that the magnetization may be written as

\[ M = N g \mu_B \left[ \frac{2J + 1}{2} \coth \frac{2J + 1}{2} \frac{x}{2} - \frac{1}{2} \coth \frac{x}{2} \right] \]

or, making the substitution,

\[ y = Jx = \frac{gJ \mu_B B}{kT} \]

the magnetization may be written

\[ M = N g \mu_B J \left[ \frac{2J + 1}{2J} \coth \frac{2J + 1}{2J} \frac{y}{2J} - \frac{1}{2J} \coth \frac{y}{2J} \right] \]

where the function in brackets is known as the Brillouin function,

\[ B_J(y) = \frac{(2J + 1)}{2J} \coth \frac{(2J + 1)}{2J} \frac{y}{2J} - \frac{1}{2J} \coth \frac{y}{2J} \]

such that

\[ M = N g \mu_B J B_J(y) \]

describes the magnetization of an ideal paramagnet of arbitrary total angular momentum \( J \) in response to an applied field \( B \) at an arbitrary temperature \( T \). If \( \mu_B B \gg kT \), meaning high fields and low temperatures, the limit of the Brillouin function \( B_J(y) \) is unity; that is, the magnetization saturates with a particular value at a given applied field strength: all
magnetic moments are aligned with the field. If $\mu_B B << kT$, meaning low fields and high temperatures, the argument $y$ of the Brillouin function $B_J(y)$ is small as it goes as $\mu B/kT$. Thus by Taylor expansion of the hyperbolic cotangent,

$$B_J(y) = \frac{(J+1)y}{3J} - \frac{[(J+1)^2+J^2](J+1)y^3}{90J^3} + ...$$

and, as $y << 1$, the first term is the only relevant one. Thus the magnetization in the low field, high temperature limit may be written as

$$M = Ng \mu_B \frac{J(J+1)y}{3J}$$

$$M = Ng \mu_B \frac{J(J+1)}{3J} \frac{gJ \mu_B B}{kT}$$

$$M = \frac{NJ(J+1)g^2 \mu_B^2 B}{3kT}$$

such that the paramagnetic susceptibility is

$$\chi = \frac{M}{B} = \frac{NJ(J+1)g^2 \mu_B^2}{3kT}$$

$$\chi = \frac{Np^2 \mu_B^2}{3kT} = \frac{C}{T}$$

where $C$ is a constant and $p$ is the effective Bohr magneton count,

$$p = g \sqrt{J(J+1)}$$

This formulation of the magnetization of an ideal paramagnet of arbitrary angular moment is known as the Curie law for paramagnetism, and shows that an ideal paramagnet will always have magnetization linearly proportional to applied field and inversely proportional to the temperature of the material so long as $\mu B/kT$ is small. For most atoms, the paramagnetic susceptibility is never very large; however this is not the
case for d-block and especially f-block atoms. Paramagnetic d-block and f-block atoms can have quite profound effects on the electronic and thermal transport properties of a solid. Conduction electron paramagnetism can be adequately described by modeling bands as Fermi gases, but the scale of the effect is dwarfed by atomic magnetism in most experiments.

C.3 Magnetic Order: Ferromagnetism and Antiferromagnetism

Long-range magnetic ordering in a material is characterized by a periodic arrangement of the vector direction of atomic magnetic dipole moments, typically with the period of the underlying crystal lattice. The ordering occurs due to overlap of the wavefunctions of unpaired outer valence electrons in a solid. The spin-spin coupling of these electrons is the cause of the magnetic ordering; due to the Pauli exclusion principle, two electrons with parallel spins must be further apart spatially than two electrons with antiparallel spins. This effect lowers the electrostatic energy of the pair of electrons, making parallel or antiparallel spins more energetically favorable than unaligned; thus, a purely quantum mechanical effect is macroscopically observable as the ordering of the dipole moments generates a very large susceptibility. This can be described in terms of an exchange integral, depending on the wavefunctions of neighboring electrons:

\[
J = \iiint \Psi_1^*(\vec{r}_1) \Psi_2^*(\vec{r}_2) V(\vec{r}_1, \vec{r}_2) \Psi_2(\vec{r}_2) \Psi_1(\vec{r}_1) \, d\vec{r}_1 \, d\vec{r}_2
\]

where \( V(\vec{r}_1, \vec{r}_2) \) is the interaction energy between the two electrons. This will modify
the Hamiltonian describing the energy of the system of electrons by adding a spin-spin interaction term of the form $-2J \vec{S}_1 \cdot \vec{S}_2$. Mean field theory gives a value of $J$ of

$$J = \frac{3kT}{2zS(S+1)}$$

where $z$ is the number of nearest neighbor atoms, with further neighbors contributing negligibly. This change in the energy of the system may be positive or negative, depending on the sign of the exchange integral $J$; when it is positive, dipole moments will tend to align; this is called ferromagnetism. When it is negative, dipole moments tend to antialign; this is known as antiferromagnetism. A ferromagnet will have a spontaneous nonzero magnetization; an antiferromagnet will have zero spontaneous magnetization, as every dipole moment has a partner that points in the opposite direction. There are variations possible on this; in a material whose dipole moments antialign, if there is more than one magnetic species of ion in the unit cell as is the case for example in magnetite ($\text{Fe}_3\text{O}_4$) which has both $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions, the dipole moments will antialign without identically canceling everywhere, resulting still in a spontaneous nonzero magnetization. This case is called ferrimagnetism, and it is an interesting side note that magnetite, the first magnet ever discovered, is not actually ferromagnetic but only ferrimagnetic. Antiferromagnetism can be looked at as adjacent dipole moments being rotated 180 degrees; this however is not always the case, and a helical structure where adjacent dipole moments are rotated by some smaller angle is also possible. The interaction between spins may not always be purely ferromagnetic or antiferromagnetic in nature, either; canted antiferromagnetism is also possible, where the system of electron spins are nominally aligned antiparallel but with a slight cant such that there still is a small
spontaneous net magnetic moment. The periodicity of the 'magnetic' unit cell may be several times that of the crystalline unit cell. It is convenient to picture the quantum effect that drives magnetic ordering in a material as an actual magnetic field throughout that forces individual dipole moments to align, known as the exchange field or the Weiss molecular field. This is not an actual field and there is no associated current density with this field; however, it is a very handy conceptual tool for calculating properties of magnetically ordered systems.

Temperature is the enemy of magnetic order in solids. Heating a magnetically ordered material above a critical temperature results in thermal disorder trumping the exchange interaction, and the material acts as a paramagnet. Permanent magnetization is not possible until the material is cooled below this critical temperature. The mean-field approximation states that the exchange field experienced by each magnetic ion is proportional to the magnetization of the material,

\[ \vec{B}_{\text{exchange}} = \lambda \vec{M} \]

with \( \lambda \) a temperature-independent constant characterizing the strength of the exchange interaction. It is then possible to identify the critical transition temperature separating ordered and unordered behavior in terms of \( \lambda \). When a ferromagnetic system is above its transition or Curie temperature, under an applied magnetic field it acts like a paramagnet, with susceptibility

\[ \chi = \frac{M}{B_{\text{applied}} + B_{\text{exchange}}} \]

which will be of the Curie form \( C / T \) as above. With the supposition that the exchange field is proportional to the magnetization, the susceptibility can be obtained in terms of \( \lambda \):
so the susceptibility has a singularity at $T = T_c$, the Curie temperature. At and below this value, the magnetization has a spontaneous value as infinite $\chi$ allows finite $M$ with zero applied field $B_{\text{app}}$. Application of the Brillouin function $B_j(y)$ allows calculation of the magnetization of a ferromagnet below the Curie temperature, swapping the applied field for the exchange field in the equation. This has the expected result of the magnetization saturating at $T = 0$ as all ions participate in the exchange interaction, and with the magnetization smoothly approaching the $1 / T$ behavior of a paramagnet as the system approaches $T_c$.

An antiferromagnet also acts paramagnetic above its transition or Néel temperature; as an antiferromagnet has nearest neighbors with opposing dipole moment directions, the system acts like two interpenetrating ferromagnetic sublattices with oppositely aligned moments. Thus the same mean-field analysis that generates the ferromagnetic susceptibility relationship will also yield the antiferromagnetic susceptibility.

$$\frac{C}{T} = \frac{M}{B_{\text{app}} + B_{\text{exc}}} = \frac{M}{B_{\text{app}} + \lambda M}$$

$$M = C \frac{B_{\text{app}}}{T - \lambda C}$$

$$MT = C (B_{\text{app}} - \lambda M)$$

$$\chi = \frac{M}{B_{\text{app}}} = \frac{C}{T - \lambda C} = \frac{C}{T - T_c}$$
\[
\chi = \frac{M_1 + M_2}{B_{\text{app}}} = \frac{(C_1 + C_2) T - 2 \lambda C_1 C_2}{T^2 - T_C^2}
\]
or, recognizing that for an antiferromagnet, \( C_1 = C_2 \),
\[
\chi = \frac{2C}{T + \lambda C} = \frac{2C}{T + T_N}
\]

where \( T_N \) is the Néel temperature where there is a cusp in the susceptibility as the dipole moments align antiparallel. Experimental results are of the form
\[
\chi = \frac{2C}{T + \Theta}
\]
and values of \( \Theta \) are generally of the order of magnitude of \( T_N \), and including next-nearest neighbor interactions increases the agreement in these two terms. This is not always the case, though. At zero temperature, the susceptibility of an ideal antiferromagnet is zero, as all dipole moments are exactly canceled. For finite temperatures below the Néel temperature, the susceptibility smoothly rises to the value at \( T_N \) as it is possible to deflect the dipole moments slightly away from being antialigned, resulting in a net magnetization. With a sufficiently large applied field, it is possible to collapse the antiferromagnetic state into a ferromagnet; however, this magnetic phase change is usually not hysteretic as once the field is removed, the system returns to being antiferromagnetically ordered. As the magnetization of the two sublattices may be written in terms of the Brillouin function, an expansion [99] to first order of the Brillouin function as a Taylor series in \( B \) yields the susceptibility of an antiferromagnet (along the easy axis of magnetization):
\[
\chi(T) = \frac{N \mu_B^2 g^2 J^2 B_j'(y)}{kT + 0.5(\lambda_{ii} + \lambda_{12}) \mu_B^2 g^2 J^2 N B_j'(y)}
\]
where $\lambda_{12}$ and $\lambda_{ii}$ are molecular field constants for nearest neighbor interactions and next-nearest neighbor interactions, respectively, and $B_j'(y)$ is the derivative of the Brillouin function with respect to its argument.

