2013

The magnetic and electric properties in novel magnetic systems

Fang Hong

University of Wollongong

Recommended Citation

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.
Institute for Superconducting & Electronic Materials

The Magnetic and Electric Properties in Novel Magnetic Systems

Fang HONG

This thesis is presented as part of the requirements for the
award of the Degree of Doctor of Philosophy
of the
University of Wollongong

JAN 2013
DECLARATION

I, Fang HONG, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting and Electronic Materials, Faculty of Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for a qualification at any other academic institution.

Fang HONG

JAN 2013
ABSTRACT

The magnetic and electric properties of novel magnetic systems have aroused great interest in the physics research community. In the classic LaMnO$_3$ to DyMnO$_3$ compounds, orbital ordering and the Jahn-Teller effect play a critical role in determining the magnetic interactions. By introducing suitable alkaline earth metal ions (such as Ca$^{2+}$, Sr$^{2+}$) into ReMnO$_3$ (Re = La$^{3+}$, Sm$^{3+}$, Nd$^{3+}$, Pr$^{3+}$), insulator-metal behavior was discovered which could be modified by changing the content of alkaline earth metal ions. Furthermore, a colossal magnetoresistance effect was subsequently found around the magnetic phase transition in these materials with the Mn$^{3+}$/Mn$^{4+}$ mixed state. On the other hand, a giant magnetoresistance effect can be achieved in many multilayer systems and in granular, heterogeneous, or phase separation magnetic alloys, on the basis of which, memory devices with high density data storage have been designed and put into large-scale industrial application. There are also other significant physical phenomena, such as the exchange bias effect (the theoretical prototype of some magnetic recording devices) and multiferroic/magnetoelectric coupling (which shows the possibility of achieving much higher data storage in the future).

In the beginning, a brief review of the magnetoresistance effect, exchange bias, and multiferroic/magnetoelectric coupling is presented, giving the basic physical principles and the latest progress as well. After the introduction, the work done during this PhD study is presented as follows:

a) Structural, magnetic, heat capacity, and dielectric properties in DyMn$_{1-x}$Fe$_x$O$_3$

DyMnO$_3$ possesses an incommensurate antiferromagnetic ordering at low temperature due to the magnetic interaction competition, which can also be regarded
as a frustrated magnetic state. This special ordering produces a ferroelectric ordering according to the spin current model. To study the magnetic competition behavior, we partially replace the Mn$^{3+}$ by Fe$^{3+}$, considering that Fe$^{3+}$ has 5 electrons on its 3$d$ orbital, while Mn$^{3+}$ only has 4 electrons on that orbital. This work adds to our understanding of the stability of spiral ordering and provides experimental evidence to demonstrate the possibility of modifying the magnetic ordering in the frustrated state.

b) Structure and magnetic properties in Nd$_{1-x}$Er$_x$MnO$_3$

The rare earth manganese oxides have interesting physics, such as the orbital ordering in LaMnO$_3$. As mentioned above, DyMnO$_3$ shows multiferroic properties. The different physical behavior is strongly dependent on the rare earth element. In this work, we have chosen to study the Er$^{3+}$ doping effect on the magnetic behavior in NdMnO$_3$, considering that both Er$^{3+}$ and Nd$^{3+}$ are magnetic ions. This study will help to clarify the interaction between magnetic rare earth ions and transition metal ions, and the competition between two different magnetic rare earth ions.

c) Heat capacity in Nd$_{1-x}$Er$_x$MnO$_3$

This work is based on a thermodynamic study. The heat capacity can reveal the low temperature behavior of such a compound, such as an anomaly in the magnetic entropy and the ground state splitting of rare earth ions. Combined with the results from b), we can explain the competition between the crystal field (dependent on structure) and exchange field (dependent on the magnetic interaction).

d) Exchange bias in NdMnO$_3$ and Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$

The exchange bias effect is usually observed in bilayer systems. For bulk materials, the exchange bias effect has not been thoroughly investigated. In this work, we study
the simple perovskite NdMnO$_3$ and the magnetocaloric Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ alloy. The exchange bias field in NdMnO$_3$ can reach -2400 Oe and 1800 Oe in various cooling fields. This work will help in the exploration of more single phase materials with the exchange bias effect. This foreshadows the possibility of a room temperature exchange bias effect in other similar or different alloys.

e) Interface structure and ferroelectricity in SmFeO$_3$ thin film

Artificial stress engineering can modify the physical behavior in bulk materials. It is also possible to achieve a relatively strong ferroelectric state in some non-ferroelectric or weak ferroelectric materials. In this work, I intended to confirm this assumption and study epitaxial SmFeO$_3$ on Nd-SrTiO$_3$ substrate based on structural characterization and electric/magnetic measurements. This work will stimulate interest in interface ferroelectric behavior.

