MAGNETIC PHASE TRANSITIONS IN PRASEODYMIUM-BARIUM DOPED MANGANITES

MICHAEL H. CHEN

Department of Physics

APPROVED:

Cristian E. Botez, Ph.D., Chair

Russell R. Chianelli, Ph.D.

William G. Durrer, Ph.D.

Pablo Arenaz, Ph.D.
Dean of the Graduate School

all good things

come to an end

MAGNETIC PHASE TRANSITIONS IN PRASEODYMIUM-BARIUM DOPED MANGANITES

by

MICHAEL H. CHEN

THESIS

Presented to the Faculty of the Graduate School of

The University of Texas at El Paso

in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE

Department of Physics

THE UNIVERSITY OF TEXAS AT EL PASO

December 2007

Acknowledgements

I wish to give thanks to the members of my committee. Dr. Cristian Botez and Dr. William Durrer of the Physics Department, and Dr. Russell Chianelli of the Chemistry Department and the Materials Research Institute. Their suggestions, comments and additional guidance were invaluable to the completion of this work. I would also like to acknowledge the camaraderie and moral support provided by my good friends and fellow physics graduate students Luis Pinales, Eric Sanchez, Francisco Carreto, Enrique Diaz, Jose Negrete, and Miguel Herrera.

Abstract

The doped manganese oxide $Pr_{0.70}Ba_{0.30}MnO_{3+\delta}$ shows distinct magnetic phase transitions before and after reoxidation. The parent sample as-prepared is oxygen stoichiometric A-site ionic disordered $Pr_{0.70}Ba_{0.30}MnO_3$ (where Pr and Ba atoms are randomly distributed on the A-sites and $\delta = 0$). After a two-step reduction-reoxidation procedure, we obtain a reoxidized sample that is oxygen non-stoichiometric A-site ionic ordered $Pr_{0.70}Ba_{0.30}MnO_{3.025}$ ($\delta = 0.025$). The reoxidized sample is actually phase separated in two distinct layers: (i) an oxygen stoichiometric A-site ordered $PrBaMn_2O_6$ phase and (ii) an oxygen non-stoichiometric A-site disordered $Pr_{0.90}Ba_{0.10}MnO_{3.05}$ ($\delta = 0.05$) phase. These two chemical phases are exchange-coupled and correspond to two magnetic phases.

The parent sample $Pr_{0.70}Ba_{0.30}MnO_3$ undergoes a conventional Weiss-Brillouin second-order magnetic phase transition from ferromagnetic to paramagnetic at $T_c = 173$ K. The reoxidized sample $Pr_{0.70}Ba_{0.30}MnO_{3.025}$ has two Curie temperatures due to the two co-existing but separate chemical phases, and its $M(T)$ curves are smooth and continuous. Yet, using the Banerjee criterion we find that the oxygen stoichiometric A-site ordered $PrBaMn_2O_6$ phase actually undergoes a *first-order* magnetic phase transition at $T_c = 133$ K, while the oxygen non-stoichiometric A-site disordered $Pr_{0.90}Ba_{0.10}MnO_{3.05}$ phase has its own second-order phase transition at a much higher temperature $T_c = 313$ K.