Thus the nature of any long-range magnetic ordering can often times be deduced just from measuring the magnetization of a sample versus temperature and field, and the ion species responsible for the magnetism can be deduced from the size of the magnetism and the free ion dipole moment values. Long-range magnetic ordering has an additional consequence: the magnetic ordering is periodic and thus acts as a magnetic structure that can diffract a beam of neutrons via interaction of the neutron's magnetic moment with that of the electron. This magnetic lattice is not necessarily commensurate with the crystalline lattice; ferromagnetic order will remain commensurate with the crystal order, as each magnetic ion's dipole moment points in the same direction; antiferromagnetic order, however, will often have nearest-neighbor magnetic ions with oppositely directed moments; this can result in a magnetic supercell that is larger than the crystalline unit cell, which will result in additional diffraction peaks. Ferromagnetic order, on the other hand, will usually enhance the intensity of peaks arising from diffraction from the periodic arrangement of atoms. A simple test for this is performing a neutron diffraction measurement above and below a suspected magnetic ordering temperature, or by use of a spin-polarized neutron beam; such measurements can tell the distribution, direction, and order of the magnetic moments.
C.4 Magnetism and Superconductivity

Superconductivity is inherently a magnetic effect, with electrical consequences; perfect diamagnetism implies zero resistance, whereas zero resistance does not imply perfect diamagnetism. A long, thin superconducting sample with long axis parallel to an applied magnetic field will be a perfect diamagnet, expelling all applied magnetic fields with susceptibility

$$\chi = \frac{M}{B_{app}} = -\frac{1}{4\pi}$$

This is known as the Meissner effect and is due to supercurrents moving in a manner to screen the applied field from the bulk material. A normal conductor cannot manage perfect screening currents as the finite mean free path of conduction electrons prohibits permanent current loops from forming; even in a conductor with infinite mean free path, field penetration still takes place [108]. This perfect diamagnetism only occurs up to a critical value of field $H_c$, above which the diamagnetism and the superconducting state are extinguished. Superconductors that behave in this manner are classified as Type I superconductors. Type II superconductors behave somewhat differently when placed in an applied magnetic field. Type II superconductors resemble Type I superconductors up to a critical field $H_{c1}$, above which some small regions of the superconductor become normal and allow field lines to penetrate through. Above $H_{c1}$ and up to a much larger field $H_{c2}$, the superconductor is in a so-called mixed state where the penetrating magnetic flux enters the material as a regular array of flux tubes. Above $H_{c2}$, diamagnetism and the superconducting state are completely extinguished. $H_{c1}$ is very low in many materials, but $H_{c2}$ may be up to hundreds of Tesla; as putting current through a
superconducting wire will generate a magnetic field at the surface of the wire proportional to the current, it is possible to make very powerful electromagnets from a coil of Type II superconductor as the wire remains superconducting up to a very high critical field at its surface, and thus up to a very high current density. This property also makes superconducting wire very appealing for power transmission, as possible current densities are orders of magnitude higher than conventional conductors; unfortunately, the expense of cryogenics and the difficulty of machining many superconductors has limited the industrial applications of superconducting technology outside of microwave filters, magnetometers, and electromagnets.

The London equation was the first understanding of perfect diamagnetism in a superconductor, and requires consideration of the magnetic vector potential $\hat{A}$ in a superconductor. It is a fair approximation to suggest that in the absence of an applied magnetic field, the ground state of the superconductor should have no net momentum. As the canonical momentum can be written as

$$\hat{p} = m \hat{v} + \frac{e}{c} \hat{A}$$

the local average velocity in the presence of an applied magnetic field is

$$\langle \hat{v} \rangle = -\frac{e}{mc} \hat{A}$$

such that the current density $\mathcal{J} = ne \langle \hat{v} \rangle$ is thus

$$\mathcal{J} = -\frac{ne^2}{mc} \hat{A}$$

Taking the curl of both sides yields
\[ \nabla \times \vec{J} = \frac{ne^2}{mc} \nabla \times \vec{A} = \frac{ne^2}{mc} \vec{B} \]

Taking the curl of Ampere's law from electrodynamics yields

\[ \nabla \times \vec{B} = \frac{4\pi}{c} \vec{J} \quad \text{(Ampere's law)} \]

\[ \nabla \times \nabla \times \vec{B} = \frac{4\pi}{c} \nabla \times \vec{J} \]

but the vector curl identity states

\[ \nabla \times \nabla \times \vec{B} = \nabla (\nabla \cdot \vec{B}) - \nabla^2 \vec{B} \]

and as the magnetic field is divergenceless,

\[ \nabla \times \nabla \times \vec{B} = -\nabla^2 \vec{B} = \frac{4\pi}{c} \nabla \times \vec{J} \]

such that

\[ -\nabla^2 \vec{B} = -\frac{4\pi}{c} \frac{ne^2}{mc} \vec{B} \]

which is a differential equation for \( \vec{B} \). The solution for this equation in the case of the example of a long superconductor parallel to an applied magnetic field is exponential decay of the field into the superconductor,

\[ \vec{B}(x) = \vec{B}_0 e^{-\frac{x}{\lambda}} \]

where \( \lambda \) is a characteristic length scale,

\[ \lambda = \sqrt{\frac{mc^2}{4\pi ne^2}} \]

Thus for a sample thicker than this London penetration depth, the magnetic field does not penetrate the bulk of the material, and it acts as a perfect diamagnet. Further understanding of the critical fields of a superconductor were first explained by Abrikosov.
and Gor'kov, and then later by the BCS formulation [13,130]. Conduction electron scattering by intrinsic magnetic moments is a common mechanism of pair breaking in superconductors containing magnetic d- or f-block ions [89]; magnetism and superconductivity generally do not mix well. There are very few spin-triplet superconductors, in which the spins of both electrons in the Cooper pair are parallel; most superconductors, low-$T_c$ and high-$T_c$ alike, are spin-singlet, with antiparallel electron spins. As a result, long-range magnetic order is a serious problem for superconductors: carriers with opposite spin precess in different directions in a local magnetic field, and the Cooper pair is pulled apart as it passes through a region of magnetic field. The conventional understanding of materials that are both superconducting and magnetically ordered relies on the argument that the superconductivity resides in chemical layers separate from the magnetically ordered layers.

The magnetic behavior of a superconductor is unique. In most superconductors the diamagnetic transition is sharp, and the diamagnetic behavior at temperatures below the transition is essentially temperature independent as all available Cooper pairs are participating in the diamagnetic screening. Conduction electron diamagnetism can emulate the behavior, but only with susceptibility many orders of magnitude smaller; at small fields, conduction electron diamagnetism is essentially unmeasurable in conventional experiments whereas superconducting diamagnetism may be very large. The dynamics of the superconducting transition in conventional superconductors and high-temperature superconductors are well known, but it is only in conventional or low-temperature superconductors that the dynamics are well understood in terms of the BCS
formalism. There has been a very large amount of work done since the discovery of YBCO and other high-temperature cuprate superconductors since the discovery of LSCO by Bednorz and Muller [16] in 1986, but a complete theoretical understanding has not yet been made. The situation has become more complicated in the last decade as the discovery of ruthenocuprate superconductors and more recently noncuprate high-temperature superconductors has raised more questions than answers.

C.5 Measuring Magnetism via a SQUID Magnetometer

A SQUID magnetometer is currently the most popular instrument in laboratories around the world for measuring magnetization of materials at a range of temperatures and fields. The Department of Chemistry at the University of Notre Dame owns and operates a Quantum Design Magnetic Properties Measurement System (MPMS) rf SQUID Magnetometer that operates over the temperature range 1.9-400 K and the field range of 0-7 T. The instrument is capable of measuring magnetizations over many orders of magnitudes, from $10^7$ to 300 emus. This is possible due to the exquisite sensitivity of a SQUID junction to changes in magnetic flux. The magnetometer consists of a liquid He cooled cryostat, a superconducting NbTi coil magnet, and a SQUID junction.

There is a plurality of units used in magnetization literature; many sources freely mix SI and CGS units. The emu is the functional unit of magnetic moment in the CGS unit system and is related to the SI unit of magnetic moment, Amperes*meters$^2$, as
1 A*m² = 10³ emu

The SI system is often not very commonly used in magnetization measurements as 1 Tesla represents quite a large field, and measurements are regularly taken in millitesla fields or smaller. As a result the most commonly used unit of magnetic induction $B$ is the Gauss, where

$$1 \text{ Tesla} = 10^4 \text{ Gauss}$$

In the CGS system, $B$ and $H$ are used interchangeably, and when literature discusses fields and field strengths of a given value, generally $\mu_0 H$ is being described despite the factor of $\mu_0$ not being written. This is standard practice and is rarely noted. As such the units of magnetic induction $B$ and magnetic field $H$ are Gauss and Oersted in CGS, and are used interchangeably in literature.

The liquid He cooled cryostat (Figure C.1) in the instrument is of a standard design. A large reservoir of liquid He (65 L) surrounds the sample chamber, and is insulated from the room by a shielding layer of liquid N₂, vacuum spaces, and several various heat-reflective layers. The liquid He is used to control the temperature of the sample space as well as refrigerate the superconducting coil magnet below its transition temperature of 10 K. To achieve cooling, liquid He is bled at a controlled rate into the bottom end of the cooling annulus, a vacuum-insulated cylindrical region surrounding the sample space. This liquid He is forced to evaporate by action of a small heater and a vacuum pump pumping on the top end of the cooling annulus. This combination of low pressure and electrically powered heating vaporizes the liquid He and forces it to rise as cold gas, contacting the Al wall of the cylindrical sample space as it does; this has the
effect of cooling the sample space at a controllable rate, as the heater power and the vacuum pumping rate (via a set of electromechanical valves) are controlled automatically by the MPMS control software. The exterior of the sample space is wound with heater wire to provide a controlled source of heat to the sample space. By combination of the active cooling and active heating, temperature stability can be accomplished. The temperature is read out at two points, one located inside the SQUID detection coils (and thus inside the magnet), and one located at the bottom of the sample chamber, outside of the magnet. The thermometers are negative temperature coefficient thermistors, and have a field-dependent resistance below 14K; thus, at higher temperatures, the thermometer closer to the sample between the SQUID detection coils is used; at lower temperatures, the thermometer at the bottom of the sample chamber is used. Thermal gradients are sufficiently small at low temperatures that there is an insignificant temperature difference between the sample and the bottom of the sample chamber, such that it is a valid reading despite not being physically as close to the sample. Below 4.2 K, the boiling point of liquid He, the temperature stability is accomplished in a slightly different manner, as this requires cooling the liquid He itself. Lowering the temperature of liquid He can be accomplished by lowering the vapor pressure over a column of liquid He. In order to reach sample temperatures below 4.2 K, liquid He fills the lower portion of the cooling annulus, and the pressure drop in the cooling annulus is adjusted electronically until the desired temperature is achieved, and the sample chamber is cooled by conduction. At all times the sample region contains low-pressure He gas (taken from boiloff of the liquid He) to provide thermal contact with the sample. The temperature stability is monitored
by a proportional-integral-differential control loop in the temperature controller included in the MPMS control hardware.