Finally, I will summarize all the work described in this thesis.
ACKNOWLEDGEMENTS

First of all, I would like to sincerely thank my supervisor A/Prof. Zhenxiang Cheng and Prof. Xiaolin Wang for their support and guidance during my PhD study. A/Prof. Zhenxiang Cheng has demonstrated his accessibility and enthusiasm for sharing his great professional knowledge of physics and materials research. This was the most critical factor that helped me get through all the difficulties during the experiments and following analysis work. A/Prof. Zhenxiang Cheng’s supervision provides me with systematic training on experimental skills, and scientific attitudes and modes of thinking. In addition, based on discussions with Prof. Xiaolin Wang, the scope of my research was expanded, and I achieved a much deeper understanding, which will have great benefits for me in my future research career for the long term. Meanwhile, I would like to take the chance to thank Prof. Shixue Dou for the excellent research environment and the support provided by ISEM.

Group members in the Spintronics Group, Dr. Yi Du, Peng Liu, Liya Feng, and others, need to be acknowledged for their suggestions, help, and support. I am also grateful to other ISEM members for their support: Dr. Wenxian Li, Dr. Germanas Peleckis, and A/Prof. Alex Pan provided the training on the PPMS; Dr. Tania Silver has helped to revise the manuscripts and thesis; Mr. Robert Morgan and Mr. Ron Kinnell helped to maintain the magnetic systems; Ms. Crystal Login and Ms. Narelle Badger dealt with any administrative problems; and Dr. Zeng Rong and Dr. Jianli Wang for their discussions on refinement.

During my study, the support and understanding from my family was especially highly appreciated.
TABLE OF CONTENTS

ABSTRACT ................................................................................................................. ii
TABLE OF CONTENTS ............................................................................................ vi
LIST OF FIGURES ..................................................................................................... x
LIST OF TABLES ..................................................................................................... xx
1 Introduction ............................................................................................................. 21
  1.1 Magnetoresistance effect ............................................................................ 22
    1.1.1 Giant magnetoresistance effect (GMR) ................................................. 23
    1.1.2 Colossal magnetoresistance effect (CMR) ............................................. 28
  1.2 Exchange bias effect .................................................................................. 31
    1.2.1 Exchange bias effect in bilayers............................................................. 31
    1.2.2 Exchange bias effect in bulk materials................................................... 33
  1.3 Multiferroics and the magnetoelectric coupling effect .............................. 35
    1.3.1 Representative multiferroic materials .................................................... 35
    1.3.2 Magnetoelectric coupling ....................................................................... 42
  1.4 My motivation and projects for this thesis work ........................................ 56
  1.5 References .................................................................................................. 58
2 The structural and magnetic properties in DyMn$_{1-x}$Fe$_x$O$_3$ ......................... 72
  2.1 Fe doping induced Jahn-Teller orbital ordering instability in DyMn$_{1-x}$Fe$_x$O$_3$
      at room temperature ........................................................................................................ 72
    2.1.1 Abstract .................................................................................................. 72
    2.1.2 Introduction ............................................................................................ 72
    2.1.3 Experimental .......................................................................................... 74
    2.1.4 Results and Discussion ........................................................................... 75
    2.1.5 Conclusion ............................................................................................. 82
2.1.6 Reference........................................................................................................... 83

2.2 Spin reorientation, and magnetic competition in the DyMn$_{1-x}$Fe$_x$O$_3$ system
85

2.2.1 Abstract ........................................................................................................... 85
2.2.2 Introduction..................................................................................................... 85
2.2.3 Experimental ................................................................................................ 88
2.2.4 Results and Discussion ............................................................................. 88
2.2.5 Conclusion .................................................................................................. 98
2.2.6 References................................................................................................... 99