Table of Contents

Page

Acknowledgements iv

Abstract v

Table of Contents vi

List of Tables ix

List of Figures x

Chapter

1 Introduction 1

1.1 Why Manganites? 1

1.2 Why Praseodymium Barium doping? 1

1.3 Chemical phases of $Pr_{0.70}Ba_{0.30}MnO_{3+\delta}$ 2

1.4 Magnetic phases of $Pr_{0.70}Ba_{0.30}MnO_{3+\delta}$ 2

1.5 Landau phase transistions 3

2 Theoretical Background 5

2.1 Magnetism 5

2.1.1 Magnetic moment $\vec{\mu}$ 5

2.1.2 Magnetization $\vec{M}$ 6

2.1.3 Magnetic field $\vec{B}$ 6

2.1.4 Magnetic field intensity $\vec{H}$ (or $\vec{H}$-field) 6

2.1.5 Magnetic susceptibility χ 7

2.1.6 Diamagnetism 7

2.1.7 Paramagnetism 7

2.1.8 Ferromagnetism 8

2.1.9 Ferrimagnetism 8

2.2 Interactions 8

2.2.1 Magnetic dipolar interaction . . . 8
2.2.2 Double exchange . . . 9
2.3 Jahn-Teller effect . . . 10
2.4 Landau theory . . . 10
2.4.1 Landau free energy . . . 11
2.5 Rietveld-refinement Analysis . . . 12
3 Experimental Procedure . . . 13
3.1 Material properties . . . 13
3.1.1 Sample preparation . . . 13
3.1.2 Crystal structure . . . 14
3.1.3 Phase separation . . . 15
3.2 Apparatus: Quantum Design PPMS . . . 16
3.2.1 PPMS probe . . . 19
3.3 Methodology . . . 19
3.3.1 Temperature dependence of magnetization . . . 21
3.3.2 H-field dependence of magnetization . . . 21
4 Results and Discussion . . . 23
4.1 Curie Temperature . . . 23
4.2 Magnetic Isotherms . . . 23
4.3 Arrott Plots . . . 26
4.4 Banerjee Criterion . . . 27
5 Conclusion . . . 32
5.1 Major Findings . . . 32
5.2 Drawbacks and Limitations . . . 33
5.3 Potential Application . . . 33
5.4 Future Work . . . 33
Appendix
A Units in Magnetism . . . 35

B Symbols & Constants 36
C Periodic Table of the Elements 38
References 39
Curriculum Vitae 43

List of Tables

3.1 The Rietveld-refined parameters for crystal structures of the PBMO phases at room temperature [1]. 18

3.2 Summary of the series of experiments conducted on PPMS. 22

A.1 Units in Magnetism 35

List of Figures

2.1 Simple cubic lattice of undoped manganese oxide. Nearest neighbor pairs of Mn^{2+} ions are connected via O^{2-} ions. 9

2.2 The Jahn-Teller effect for the Mn^{3+} center of a typical perovskite MnO_6 octahedron. 10

3.1 Diagram of powder X-ray diffraction at room temperature. (a) Parent sample, in Phase I. (b) Reoxidized sample, in Phases II and III. [1] 14

3.2 Crystal structure of Phase I, oxygen stoichiometric A-site disordered $Pr_{0.70}Ba_{0.30}MnO_3$ 15

3.3 Crystal structure of Phase II, oxygen stoichiometric A-site ordered $PrBaMn_2O_6$ 16

3.4 Crystal structure of Phase III, oxygen non-stoichiometric A-site disordered $Pr_{0.90}Ba_{0.10}MnO_{3.05}$ 17

3.5 RP series of manganites. Parent sample is a perovskite ($n = \infty$) in Phase I. Reoxidized sample is phase separated ($n = 2$) into Phase II and Phase III. 17

3.6 PPMS apparatus cutaway view. 20

3.7 PPMS probe schematic. 20

4.1 Magnetization versus temperature for parent sample ($Pr_{0.70}Ba_{0.30}MnO_3$). Fastest drop occurs at $T_c = 173$ K. 24

4.2 Magnetization versus temperature for reoxidized sample ($Pr_{0.70}Ba_{0.30}MnO_{3.025}$). First derivative has two minimas at $T_c = 133$ K and $T_c = 313$ K. 24

4.3 Magnetization versus H-field isotherms for parent sample ($Pr_{0.70}Ba_{0.30}MnO_3$). $T_c = 173$ K. 25

4.4 Magnetization versus H-field isotherms for reoxidized sample ($Pr_{0.70}Ba_{0.30}MnO_{3.025}$). Phase II $T_c = 133$ K. 25