Figure C.1: Block diagram of SQUID cryostat
The magnetization of the sample is measured by the current induced in a set of coils wound around the sample chamber as a sample is moved through them linearly along the coil axis. As the sample moves through the coil loops, any magnetization of the sample (directed through the plane of the coil loops) will induce a current in the superconducting sensor coils as the flux through the coils changes, as per the definition of inductance:

\[ \Delta \phi = L \Delta I \]

Any sample with a net spontaneous magnetization, or any sample showing a magnetization due to application of field from the superconducting magnet, will induce currents in the sensor coils. The sensor coils (Figure C.2) are wound to form a second-derivative axial gradiometer, which acts as two opposing first-derivative gradiometers placed back to back. As a result the sensor coils are insensitive to drifts or gradients in the field generated by the superconducting magnet surrounding them. Expanding the field along the axis of the sensor coils in a Taylor-Maclaurin series,

\[ B_z(z) = B_z(0) + z \frac{dB}{dz}|_{z=0} + \frac{z^2}{2} \frac{d^2B}{dz^2}|_{z=0} + \ldots \]

where the origin is the center of the lowest coil, the flux \( \Phi \) through the sensor coils can be written

\[ \phi = A \left[ B_z(0) - 2B_z(a) + B_z(2a) \right] \]

such that

\[ B_z(0) = B_z(0) \]

\[ B_z(a) = B_z(0) + a \frac{dB}{dz} + \frac{a^2}{2} \frac{d^2B}{dz^2} \]
\[ B_z(2a) = B_z(0) + 2a \frac{dB}{dz} + 2a^2 \frac{d^2B}{dz^2} \]

and thus,

\[ \phi = Aa^2 \frac{d^2B}{dz^2} \]

such that only second-order and higher terms in the expansion field can affect the flux through the coils. As the field of a magnetic dipole goes as \( r^{-2} \), that means the sensor coils are only sensitive to terms of \( r^{-4} \) and higher powers in the field of any external dipole source. The sensor coils are connected to a superconducting radio-frequency interference (RFI) isolation transformer, the other half of which is the SQUID input circuit. This transformer enables the system to be used in very noisy RFI environments without generating flux jumps while measurements are taken, as RFI can lead to a reduction of the SQUID modulation voltage. The superconducting isolation transformer is heated to its normal state whenever the magnet is charging as well as immediately before each measurement is taken to remove any persistent currents in the SQUID input circuit.
Understanding the \textit{rf} SQUID itself requires an understanding of flux quantization, Josephson junctions, and the Josephson effect. Magnetic flux threading through a superconducting ring is quantized in integer multiples of the fluxon, 

\[ \Phi_0 = \frac{\hbar}{2e} \]

This arises due to the macroscopic nature of the superconducting wave function. The superconducting state in a solid may be described with a macroscopic wave function
\[ \Psi(\vec{r}, t) = \Psi_0 e^{i\Phi(\vec{r}, t)} \]

with \( \Psi_0 \) describing the density of Cooper pairs, and the phase \( \phi \) describing their center of mass motion. In order to guarantee single-valued wavefunctions, moving once around any closed path in a superconductor can only introduce a phase shift of integer multiples of \( 2\pi \); any other value would mean that the wavefunction \( \Psi \) is not single-valued. That indicates that integrating the gradient of \( \Phi \) over a closed path, \( i.e. \) going around a superconductor bent into a ring, should result in an integer multiple of \( 2\pi \),

\[ \oint \nabla \Phi \cdot d\ell = n \cdot 2\pi \]

Writing [39] the phase gradient as

\[ \nabla \Phi = \frac{1}{\hbar} (m \vec{v} + q \vec{A}) \]

with the Cooper pair mass \( m = 2m_e \), charge \( q = 2e \), and by replacing the kinetic term via

\[ m \vec{v} = \frac{m}{qn} \vec{j} \]

and using the supercurrent density

\[ \vec{j} = qn \vec{v} \]

the line integral becomes

\[ \oint \nabla \Phi \cdot d\ell = \frac{m}{qn \hbar} \oint \vec{j} \cdot d\ell + \frac{q}{\hbar} \oint \vec{A} \cdot d\ell \]

The first integral represents the contribution of supercurrents; the second integral, the magnetic flux \( \Phi \) through the closed contour. As per the London equation, deep enough inside a superconductor the current exponentially goes to zero, and thus the first term is exponentially small so
or, substituting in the fluxon value $\Phi_0$,

$$\Phi = n \Phi_0$$

This does not mean that the flux through a superconducting ring due to supercurrents in the ring is quantized; this means that the total flux through the ring, which is the sum of any externally applied flux $\Phi_a$ and flux from the supercurrents $\Phi_{sc}$, is quantized:

$$\Phi_a + \Phi_{sc} = n \Phi_0$$

Thus, applying a magnetic field to a superconducting ring will make supercurrents that will adjust to ensure that the total magnetic flux through the ring will be quantized in units of $\Phi_0$.

A Josephson junction exploits the single-valued requirement of the superconducting wavefunction. A Josephson junction is typically made of two superconductors separated by a very thin insulating layer. Supercurrent tunneling occurs across this junction even with no voltage applied across the junction: this is the \textit{dc} Josephson effect, and it is driven by the phase difference between the two superconductors. As before, writing the wavefunctions for each superconductor as

$$\Psi_1(\vec{r}, t) = \Psi_{1e} e^{i\Phi_1(\vec{r}, t)} = \rho_1^{1/2} e^{i\Phi_1}$$

$$\Psi_2(\vec{r}, t) = \Psi_{2e} e^{i\Phi_2(\vec{r}, t)} = \rho_2^{1/2} e^{i\Phi_2}$$

after making the substitution of carrier density $\rho$ for $\Psi$, application of the time-dependent Schroedinger equation,
\( i \hbar \frac{\partial \Psi}{\partial t} = H \Psi \)

across the boundary between the two superconductors ultimately yields a relationship [47,76] for the spontaneous current in terms of the phase difference:

\[
i \hbar \frac{\partial \Psi_1}{\partial t} = eV \Psi_1 + K \Psi_2
\]

\[
i \hbar \frac{\partial \Psi_2}{\partial t} = eV \Psi_2 + K \Psi_1
\]

The energy \( eV \) represents the difference in ground state energies of the unperturbed systems in the absence of charge transfer; for no potential difference, as is the case in the \textit{dc Josephson effect}, this term is zero. \( K \) represents the transfer interaction across the insulator and is a measure of the extent of leakage of wavefunctions across the insulator.

Thus,

\[
i \hbar \frac{\partial \Psi_1}{\partial t} = K \Psi_2
\]

\[
i \hbar \frac{\partial \Psi_2}{\partial t} = K \Psi_1
\]

and, differentiating,

\[
- \frac{i \hbar}{2} \rho_1^{-1/2} e^{i\Phi} \frac{\partial \rho_1}{\partial t} e^{i\Phi} \frac{\partial \Phi_1}{\partial t} = K \rho_2^{1/2} e^{i\Phi},
\]

\[
- \frac{i \hbar}{2} \rho_2^{-1/2} e^{i\Phi} \frac{\partial \rho_2}{\partial t} e^{i\Phi} \frac{\partial \Phi_2}{\partial t} = K \rho_1^{1/2} e^{i\Phi}
\]

Multiplying each line by \( \rho_2^{1/2} e^{-i\Phi} \) simplifies the equations:

\[
- \frac{i \hbar}{2} \frac{\partial \rho_1}{\partial t} e^{i\Phi} \frac{\partial \Phi_1}{\partial t} = K (\rho_1 \rho_2)^{1/2} e^{i(\Phi_1 - \Phi)} = \alpha e^{i\delta}
\]

279
\[-\frac{i\hbar}{2} \frac{\partial \rho_2}{\partial t} - \hbar \rho_2 \frac{\partial \Phi_2}{\partial t} = K (\rho_1 \rho_2)^{1/2} e^{i(\Phi_1 - \Phi_2)} = \alpha e^{-i\delta}\]

with the substitutions

\[\alpha = K (\rho_1 \rho_2)^{1/2}\]

\[\delta = \Phi_2 - \Phi_1\]

The formulas then may be expanded into sines and cosines via Euler’s theorem, so

\[-\frac{i\hbar}{2} \frac{\partial \rho_1}{\partial t} - \hbar \rho_1 \frac{\partial \Phi_1}{\partial t} = \alpha \cos \delta + i \alpha \sin \delta\]

\[-\frac{i\hbar}{2} \frac{\partial \rho_2}{\partial t} - \hbar \rho_2 \frac{\partial \Phi_2}{\partial t} = \alpha \cos \delta - i \alpha \sin \delta\]

Equating imaginary and real components in the two equations yields a set of four differential equations:

\[\frac{\partial \rho_1}{\partial t} = -\frac{2\alpha}{\hbar} \sin \delta\]

\[\frac{\partial \rho_2}{\partial t} = \frac{2\alpha}{\hbar} \sin \delta\]

\[\frac{\partial \Phi_1}{\partial t} = -\frac{\alpha}{\hbar \rho_1} \cos \delta\]

\[\frac{\partial \Phi_2}{\partial t} = -\frac{\alpha}{\hbar \rho_2} \cos \delta\]

These four relations define the change in electron concentrations and wavefunction phases at the interface. There are two consequences of this; first,

\[\frac{\partial \rho_1}{\partial t} = -\frac{\partial \rho_2}{\partial t}\]

such that the rate of decrease of charge carriers in one side is exactly countered by an
increase in charge carriers on the other side, which is not only a statement of charge conservation, but a revelation that the current density moving across the junction is proportional to the phase difference between the two superconductors. As the current density is related to the rate of change of the charge density,

$$\frac{\partial \rho_1}{\partial t} = \frac{2 \alpha}{\hbar} \sin \delta$$

is really an expression of the current density such that

$$J = J_0 \sin \delta$$

where \(J_0\) is proportional to the transfer interaction \(K\), and is the maximum zero-voltage current passable across the junction. The second consequence is that the rate of change of the superconducting phase angles is equal:

$$\frac{\partial \Phi_1}{\partial t} = \frac{\partial \Phi_2}{\partial t}$$

This implies that the rate of change of the difference \(\delta\) is zero,

$$\frac{\partial (\Phi_2 - \Phi_1)}{\partial t} = 0$$

This will be nonzero in the \(ac\) Josephson effect, which will make the current density across the junction oscillate.

The \(ac\) Josephson effect is thus clearly related; upon biasing the junction with a constant voltage, an alternating current occurs. The result of the above difference in ground state energies, \(eV\), no longer being zero is to introduce a change in the derivatives of the phase angles:

$$\frac{\partial (\Phi_2 - \Phi_1)}{\partial t} = \frac{2eV}{\hbar}$$

281
such that the relative phase across the junction is now time dependent,

\[ \delta = \Phi_2 - \Phi_1 - \frac{2eV}{\hbar}t \]

which generates an alternating current across the junction as now

\[ J = J_0 \sin \left( \Phi_2 - \Phi_1 - \frac{2eV}{\hbar}t \right) \]

These effects allow for the construction of devices for exquisitely sensitive measurements of magnetic flux.

A SQUID, or Superconducting QUantum Interference Device, is one such tool. There are two variations, the dc SQUID and the rf SQUID. The dc SQUID is simpler theoretically but more difficult to construct; the rf SQUID is more complicated but more commonplace due to ease of machining. The rf SQUID (Figure C.3) consists of a superconducting loop interrupted by a single Josephson junction. The name is misleading; there is no quantum interference as would be the case for a dc SQUID which contains two parallel junction. The rf SQUID is coupled both to an rf-oscillating LC circuit (hence the name), and to an input coil.
For macroscopic magnetization measurements, it is much easier mechanically to couple to an input coil than to move the sample through or near the SQUID loop, as the dimensions of most SQUID loops are millimeters at most. Typically, rf and dc SQUIDs are constructed of a ring of Nb or other low-temperature superconductors, with a very short section of the ring (or two, as in the case of the dc SQUID) having a significantly smaller diameter. This very short section acts as a weak electrical link, essentially acting as a barrier and thus as the Josephson junction(s). This construction thus allows for flux quantization in the loop, as a continuous superconducting path can be drawn through the whole loop, which mandates flux quantization due to the wavefunction being single-phase; also, as an added advantage, flux quantization can be broken by exceeding the
critical current of the weak link. Doing this drives the weak link into its normal state, which means that there is no longer a continuous path and thus no longer flux quantization. The result of the phase difference around the closed path being an integer multiple of $2\pi$ was that

$$\delta = \phi_1 - \phi_2 = n \ 2\pi$$

which resulted in the expression that

$$\frac{q\Phi}{h} = n \ 2\pi$$

This implies that the phase difference $\delta$ across the Josephson junction may be written in terms of total flux through the loop and the flux quantum,

$$\delta = \frac{2\pi \Phi}{\Phi_0}$$

As above, the current in this $dc$ Josephson junction will have a sinusoidal dependence on the relative phase:

$$J = J_0 \sin \frac{2\pi \Phi}{\Phi_0}$$

This current will act to oppose any applied external flux. Thus the total flux through the ring will be

$$\Phi = \Phi_a - L J_0 \sin \frac{2\pi \Phi}{\Phi_0}$$

where $L$ is the inductance of the ring, and it is this total flux that is quantized in integer increments of $\Phi_0$. The induced currents can never perfectly cancel out the applied flux due to the weak link carrying significantly less supercurrent than the rest of the loop [120]. As applied flux is increased from zero, the induced current increases up to a
critical value, specifically the critical current of the weak link. Increasing the applied
flux above this value increases the current in the loop sufficiently to drive the weak link
normal; to accommodate this increase in applied flux to a value above that which the
current can screen, a quantum transition from \( n \) to \( n+1 \) quanta of fluxons through the ring
occurs [39], and the weak link again becomes superconducting. As a result of this jump
in flux, the total flux through the ring exceeds the applied flux, and the screening current
must change directions to preserve the quantization of total flux through the loop.
Further raising the applied flux value to one flux quantum will mean that the screening
current goes to zero, as it no longer has to screen or provide any 'excess' flux to preserve
flux quantization. Further increasing of the applied flux repeats this switching with a
period of \( \Phi_0 \). Decreasing the flux eventually causes quantum transitions from \( n+1 \) to \( n \)
fluxons through the ring; thus, a cyclic variation of applied flux is accompanied by a
hysteresis loop (Figure C.4), and the energy dissipated resistively by the weak link during
jumps (while it is in the normal state) is proportional to the area of the hysteresis loop.
The applied flux comes from two sources, from the inductive coupling to the \( rf \)-
oscillating LC or tank circuit, and the inductive coupling to the input coil. The physics of
the junction is independent of the source of the applied flux; the reason for the tank
circuit is to read out values proportional to the flux through the ring.
It is easiest to understand the readout by first examining the case with zero flux from the input coil, such that the only flux applied to the superconducting ring is that of the rf tank circuit. This circuit is driven at or near its resonant frequency with a very high Q factor such that the resonant current flowing around the tank circuit is much greater than the source current [136]. The voltage $V$ across the tank circuit is the output of the rf SQUID. As the driving current is linearly increased, the current in the tank circuit grows, the flux through the SQUID loop grows, and the voltage $V$ grows linearly; eventually the induced superconducting current can no longer screen the added flux, and the system undergoes a hysteresis loop as above. The energy lost by the hysteresis loop is taken

\[ \Phi / \Phi_0 \]

\[ -2 \quad -1 \quad 0 \quad 1 \quad 2 \]

Figure C.4: Total flux $\Phi$ through an rf SQUID loop versus the applied flux $\Phi_a$. The hysteresis loops remove energy from the LC tank circuit.
from the tank circuit, which decreases the current in the tank circuit; this current is then too small to drive the SQUID loop above its critical current value, and will require many cycles to be built up sufficiently from the driving current. Raising the driving current more will simply build energy up in the tank circuit faster; eventually, the driving current is sufficient to push the SQUID loop above its critical current value every cycle. Before this occurs, however, increasing the driving current does not change the voltage V as the required tank current to push the SQUID around the hysteresis loop is continually reached after some number of cycles, and the process starts over. Thus, the I-V plot (Figure C.5) is a straight line for this section. Once the driving current is sufficient to overload the SQUID every cycle, the linear I-V relationship is again achieved until the next higher quantum transition is reached in the SQUID. Thus, the I-V plot for the readout is like a staircase. Adding an external source of \textit{dc} flux changes this slightly. Any input signal will essentially be \textit{dc} compared to the \textit{rf} oscillation frequency of the output loop, as the input signal is generated by physically moving the sample. Having an added source of essentially constant flux means that the critical value of flux corresponding to the critical current in the SQUID is reached at a significantly smaller current in the tank circuit [120]. Sourcing an \textit{ac} current $I_w$ as in Figure C.5 that is large enough such that the system has enough flux to start the hysteresis looping, but not enough to do it every cycle illustrates this. If $\Phi_a=0$, the output voltage is $V_0$; if $\Phi_a=\Phi_0/2$, the output voltage will be $V_{02}$, changing linearly with applied flux. However, if $\Phi_a$ is increased to $\Phi_0$, the superconducting current is zero as there is no need for screening to preserve the quantization of flux through the loop; the output will again be $V_0$ as this is

287
then the same as zero applied flux. The dependence of the output voltage $V$ on the applied flux is then a sawtooth (Figure C.6), with period of $\Phi_0$. Thus the rf SQUID is very sensitive a linear detector of magnetic flux, provided that the changes in flux are limited to $\pm\Phi_0/2$ [50]. For greater range, negative-feedback and a lock-in amplifier are used to linearize the sawtooth function to allow measurement of signals significantly greater than a flux quantum.

![Figure C.5: rf SQUID current-voltage for two different values of input flux](image)

*Figure C.5: rf SQUID current-voltage for two different values of input flux*
The *dc* SQUID is much simpler by comparison. It consists of a superconducting loop interrupted by two Josephson junctions on opposite sides of the loop, with an inlet and outlet connected to a sensitive ammeter. As the phase difference through a closed loop around the superconductor is dependent on the enclosed magnetic flux, the phase difference between two paths that each go through one junction is proportional to the applied magnetic flux:

\[ \delta_b - \delta_a = \frac{2e}{h} \Phi \]  

such that the phase difference across each path is.

![Figure C.6: Dependence of output rf voltage $V_0$ on the applied flux $\Phi_a$](image)
\[ \delta_b = \delta_0 + \frac{e}{\hbar c} \Phi \]
\[ \delta_a = \delta_0 - \frac{e}{\hbar c} \Phi \]

The current through each junction again varies sinusoidally, as is the case for the \textit{dc} Josephson effect, such that
\[ J_a = J_0 \sin \left( \delta_0 - \frac{e}{\hbar c} \Phi \right) \]
\[ J_b = J_0 \sin \left( \delta_0 + \frac{e}{\hbar c} \Phi \right) \]

Thus, the total current \( J_{\text{total}} = J_a + J_b \) is
\[ J_{\text{total}} = J_0 \left[ \sin \left( \delta_0 + \frac{e}{\hbar c} \Phi \right) + \sin \left( \delta_0 - \frac{e}{\hbar c} \Phi \right) \right] \]

and, using the trigonometric sum-to-product identity
\[ \sin \alpha + \sin \beta = 2 \sin \frac{\alpha + \beta}{2} \cos \frac{\alpha - \beta}{2} \]

the total current through the \textit{dc} SQUID loop is
\[ J_{\text{total}} = 2J_0 \sin \delta \cos \frac{e \Phi}{\hbar c} \quad \text{(CGS)} \]

This current then varies with the applied flux \( \Phi \) and has period \( \frac{(n \pi \hbar c)}{e} \). Thus the increase of magnetic flux through the SQUID loop, typically via inductively coupled sensor coils, can be directly measured by the periodicity of the current through the SQUID loop. Suitable choice of electronics and amplification can make the sensitivity of the \textit{rf} and \textit{dc} SQUIDs comparable for most uses, and the \textit{rf} SQUID is still quite commonplace as it is easier to machine one Josephson junction instead of two identical junctions.
As stated, the samples are moved through the sensor coils linearly, and the sensor coils are ultimately inductively coupled to the SQUID loop. The sample is mounted on the end of a 0.2 m rod of quantalloy (nonmagnetic silicon copper alloy), which is connected to a thin, 1.5 m stainless steel rod. The steel rod passes up the length of the sample chamber and through a Teflon double lip seal to exit the sample airlock chamber. This seal is thoroughly lubricated with Apiezon M vacuum grease to ensure that the sample and airlock chambers remain free of external gas: this is necessary to prevent both ice buildup hampering mechanical movement of the sample or plugging of liquid He lines, and also to prevent buildup of frozen O$_2$, which is paramagnetic. The top end of the sample rod is held by a linear stepping motor, which is computer controlled to move the sample through the sensor coils. The sample is physically mounted inside a gelatin capsule stuffed with cotton to prevent the sample from moving about inside the capsule, and then the capsule is then stitched into a clear drinking straw with clear nylon thread. This drinking straw is then taped to the end of the quantalloy section of the sample rod. Clear thread and straws are necessary as dyes often contain magnetic transition elements, which would interfere with measurement. Following measurement, samples are stored in sealed zip-lock bags to keep out moisture; this has shown to be effective over a time frame of years. The data processing is all done in software by the instrument, with a regression algorithm fitting the observed SQUID voltage versus position data with the response of an ideal magnetic dipole; the end user is provided with ASCII files containing tabulated values of magnetization, field, temperature, time, and fitting parameters, which then may be parsed and processed as needed in standalone graphical plotting programs.
The molar susceptibility of a sample may be calculated simply. To convert emu to molar susceptibility, the magnetization measured by the SQUID (in emu) is divided by the field strength in Oe and the mass in grams, then multiplied by the molar mass of the material. This allows for quick fitting of paramagnetic responses to the Curie-Weiss law and extraction of effective magneton count; after changing the values into emu/mol, a nonlinear least squares fit is performed (using the data plotting and processing program Grace) to the function

\[ y = A_0 + \frac{A_1}{A_2 + x} \]

where \( A_0 \) is a constant offset, \( A_2 \) is a Weiss \( \theta \) (if nonzero), and \( A_1 \) is the Curie constant \( C \). This can be expressed as

\[ C = \frac{N_A \mu_B^2 \mu^2}{3 k_B} \]

where \( \mu \) is the effective magneton count. Thus, from the magnetization data direct from the instrument, it is easy to extract information about the magnetic character of the system.
APPENDIX D:
RESISTIVITY MEASUREMENTS

The electrical resistance and resistivity of samples are measured on a self-built cryogenic apparatus that can go from 1.8 K to 400 K. Resistive zeros are the second easiest characteristic to observe when searching for superconductivity in a new class of materials (after diamagnetism observed in a SQUID). The resistive behavior as a function of temperature, and occasionally as a function of applied magnetic field, reveals much about the electronic structure of the material, and often times is the only clear way to demonstrate that the intended doping levels actually were successfully achieved. A finite resistance at low temperature does not specifically mean no superconductivity; if the volume fraction of superconducting phase is too low in the polycrystalline sample, then the sample will not percolate and the transport properties will be dominated by the nonsuperconducting bulk. With a polycrystalline sample, about 20% of the bulk must be superconducting phase in order to successfully have bulk superconducting electronic transport—in the class of materials under study, this has been regularly quite difficult to accomplish. Distinguishing between metallic, insulating, and semiconducting behavior is
also important as it indicates with what success the dopant ions have gone in place: if the sample is insulating, it indicates that the doping failed, and usually diffraction analysis can verify the presence of the precursor oxide that was supposed to be the dopant, or secondary phases. Semiconducting behavior without a superconducting transition in a single phase indicates that the material is not a superconductor when doped in that manner.

In order to perform resistance measurements, square rods approximately 1 cm long and with faces 1 mm across are cut from polycrystalline pellets of sample with a clean, thin diamond saw. Often times the sintered pellets are extremely hard and fused together such that the toughness of the diamond blade is absolutely necessary. While cutting, the samples are held in place with cooled paraffin wax that had been melted into place. This wax is removed following cutting by immersion into an acetone bath inside an ultrasonic shaker. The rods are cut from the center of the middle pellet (from the original stack of 3 pellets in a batch in the furnace at a time) to ensure the material is as homogenous as possible. A 4-point resistance measurement is taken to ensure the effects of contact resistance are minimal. Making the electrical contacts is an acquired skill, as the oxides cannot be directly soldered to. Either gold or silver wire is used for the four contacts, and actual electrical contact is made by using silver paint nominally used for mounting SEM samples. As the silver paint dries, silver crystallites are left behind and get wedged into the surface of the rod and the surface of the wires, creating solid electrical contact between the bar and the wires. The sample is glued down on a rigid plastic backing, and the very fine lead wires are fed through screw pegs to large contact
pads which feed to the measurement apparatus. An alternate method of attaching contacts to sample rods involving melting wire directly to the sample surface was also tried, with limited success. In this method, a power supply is first used to charge up a capacitor. The sample rod is wired in parallel with this capacitor, with the rod being the low voltage end via an alligator clip and the gold or silver contact wire being the high voltage end. Pressing the contact wire to the surface of the sample discharges the capacitor, and the arc melts the end of the contact wire to the surface of the rod, nominally binding the two well. The failure of this method is that for many samples, the temperature of the arc is hot enough to melt the sample at the point of contact, with no guarantee that it will take the same crystalline phase when it resolidifies. Thus, this method was eventually abandoned as the ability to generate good electrical contacts was inconsistent.

Both the measurement apparatus and controlling software were hand-made. The direct-current measurement apparatus consists of an approximately 1.2 m long hollow stainless steel tube for insertion into a low-temperature cryostat. The 'warm' end of the tube is sealed and has a large Cu endcap with flanges matching those found on a standard liquid He supply Dewar. There are three hermetic feedthroughs in the endcap, with wires running down the length of the tube to the 'cold' end where the sample is mounted. These wires carry thermometry, source current, and measured voltage. At the 'cold' end, temperature is controlled by means of a standard DT-470 silicon diode temperature sensor and a small 10 Ω resistor used to supply heat, both mounted inside a small Cu block. An alternate capacitive sensor can also be used to maintain temperature stability.
in the presence of a magnetic field. The sample 'card' is soldered to the lead wires at the 'cold' end of the apparatus, directly adjacent to the Cu block housing the thermometry package. The sample and thermometry package are then covered with a Cu cap which is then taped in place. The Cu cap is internally lined with paper to prevent grounding any exposed wires, and it assists as a heat sink in keeping the temperature of the sample area homogenous. The design is chosen as such to easily facilitate making quick, cheap measurements by simply inserting the rod into a Dewar of liquid He. The mating flange at the 'warm' end of the rod is attached via an appropriately sized quick disconnect fitting such that the depth of the rod in the Dewar of liquid He can be immediately adjusted; this allows for rapidly changing the temperature of the sample with very little expenditure of increasingly expensive liquid He. Temperature stability is thus not actively controlled by bleeding cold He gas across the sample, but rather by passive cooling due to the ambient liquid or gaseous He, and heat supplied via the attached resistor.

Direct-current measurements were first performed with a Keithley Model 192 Programmable Current Source providing anywhere from 500 nA to 500 mA of current through the two outer leads on a sample, and a low impedance Keithley Model 196 Digital Multimeter measuring the induced voltage across the inner two leads on the sample. A self-written control and acquisition program running on a PC samples the data at a controllable rate, obtaining the data over GPIB from the Digital Multimeter. This method was found to induce errors due to thermoelectric effects presumably on the solder joints at both ends of the gold or silver wires. Alternating the current at an insignificantly low frequency allows this problem to be solved. Alternating at 1 or 2 Hz, measuring
voltage in both current orientations, then subtracting one data point from the other allows
the thermal biases to be canceled off, as the thermal biases do not depend on current
direction but only on temperature: 

\[
\frac{[(\text{Signal} + \text{Bias}) - (-\text{Signal} + \text{Bias})]}{2} = \text{Signal}. 
\]

This pulsing of the current can be accomplished by the same control and acquisition program
via GPIB control of the Model 192 Current Source. With this method, consistently clean
data can be obtained over many orders of magnitude of resistance. The system can
measure resistances from 1 Ω or less to 200 MΩ.

Reliable thermometry is obtained via the previously-mentioned DT-470 silicon
diode and a LakeShore Model 340 Temperature Controller. The constant-current voltage
versus temperature of the silicon diode is well known and can readily be calculated
knowing the doping of the semiconductor. As a result mass-produced DT-470 diodes are
used as standard temperature sensors in cryogenic applications in laboratories around the
world. The device requires four leads, two for sourcing current and two for measuring
voltage; the four leads are used instead of two to compensate for any contact resistance.
The LakeShore Temperature Controller sources a constant 10 μA to the diode, and the
voltage induced across it is compared to a set table of voltage versus temperature
programmed into the device, and temperature readout is displayed on the device as well
as sent to the PC acquisition program via GPIB. The controller has a proportional-
integral-differential feedback loop with the 10 Ω resistor, and automatically adjusts the
power going to the resistor to stabilize the temperature. Of course, with this passive
cooling method, the temperature at any given depth in the liquid He Dewar will
eventually destabilize as the liquid He level lowers; thus, the system is not completely

297
automated and requires an operator to check the temperature stability several times an hour. Measurements have been performed via the acquisition software in both a 'stabilizing' mode and a 'sweep' mode. The sweep mode was designed first, being easier to program; however, while ramping in temperature, there generally are thermal gradients across the 'cold' or probe end between the heater, the diode temperature sensor, and the sample, so data is not entirely accurate as the sample is not specifically at the same temperature as the diode temperature sensor. The spread is never more than 2 K so the error is not substantial. In the interest of lowering noise and error in measurements, a stabilizing mode was designed, all controlled by the acquisition software. This method starts at some minimal temperature then incrementally raises the temperature, waits for temperature stability, measures, then raises the temperature again and repeats the process to whatever cutoff temperature is desired. This makes very repeatable data. This method has the additional advantage that it can be and has been used to reliably calibrate other temperature sensors in the laboratory, something that outside firms charge hundreds to thousands of dollars to perform. The resistance probe can also be inserted into a cooled cryostat to allow active cooling with cold He gas and better temperature stability. Inserting the probe in the cryostat also allows for application of magnetic fields to observe any magnetic effects on resistance, on transition temperature, or on transition width. This direct-current method has its limitations, however; as mentioned above, superconductivity in the sample can be impossible to observe as having an inhomogeneous sample means the bulk properties dominate; if superconducting phase is located randomly and is under 20% of the bulk, superconducting transport across the
sample is generally not possible. Also for many samples, the resistance grows exponentially at low temperatures as dopant carrier populations fall; measuring hundreds of megohms can become important. Contact resistance occasionally is an insurmountable issue in direct-current measurements; this is not an issue in alternating-current measurements. As a result of these issues, performing alternating current measurements is also done on a separate but similar apparatus.

The alternating-current measurement apparatus is quite similar to the direct-current apparatus. The mounting of the samples is done in the same manner. A custom-designed and built brass head is attached to a long thin walled stainless steel tube at the 'cold' end, and at the 'warm' end there is a large sealed Cu head containing a set of hermetic feedthroughs and a flange to allow insertion of the apparatus into a research cryostat or liquid He supply Dewar. The alternating-current apparatus does not have the ability to adjust the depth of the 'cold' end inside the cryostat or Dewar; thus, it is not very useful for doing measurements with passive liquid He cooling. The wiring of the sample is identical at the 'cold' end; again there is a DT-470 silicon diode for thermometry, a picofarad capacitor for temperature stability in the presence of a magnetic field, and a 10 Ω resistor for adding heat to the system. The thermometry is again controlled by a LakeShore Model 340 Temperature Controller. The measurement is performed differently than the direct-current measurement; a Stanford Research Systems lock-in amplifier is used to make the voltage measurement, and a Hewlett-Packard function generator is used to source the alternating current. The lock-in amplifier takes its reference signal from the function generator: this minimizes signal noise. Using the lock-
in amplifier generates a grounding issue, however, as the ground of the lock-in amplifier is floating. To overcome this, a transformer must be inserted between the two voltage contacts on the sample rod and the two voltage leads on the lock-in amplifier. This is done inside the large Cu head at the 'warm' end of the apparatus. The center tap of the transformer is then wired directly to ground. Thus the five pins of the transformer have the following connections: one each to V+ and V- on the sample rod, one each to V+ and V- on the lock-in amplifier input, and one to ground. As the impedance of the sample rod is by definition not known and a function of temperature, balanced load resistors are put in serial with the voltage leads to the sample rod. Likewise, there is a current-limiting resistor in line with the current source to the sample rod. Without these current-limiting resistors, sudden large changes in the resistance of the sample rod could cause damage to the circuit elements and measurement instruments. These resistors are also located inside the large Cu head. Data readout from the lock-in amplifier is done by a custom-made control software on a PC, with communication again done via GPIB. The frequency and source current can be changed over many orders of magnitude to allow for a large variety of measurements. It can be difficult though to compare resistance data at extremely different frequencies as the output of the transformer is not perfectly frequency independent. With this measurement apparatus, miliohms to hundreds of megohm resistance samples can be measured, which cannot be done with the direct-current apparatus. There is an added difficulty in establishing the proper phase between the real and imaginary components of the resistance.
APPENDIX E:
MAGNETIC RESONANCE

E.1 Introduction

Magnetic resonance, particularly electron spin resonance or ESR, is an extremely sensitive method for probing magnetic structure in materials with magnetic ions. Via ESR it is very easy to distinguish between paramagnetism, ferromagnetism, and antiferromagnetism, and well performed ESR can be orders of magnitude more sensitive to the existence of superconductivity than SQUID magnetometry or resistance measurements. Precision measurements are of course dependent on quality equipment; substantial work has been invested in custom building an ESR spectrometer system whose sensitivity substantially exceeds that of a commercial system in the Chemistry Department at Notre Dame which works across a variety of microwave frequencies and applied magnetic fields. The sensitivity of recent work is such that an impurity phase consisting of $\sim 10^{16}$ paramagnetic ions would be detectable in a macroscopic sample containing $\sim 10^{30}$ atoms, making ESR orders of magnitude more sensitive than diffraction at detecting certain minority phases.
E.2 Electron Paramagnetic Resonance

Electron Paramagnetic Resonance or EPR is the simplest magnetic resonance to describe, and has its origins in the Zeeman effect: the lifting of degeneracy in an energy level by application of a magnetic field. This level splitting can be observed by resonant absorption of photons of the appropriate frequency. The energy of a magnetic dipole in an applied magnetic field are

\[ U = -\vec{\mu} \cdot \vec{B} \]

which is, in terms of the angular momentum quantum number \( m_J \),

\[ U = m_J g \mu_B B_z \]

where \( g \) is again the Lande g-factor, and \( B_z \) the applied field along the vector direction of the magnetic moment. In the language of electron spin resonance, \( g \) is replaced with the gyromagnetic ratio \( \gamma \)

\[ \gamma = g \mu_B \hbar \]

such that

\[ U_J = m_J \gamma \hbar B_z \]

Thus, the separation in energy between two consecutive angular momentum states \( m_J \) and \( m_{J-1} \) is given by

\[ \Delta U = U_J - U_{J-1} = m_J \gamma \hbar B_z - (m_{J-1}) \gamma \hbar B_z \]

\[ \Delta U = \gamma \hbar B_z \]

which immediately suggests the energy of the photon necessary to promote electrons between spin levels:

\[ \hbar \omega = \gamma \hbar B_z \]
\[ \omega = \gamma B_z \]

Examining the equation of motion of the magnetic moment further explains this effect. From classical mechanics, the rate of change of the angular momentum of a system is equal to the torque; so

\[ \tau = \mu \times \vec{B} \]

\[ \hbar \frac{d \vec{J}}{dt} = \mu \times \vec{B} \]

but as

\[ \mu = \gamma \hbar \vec{J} \]

this may be written as

\[ \frac{d \mu}{dt} = \gamma \mu \times \vec{B} \]

Thus applying a field along the z-axis will result in the following solutions for the magnetic dipole moment components:

\[ \mu_x = \mu \sin \theta \cos \omega t \]
\[ \mu_y = \mu \sin \theta \sin \omega t \]
\[ \mu_z = \mu \cos \theta = \gamma \hbar m_j \]

and the dipole moment precesses about the direction of the applied magnetic field. In the classical picture, the dipole moments would align themselves along the applied field; in the quantum mechanical picture, it is rather the maximum component of the moment along the direction of the applied field that is quantized. Thus, there must be dipole moment components in the xy-plane [99]. As the magnetization of the entire system is the sum of all vector dipole moments, this equation is be written for the entire system as
Thus in a static field, the magnetic dipole moments will precess about the vector direction of the applied field. This is not the only source of motion, however. When placed in an applied field, it takes time for the system to reach an equilibrium magnetization; this is because the dipole moments do not instantaneously assume new values; essentially, the system is not in thermal equilibrium while the populations of the various no longer degenerate energy levels change. This can be described by

\[
\frac{d \tilde{M}}{dt} = \gamma \tilde{M} \times \tilde{B}
\]

where \( M_0 \) is the equilibrium magnetization, taking the z direction to be that along the applied magnetic field, and \( T_1 \) is a characteristic time describing the relaxation towards equilibrium that is material-specific known as the spin-lattice relaxation time. It earns this name as it characterizes the rate of interaction of the spin with the lattice—a dipole moment can lose energy to the crystal lattice, preventing the spin system from achieving the equilibrium magnetization. The solution to the magnetization equilibrium differential equation is exponential:

\[
M_z(t) = M_0 (1 - e^{-t/T_1})
\]

This effect is not an issue in conventional measurements of magnetization, as values of \( T_1 \) are very short compared to measurement timescales; usually values are micro- to milliseconds, whereas SQUID magnetization measurements take seconds each. Thus, the z-component of the equation of motion of the system may be written

\[
\frac{d M_z}{dt} = \frac{M_0 - M_z}{T_1}
\]
As field is applied, the moments precess; however, individual spins may precess at different rates. This causes spins to lose phase coherence in the precessional motion, not involving any energy transfer but increasing the entropy of the system. As the magnetization is the sum of all vector dipole moments, de-phasing of the transverse components of the dipole moments will cause a decrease in the net transverse magnetization [117]. This interaction is characterized by a rate $T_2$, known as the transverse or spin-spin relaxation time, and the $x$- and $y$- component equations of motion become

$$
\frac{d M_x}{dt} = g (M_y B_z - M_z B_y) - \frac{M_x}{T_2}
$$

$$
\frac{d M_y}{dt} = g (M_z B_x - M_x B_z) - \frac{M_y}{T_2}
$$

These three equations of motion are known as the Bloch equations. Applying a small circularly polarized magnetic field of the form

$$B_x = B_{rf} \cos \omega t$$

$$B_y = -B_{rf} \sin \omega t$$

will drive the system to absorb energy; this represents the $B$-component of the incident photon. By applying a time-varying field $\vec{B}_{rf}$ in the plane perpendicular to the static field $\vec{B}$ that generates the precession, an additional torque on the dipole moment is caused that will attempt to turn the moment $\vec{\mu}$ either towards or away from the static field. If the frequency of this rotating field is substantially different than the calculated
resonant frequency, the average torque will be zero as the phase between $\vec{\mu}$ and $\vec{B}_{rf}$ will constantly be changing; if the frequency is that of the resonant frequency, the torque will be nonzero and constant. This is the actual mechanism of resonant absorption.

Adding the rotating fields to the equations of motion gives the result

$$\frac{d M_x}{dt} = \gamma B_z M_y + \gamma B_{rf} M_z \sin \omega t - \frac{M_x}{T_2}$$

$$\frac{d M_y}{dt} = -\gamma B_z M_x + \gamma B_{rf} M_z \cos \omega t - \frac{M_y}{T_2}$$

$$\frac{d M_z}{dt} = -\gamma B_{rf} (M_x \sin \omega t + M_y \cos \omega t) + \frac{M_0 - M_z}{T_1}$$

Examining the steady state situation where $M_z = M_0$, it is acceptable to ignore the terms containing both $B_{rf}$ and a transverse magnetization component as the product will be very small. A solution for the transverse equations of motion such as

$$M_x = m \cos (\omega t + \phi)$$

$$M_y = -m \sin (\omega t + \phi)$$

only differs in form from the driving field by a phase angle. Inserting these into the differential equations,

$$-\omega m \sin (\omega t + \phi) = -\gamma B_z m \sin (\omega t + \phi) + \gamma B_{rf} M_z \sin \omega t - \frac{m \cos (\omega t + \phi)}{T_2}$$

$$-\omega m \cos (\omega t + \phi) = \gamma B_z m \cos (\omega t + \phi) + \gamma \omega B_{rf} M_z \cos \omega t + \frac{m \sin (\omega t + \phi)}{T_2}$$

and examining $t = 0$ in the $x$ equation yields a condition on the phase angle:

$$-\omega m \sin \phi = -\gamma B_z m \sin \phi - \frac{m \cos \phi}{T_2}$$

such that, upon rearrangement,
\[ \tan \phi = -\frac{1}{(\gamma B_z - \omega)T_2} \]

Setting \( t = 0 \) in the \( \gamma \) equation,

\[ -\omega m \cos \phi = \gamma B_z m \cos \phi + \gamma B_{rf} M_z + \frac{m \sin \phi}{T_2} \]

the transverse magnetization may be written in terms of the phase angle:

\[ m = \frac{\gamma B_{rf} M_0 T_2}{T_2(\gamma B_z - \omega) \cos \phi - \sin \phi} \]

By manipulating trigonometric identities, it is possible to generate expressions for the cosine and sine terms from the tangent:

\[ \sec^2 \phi - \tan^2 \phi = 1 \]

\[ \frac{1}{\cos^2 \phi} = 1 + \tan^2 \phi \]

\[ \cos^2 \phi = \frac{1}{1 + \tan^2 \phi} \]

\[ \cos^2 \phi = \frac{1/\tan^2 \phi}{1 + 1/\tan^2 \phi} = \frac{(\gamma B_z - \omega)^2 T_2^2}{1 + (\gamma B_z - \omega)^2 T_2^2} \]

\[ \cos \phi = \frac{(\gamma B_z - \omega) T_2}{\sqrt{1 + (\gamma B_z - \omega)^2 T_2^2}} \]

such that, as

\[ \sin^2 \phi + \cos^2 \phi = 1 \]

the sine term is given by

\[ \sin^2 \phi = \frac{1}{1 + (\gamma B_z - \omega)^2 T_2^2} \]
\[
\sin \phi = \frac{-1}{\sqrt{1 + (\gamma B_z - \omega)^2 T_2^2}}
\]

Thus, combining these expressions into that for the transverse magnetization,

\[
m = \frac{\gamma B_{rf} M_0 T_2}{\sqrt{1 + (\gamma B_z - \omega)^2 T_2^2}}
\]

with the transverse magnetization reaching a maximum at

\[
\omega = \gamma B_z
\]

which is the resonant frequency.

The power dissipated by this resonant absorption is given by

\[
P = \vec{B} \cdot \frac{d \vec{M}}{dt}
\]

and may be calculated from the above equations:

\[
P = (B_{rf} \cos \omega t)(-\omega m \sin (\omega t + \phi)) + (-B_{rf} \sin \omega t)(-\omega m \cos (\omega t + \phi))
\]

\[
P = \omega m B_{rf} \left[ \sin (\omega t) \cos (\omega t + \phi) - \cos (\omega t) \sin (\omega t + \phi) \right]
\]

Using the trigonometric identity

\[
\sin (\alpha - \beta) = \sin \alpha \cos \beta - \cos \alpha \sin \beta
\]

the power expression may be rewritten as

\[
P = \omega m B_{rf} \sin (\omega t - \omega t - \phi) = -\omega m B_{rf} \sin \phi
\]

and, substituting in for the phase angle and the transverse magnetization,

\[
P = \frac{\omega \gamma B_{rf}^2 M_z T_2}{1 + (\gamma B_z - \omega)^2 T_2^2}
\]

A more general solution that involves \(M_z \neq M_0\), meaning before equilibrium is established, is more complicated. Building a set of ladder operator-like functions for the
magnetization,

\[ M_+ = M_x + i M_y \]
\[ M_- = M_x - i M_y \]

and adding in exponential time dependence such that

\[ M_+(t) = M_+ e^{-i\omega t} \]
\[ M_-(t) = M_- e^{+i\omega t} \]

the transverse components of the magnetization may be written as

\[ M_x = \frac{M_+ + M_-}{2} \]
\[ M_y = \frac{M_+ - M_-}{2i} \]

such that the Bloch equations may be rewritten as

\[ \frac{d M_+(t)}{d t} = -i y B_z (M_y - i M_x) + y B_{rf} M_z (\sin \omega t + i \cos \omega t) - \frac{M_x + i M_y}{T_2} \]
\[ \frac{d M_-(t)}{d t} = -i y B_z (M_y - i M_x) + y B_{rf} M_z (\sin \omega t + i \cos \omega t) - \frac{M_x + i M_y}{T_2} \]
\[ \frac{d M_+}{d t} = -i y B_z M_+ + i y B_{rf} M_z e^{-i\omega t} - \frac{M_+ + i M_y}{T_2} \]
\[ -i \omega M_x e^{-i\omega t} = -i y B_z M_+ e^{-i\omega t} + i y B_{rf} M_z e^{-i\omega t} - \frac{M_x e^{-i\omega t}}{T_2} \]
\((-\omega + yB_z - \frac{i}{T_2})M_+ = yB_{rf}M_z\)

such that

\[M_+ = \frac{yB_{rf}M_z}{-\omega + yB_z - i/T_2}\]

Likewise substituting in for the minus equation,

\[\frac{dM_-(t)}{dt} = yB_z (M_y + iM_x) + yB_{rf}M_z (\sin \omega t - i \cos \omega t) - \frac{M_x - iM_y}{T_2}\]

\[\frac{dM_-(t)}{dt} = i\gamma B_z (M_x - iM_y) - i\gamma B_{rf}M_z (\cos \omega t + i \sin \omega t) - \frac{M_x - iM_y}{T_2}\]

\[\frac{dM_-(t)}{dt} = i\gamma B_z M_-(t) - i\gamma B_{rf}M_z e^{i\omega t} - \frac{M_-(t)}{T_2}\]

\[i\omega M_-(t) = i \gamma B_z M_-(t) e^{i\omega t} - i\gamma B_{rf}M_z e^{i\omega t} - \frac{M_-(t)}{T_2}\]

\[(-\omega + yB_z + \frac{i}{T_2})M_- = yB_{rf}M_z\]

such that

\[M_- = \frac{yB_{rf}M_z}{-\omega + yB_z + i/T_2}\]

These two new relations allow for the generalized solutions to the transverse magnetizations:

\[M_x = \frac{-yB_{rf}M_z e^{-i\omega t}}{2(-\omega + yB_z - i/T_2)} + \frac{yB_{rf}M_z e^{i\omega t}}{2(-\omega + yB_z + i/T_2)}\]

\[M_x = \frac{(yB_z - \omega + i/T_2)yB_{rf}M_z e^{-i\omega t} + (yB_z - \omega - i/T_2)yB_{rf}M_z e^{i\omega t}}{2((yB_z - \omega)^2 + 1/T_2^2)}\]
\[ M_x = \frac{\gamma B_{rf} M_z [(\gamma B_z - \omega) \cos \omega t + (\sin \omega t)/T_2]}{(\gamma B_z - \omega)^2 + 1/T_2^2} \]

Likewise, for the y-component,
\[ M_y = \frac{\gamma B_{rf} M_x e^{-i\omega t}}{2i(-\omega + \gamma B_z - i/T_2)} - \frac{\gamma B_{rf} M_z e^{i\omega t}}{2i(-\omega + \gamma B_z + i/T_2)} \]

\[ M_y = \frac{(\gamma B_z - \omega + i/T_2) \gamma B_{rf} M_z e^{-i\omega t} - (\gamma B_z - \omega - i/T_2) \gamma B_{rf} M_z e^{i\omega t}}{2i((\gamma B_z - \omega)^2 + 1/T_2^2)} \]

\[ M_y = \frac{\gamma B_{rf} M_z [-(\gamma B_z - \omega) \sin \omega t + (\cos \omega t)/T_2]}{(\gamma B_z - \omega)^2 + 1/T_2^2} \]

It is then possible to explicitly solve for the z-component of the magnetization:
\[ \frac{d M_z}{dt} = -\gamma B_{rf} (M_x \sin \omega t + M_y \cos \omega t) + \frac{M_0 - M_z}{T_1} \]

Noting that the two transverse magnetization components have a common denominator, this becomes:
\[ \frac{d M_z}{dt} = -\gamma^2 B_{rf}^2 M_z \frac{\sin^2 \omega t/T_2 + \cos^2 \omega t/T_2}{(\gamma B_z - \omega)^2 + 1/T_2^2} + \frac{M_0 - M_z}{T_1} \]

\[ \frac{d M_z}{dt} = -\gamma^2 B_{rf}^2 M_z T_2 \frac{M_0 - M_z}{(\gamma B_z - \omega)^2 + 1/T_2^2} \]

Setting this derivative equal to zero assumes that equilibrium exists in the spin system. This is different than setting \( M_0 = M_z \), because as long as the rf-field is applied, there will always be a torque preventing this from occurring. Thus, if equilibrium is reached, \( M_0 = M_z \)

\[ \frac{M_0 - M_z}{T_1} = \frac{\gamma B_{rf}^2 M_z T_2}{(\gamma B_z - \omega)^2 + 1/T_2^2} \]

so
\[ M_z = \frac{M_0 [1 + (y B_z - \omega)^2 T_2^2]}{1 + (y B_z - \omega)^2 T_2^2 + y B_{rf}^2 T_1 T_2} \]

With this explicit value for the \( z \)-component, explicit values for the transverse components are

\[
M_x = y B_{rf} M_0 T_2^2 \frac{(y B_z - \omega) \cos \omega t + (\sin \omega t) / T_2}{1 + (y B_z - \omega)^2 T_2^2 + y^2 B_{rf}^2 T_1 T_2} \\
M_y = y B_{rf} M_0 T_2^2 \frac{-(y B_z - \omega) \sin \omega t + (\cos \omega t) / T_2}{1 + (y B_z - \omega)^2 T_2^2 + y^2 B_{rf}^2 T_1 T_2}
\]

and the power dissipated by a circularly polarized \( B \)-field may finally be calculated:

\[
P = \frac{\overline{B} \cdot \overline{d M}}{d t}
\]

\[
P = B_{rf} \cos \omega t \frac{dM_x}{dt} - B_{rf} \sin \omega t \frac{dM_y}{dt} = \frac{\omega y B_{rf}^2 M_0 T_2}{1 + (y B_z - \omega)^2 T_2^2 + y^2 B_{rf}^2 T_1 T_2}
\]

At 300 K, typical values of the spin-orbit relaxation time are \( \sim 10^{-6} \) sec, and typical values of the spin-spin relaxation time are \( \sim 10^{-10} \) sec for paramagnetic salts; as such, the denominator term \( T_1 T_2 \) is usually small enough to neglect; then, the expression reduces to the previously calculated value unless the amplitude of the \( rf \)-field is sufficiently high.

An analysis originally done by F. Dyson [44] for the line shape of paramagnetic resonance in a conductor as opposed to a noninteracting paramagnetic salt yields a similar but no longer symmetric function,

\[
y(B) = \frac{1 + (y B_z - \omega) T_2}{1 + (y B_z - \omega)^2 T_2^2 + y^2 B_{rf}^2 T_1 T_2}
\]

There exist several mechanism that either broaden or narrow the width of the magnetic resonance, the most significant of which is usually the magnetic dipolar interaction. The
internal magnetic fields will vary from dipole to dipole as a function of time, as
transitions between energy levels occur; as a result, any given dipole sees an effective
field that is the sum of the internal and the applied field, and the dipoles will precess with
a range of frequencies corresponding to the range of internal fields at various dipoles.
This will broaden the resonance line. There are weak exchange interactions in all but the
most dilute paramagnetic materials; this affects the magnetic resonance. Van Vleek
demonstrated [135] that the exchange interaction cannot broaden the paramagnetic
resonance line because it commutes with the components of the total magnetic moment,
and thus has no direct effect on the Zeeman energy. Instead, the exchange interaction
causes rapid motion in the spin system, which will average out the effects of magnetic
dipolar interactions, narrowing the resonance line [6]. The crystalline electric field can
also play a role; lattice defects and electric field splitting of energy levels will yield a
random variation of the necessary resonance frequencies, thus also broadening the
resonance line. These effects are not always of great consequence, however. In all cases
the requirement for observation of paramagnetic resonance is that there must be a
component of the rf-field $B_{rf}$ perpendicular to the static field $B_z$; the maximum resonance
will be obtained when the two fields are perpendicular, which is easy to accomplish in an
experiment.
Magnetic resonance in an ordered ferromagnet is similar to that of a paramagnet. The magnetic dipole moments precess about the direction of the applied field, and strong absorption of energy again occurs when the \textit{rf}-field frequency is equal to the precession frequency. It is generally assumed in analysis of ferromagnetic resonance that the direction of the magnetization is parallel to that of the applied field, that is, that the magnetization is saturated; this assumes that crystalline anisotropy is small, a fair assumption for polycrystalline samples as all sample orientations exist. As the susceptibility of a ferromagnet is much larger than a paramagnet, it follows that ferromagnetic resonance is of much larger magnitude than paramagnetic resonance. The exchange coupling is much more important, generally completely suppressing the dipolar interaction and strongly sharpening the resonance line. The exchange coupling also causes saturation effects at low \textit{rf}-power levels, as the ferromagnetic excitations break down into spin wave modes due to strong coupling before the magnetization vector can be rotated significantly from the \textit{z}-direction [76]. For a polycrystalline sample of randomly oriented noninteracting spherical crystallites with cubic anisotropy, first-order approximations done by Schloemann [119] yield a resonance frequency of

$$\omega_r = -\gamma (B_z - \frac{K_1}{2M_s})$$

where \(K_1\) is the first anisotropy constant, and \(M_s\) the saturation magnetization. In weakly ferromagnetic or antiferromagnetic systems, two distinct resonance modes are excitable, with opposite directions of circular polarization [78]. With molecular fields as described in Appendix C.3, and describing the energy involved in rotating both spin systems
together with an energy density constant $K$, there is an anisotropy field $B_A = K/M$ acting on each sublattice. Ignoring demagnetizing effects, the equations of motion with a transverse $rf$-field are

$$\frac{d \vec{M}_1}{dt} = y \vec{M}_1 \times [(B_x - y M_{2x}) \hat{i} + (B_y - y M_{2y}) \hat{j} + (B_0 + B_A + B_E) \hat{k}]$$

$$\frac{d \vec{M}_2}{dt} = y \vec{M}_2 \times [(B_x - y M_{1x}) \hat{i} + (B_y - y M_{1y}) \hat{j} + (B_0 - B_A - B_E) \hat{k}]$$

where $B_E = \lambda M = \lambda M_{1z} = -\lambda M_{2z}$ is the exchange field. Defining complex operators as for the paramagnetic case

$$M_x = M_x - i M_y$$

$$B_x = B_x - i B_y$$

allows solution for the resonant frequencies:

$$\omega_0 = y^{-1} \left( B_0 \pm \left| B_A (B_A + 2B_E) \right|^{1/2} \right)$$

These resonant modes may not simultaneously be excited by clever setup of the experimental apparatus; the lower frequency mode is only excited when the $rf$-field is parallel to the static field, and the higher frequency mode is only excited when the two fields are perpendicular [132]. Thus, by rotating the angle between the $rf$-field and the static field, it is possible to determine if the resonance is antiferromagnetic or weakly ferromagnetic, as only these two types of magnetic order resonate with either parallel or perpendicular orientations of the $rf$-field and the static field; ferromagnetic resonance and paramagnetic resonance only occurs if the $rf$-field has a component perpendicular to the static field.
The essential equipment necessary for observation of magnetic resonance are a large static field and a microwave-frequency \textit{rf}-source. The static field is slowly swept until the level splitting is equal to the energy of the microwave photons. In conventional nuclear magnetic resonance, the static field is actually kept static, and the (radio) frequency of the photons is adjusted, the reverse configuration of ESR. In ESR the field is varied as it is substantially easier to do that than to make high-power microwave sources that are tunable over a very wide range of frequencies. A klystron tube or Gunn diode is used as the microwave source, and the microwaves are coupled to a resonant cavity operating in the TE$_{101}$ mode containing the sample; the reflected power is measured. The resonant cavity is inserted in a conventionally designed cryostat that allows the cavity to be exposed to magnetic fields up to 7 T over a temperature range of 2-400 K. A unique feature of this spectrometer (Figure E.1) is that it does not modulate either the steady field or the \textit{rf}-field; most ESR spectrometers either apply modulation to the carrier microwave frequency or to the static field in order to measure changes in the reflected power, and not the reflected power itself. By not modulating either field, this unconventional spectrometer is able to directly measure the reflected signal instead of the derivative of the signal, and thus accurately measure signals with extremely broad line widths.
Figure E.1: Block diagram of example ESR spectrometer
The reflex klystron is a device for generation of microwaves, typically of ~1W or less for ESR measurements. In the reflex klystron, an electron gun emits a beam of electrons into a tube, the far end of which contains a negatively charged reflector plate, to set up a self-sustaining, oscillating electron beam. An rf-potential is applied across the center of the tube, which causes the electrons to form bunches each pass across the tube. This bunching of the electrons is equivalent to an rf-current and will produce an rf-field, and can be used to induce standing waves of the same frequency in an attached resonant cavity internal to the device; this cavity then acts as a source of microwaves to coupled waveguides, and the frequency can be tuned slightly by varying the voltage on the reflector plate. At microwave frequencies above 10 GHz, a Gunn diode is used as the microwave source. This semiconductor device has a region of negative differential resistance, and exploits this feature to generate microwaves. The diode is constructed entirely of uniformly $n$-doped material, with a thin region of the middle having significantly lower doping. At a sufficient value of applied voltage (the 'peak' voltage), the middle layer's conductivity decreases until at another higher voltage (the 'valley' voltage), where the current increases again. This semiconductor effect allows construction of an oscillatory $RLC$ circuit, and coupling this circuit to a resonating cavity generates microwaves at the frequency of oscillation. The maximum power available is frequency dependent as each klystron or Gunn diode is unique; the range is hundreds of milliwatts up to 1 watt. The frequency of the microwave source is modulated at 10 kHz, either by varying the reflector voltage in the klystron, or by tuning the capacitance in the $RLC$ circuit that makes up the Gunn diode assembly. This modulation frequency is
connected into and drives the reference channel of a lock-in amplifier; the output of the microwave detector provides the input of the lock-in amplifier. The frequency modulation is done for the purpose of accurately matching the frequency of the microwave source to the resonant frequency of the sample cavity. The resonant frequency varies slowly as a function of sample and temperature, and a circuit is necessary to eliminate drift.

Microwave generating devices do not necessarily work at cryogenic temperatures and as such are kept external to the cryostat and waveguides are used to transmit microwave energy to the resonant cavity containing the sample. Hollow conductive waveguides cannot support transverse electromagnetic waves, meaning waves that have neither $B$ or $E$ components in the direction of propagation; they only allow transverse electric or transverse magnetic waves, meaning that either $B$ or $E$ must lie in the direction of propagation down the waveguide. This is true as, for propagation in the $z$-direction, were $E_z$ zero, Gauss' law dictates that

$$\nabla \cdot \vec{E} = \frac{\partial E_y}{\partial x} + \frac{\partial E_x}{\partial y} = 0$$

and Faraday's law requires

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$$

$$\left( \frac{\partial E_y}{\partial y} - \frac{\partial E_x}{\partial z} \right) \hat{i} - \left( \frac{\partial E_z}{\partial x} - \frac{\partial E_x}{\partial z} \right) \hat{j} + \left( \frac{\partial E_y}{\partial x} - \frac{\partial E_z}{\partial y} \right) \hat{k} = -\frac{\partial B_x}{\partial t} \hat{i} - \frac{\partial B_y}{\partial t} \hat{j} - \frac{\partial B_z}{\partial t} \hat{k}$$

such that, when $B_z$ is zero, comparing the $z$-components,

$$\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = 0$$
But the boundary conditions on the surface of a conductor must be

\[ E_n = 0 \]
\[ \frac{\partial B_z}{\partial n} = 0 \]

such that at a waveguide surface on the x- or y-axis, the electric field is at most, constant.

The curl and divergenceless wave can be written as the gradient of a scalar, and must obey Laplace's equation

\[ \nabla^2 V = 0 \]

indicating that there are no local maxima or minima in the field; as the entire surface of the conductive waveguide must be an equipotential, the only solution is if the electric field everywhere is zero—no waves are allowed. Relaxing either the condition on \( B_z \) or on \( E_z \) allows for nonzero solutions to Maxwell's equations and thus wave propagation. A generic monochromatic wave propagating in the \( z \)-direction has fields of the form

\[ \vec{E}(x, y, z, t) = \vec{E}_0(x, y)e^{i(kz - \omega t)} \]
\[ \vec{B}(x, y, z, t) = \vec{B}_0(x, y)e^{i(kz - \omega t)} \]

and the coefficient is a vector function of coordinates,

\[ \vec{E}_0 = E_x(x, y)\hat{i} + E_y(x, y)\hat{j} + E_z(x, y)\hat{k} \]

Faraday's law and Ampere's law require

\[ \frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = i\omega B_z \]
\[ \frac{\partial B_y}{\partial x} - \frac{\partial B_x}{\partial y} = -\frac{i\omega E_z}{c^2} \]
\[ \frac{\partial E_z}{\partial y} - ik E_y = i\omega B_x \]
\[ \frac{\partial B_z}{\partial y} - ik B_y = -\frac{i\omega E_x}{c^2} \]
\[ ik E_x - \frac{\partial E_x}{\partial x} = i\omega B_y \]
\[ ik B_x - \frac{\partial B_x}{\partial x} = -\frac{i\omega E_x}{c^2} \]
which may be written in uncoupled form as, for the \( z \)-components [56],

\[
\left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\omega^2}{c^2} k^2 \right] E_z = 0
\]

\[
\left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\omega^2}{c^2} k^2 \right] B_z = 0
\]

subject to the boundary conditions mentioned above on the surface of the conductor. Separation of variables allows for solution of the \( z \)-components of the field. Trying a function of the form

\[
B_z(x, y) = P(x) Q(y)
\]

for the \( z \)-component of the magnetic field yields generic solutions of the form:

\[
P(x) = A \sin(k_x x) + B \cos(k_x x)
\]

\[
Q(y) = C \sin(k_y y) + D \cos(k_y y)
\]

In a rectangular conductive waveguide of cross-sectional dimensions \( L_x \) and \( L_y \), the fields must be zero at the boundaries; thus, the even terms in the generic solutions must be zero, and the coefficients then are restricted such that

\[
k_x = \frac{m \pi}{L_x} \quad (m = 0, 1, 2...)
\]

\[
k_y = \frac{n \pi}{L_y} \quad (n = 0, 1, 2...)
\]

such that the field amplitude may be written

\[
B_z = B_0 \cos \frac{m \pi x}{L_x} \cos \frac{n \pi y}{L_y}
\]

and the component \( E_z \) must be zero as discussed above. Solutions of this form are labeled as \( \text{TE}_{mn} \) modes. Similar arguments show identical wave solutions for \( \text{TM}_{mn} \) modes, with
$E$ and $B$ swapped. The wave number of this mode is given by

$$k = \sqrt{\frac{\omega^2}{c^2} - \pi^2 \left( \frac{m^2}{L_x^2} + \frac{n^2}{L_y^2} \right)}$$

This indicates that there is a minimum wave frequency that can propagate down the waveguide, for

$$\omega < c \pi \sqrt{\frac{m^2}{L_x^2} + \frac{n^2}{L_y^2}}$$

the wave number is complex, representing exponentially decaying fields. Thus, different sized waveguides are necessary for propagating different frequencies of microwaves. The waveguide should be constructed out of the highest-conductivity material possible, as the skin depth of the material will dissipate energy; at higher frequencies, this becomes critical. Superconducting waveguide is not used as the decrease in attenuation is trivial compared to a conventional conductor, especially in light of the engineering difficulty of using cryogenically cooled waveguide. Waveguides made entirely of gold or silver would be ideal, but mechanically unsturdy; waveguides electroplated with silver or gold are difficult to engineer as this would require plating uniformly onto an already-formed asymmetric waveguide. Brass, copper, or silver is typically used, and new sections are typically cut and silver soldered together in the laboratory as necessary.

There are several components to a microwave spectrometer, as indicated in the figure. The isolator consists of a waveguide section surrounded by a permanent magnet with field along the propagation direction; it exploits the Faraday effect to rotate the plane of polarization of the microwaves, as one polarization of microwaves will propagate at a faster phase velocity than the other polarization. By rotating the
polarization 45°, the isolator acts as a one-directional transmitter; any reflected beam traveling backwards through the isolator will have its polarization rotated another 45°, for a total of 90°. Polarizing filters at each end will then extinguish this wave, preventing any reflected microwaves from damaging the microwave source. Two attenuators are placed in the system, one between the microwave source and the cavity, and the other between the cavity and the detector. The purpose of this is to allow variable microwave power into the sample cavity while keeping the power level on the microwave amplifier and detector constant. The attenuators work by simply inserting a thin card coated with graphite into the waveguide, with the amount inserted adjustable by a graduated knob. The attenuation is measured in decibels and is given by

\[ A = 10 \log_{10} \frac{P_1}{P_2} \]

where \( P_1 \) is the power (in watts) incident on the attenuator, and \( P_2 \) the power exiting the attenuator. To protect the microwave amplifier, a value of -25 dB total attenuation is always maintained; thus by varying both attenuators simultaneously, a dynamic power range of 1 W to ~0.003 W incident on the sample cavity is possible. A wavemeter is attached to a piece of waveguide by a small hole (which attenuates very little power), and is calibrated in order to measure the resonant frequency of the microwave cavity. This is possible as the wavemeter is actually a cylindrical resonant cavity with an extremely narrow resonance, the top of which is an adjustable plunger; changing the height of the cylindrical cavity adjusts the resonant frequency, and is used to measure the resonant frequency of the sample cavity. After measurement, the wavemeter is adjusted to have a resonant frequency far away from that of the sample cavity to prevent errors in
spectrometry measurements. A directional coupler acts to split the signal between incident and reflected components; each pass through the coupler loses 3 dB or about one half of the microwave energy. This is necessary due to the construction of the coupler [109]; lowering the amount of power lost through the coupler is possible, but this would mean lowering the amount of reflected power transmitted through the coupler to the detector. The reflected microwave energy is then incident on a semiconducting microwave amplifier with a gain of 25+ dB, which greatly increases the sensitivity. The amplifier feeds the signal into a point-contact diode that rectifies at microwave frequencies, which acts as the power detector.

The sample cavity is cut from a block of high-conductivity metal, typically copper or silver, and has dimensions of $0.5\lambda$ of the microwaves at the desired frequency. A thin metal iris couples the resonant cavity to the waveguide, and the strength of this coupling is adjustable via insertion of a capacitive tuning screw immediately before the iris in the waveguide. At resonance standing waves are formed in the cavity; the spatial arrangement of these standing waves depends on the size of the cavity and the mode of the wave as discussed earlier. Standing waves confined to a rectangular box of dimensions $L_x$, $L_y$, $L_z$ will obey Maxwell's equations, just as the propagating waves in the waveguide. With the condition that the fields are zero at the edges in 3 dimensions as opposed to the 2 earlier, the magnetic field will take the form

$$B_z = B_0 \cos \frac{m \pi x}{L_x} \cos \frac{n \pi y}{L_y} \cos \frac{p \pi z}{L_z}$$

where modes are classified as $TE_{mnp}$ modes. For a cylindrical cavity of radius $a$, the field solutions are Bessel functions of the form [109]
\[ B_z = \frac{k_c B_0}{\sqrt{k_c^2 + k_z^2}} J_m(k_c r) \cos(m \phi) \sin(k_z z) \]

where the quantity \( k_c \) is the \( n \)th root of the \( m \)th-order Bessel function. Based on the standing wave pattern, it is possible to pick a spot where the microwaves' magnetic field amplitude is at a maximum, and quite uniform: for a rectangular cavity, this is along the bottom of the cavity, and for a cylindrical cavity, this is a circle on the bottom of the cavity at a calculable radius. The sample is placed at these locations. A slice of DPPH (2,2-Diphenyl-1-Picrylhydrazyl) is routinely placed on the side wall of the cavity. In both cavity types, the field along the sidewall is directed along \( z \), whereas on the bottom of the cavity, the field is directed in-plane; thus, if the static magnetic field is rotated in the plane of the cavity, the sample's magnetic environment is changed but the DPPH's magnetic environment is not. The DPPH is a well-studied paramagnet with an extremely narrow resonance line, and is used to calibrate the static magnetic field strength as well as relative signal intensities as a function of temperature.


50. J.C. Gallup. *SQUIDS, the Josephson effects and superconducting electronics*. Talyor and Francis, 1991 p56