3 Dielectric property study in DyMn$_{1-x}$Fe$_x$O$_3$ System ............................................. 102

3.1 Dielectric Relaxation in the DyMn$_{1-x}$Fe$_x$O$_3$ System ........................................ 102
3.1.1 Abstract ...................................................................................................... 102
3.1.2 Introduction ................................................................................................ 102
3.1.3 Experimental ............................................................................................. 103
3.1.4 Results and discussion .............................................................................. 104
3.1.5 Conclusion .................................................................................................. 110
3.1.6 References................................................................................................... 111

3.2 Temperature and Frequency Dependent Giant Magnetodielectric Coupling
in DyMn$_{0.33}$Fe$_{0.67}$O$_3$.................................................................................................. 114
3.2.1 Abstract ...................................................................................................... 114
3.2.2 Introduction ................................................................................................ 114
3.2.3 Experimental ............................................................................................. 115
3.2.4 Results and discussion .............................................................................. 116
3.2.5 Conclusion .................................................................................................. 123
3.2.6 References................................................................................................... 123
4 Strong 4f Electron Interaction and Magnetic Ordering Modification in Nd$_{1-x}$Er$_x$MnO$_3$ ($0 \leq x \leq 0.5$) .......................................................... 126

4.1 Abstract .......................................................................................... 126
4.2 Introduction ..................................................................................... 126
4.3 Experimental .................................................................................. 128
4.4 Results and discussion ................................................................... 129
  4.4.1 Structural properties ................................................................. 129
  4.4.2 Magnetic properties ................................................................. 134
4.5 Conclusion ..................................................................................... 145
4.6 References ..................................................................................... 145

5 Competition between the Crystal field and the Exchange Field in Er$^{3+}$ Doped NdMnO$_3$ ................................................................. 148

5.1 Abstract .......................................................................................... 148
5.2 Introduction ..................................................................................... 148
5.3 Experimental .................................................................................. 151
5.4 Results and Discussion ................................................................... 151
  5.4.1 Specific heat around antiferromagnetic transition ....................... 151
  5.4.2 Specific heat in the low temperature range ................................. 154
5.5 Conclusion ..................................................................................... 163
5.6 References ..................................................................................... 164

6 Exchange bias effect in Rare earth and transition metal compounds .......... 167

6.1 Positive and Negative Exchange Bias Effects in the Simple Perovskite Manganite NdMnO$_3$. ................................................................. 167
  6.1.1 Abstract .................................................................................. 167
  6.1.2 Introduction ............................................................................. 167
LIST OF FIGURES

Figure 1.1-1 The GMR effect reported by M.N. Baibich et al. in Fe/Cr superlattices. ................................................................. 23

Figure 1.1-2 Oscillatory dependence of the GMR effect (top) and saturation field (bottom) on the thickness of the non-magnetic layer in Fe/Cr superlattices, with the insets showing enlargements for higher thicknesses. ......................................................... 25

Figure 1.1-3 Magnetic hysteresis loop and GMR effect in NiFe/Cu/NiCo. ......................... 26

Figure 1.1-4 The GMR effect (top) and magnetic hysteresis loop at 5 K (bottom) in phase separation state of Co_{16}Cu_{84} alloy thin film. .................. 28

Figure 1.1-5 Magnetic field effect on the resistivity in Sm_{1-x}Sr_{x}MnO_{3} and Nd_{1-x}Sr_{x}MnO_{3}. .......................................................... 30

Figure 1.2-1 Exchange bias effect observed in LaNiO_{3}-LaMnO_{3} superlattice interface. .......................................................... 32

Figure 1.3-1 Control of magnetization direction in (Cu, Ni)B_{2}O_{4} at 15 K by an electric field. .......................................................... 43

Figure 1.3-2 Dependence of $\Delta \theta$ on the magnetic field in various electric fields. ......................... 44

Figure 1.3-3 Structure and spin arrangement in single crystal Ba_{2}Mg_{2}Fe_{12}O_{22}. (A) the schematic crystal structure with alternative L (brown) and S (green) blocks; (B) proper screw spin structure at zero field (from 50-195 K); (C) longitudinal conical spin structure at zero field for $T < 50$ K; (D) slanted conical spin structure when the field is 30 mT below 195 K. ......................................................... 46

Figure 1.3-4 (A) Magnetoelectric phase diagram in magnetic field; (B) magnetization versus magnetic field curve at 5 K when the magnetic field is applied along [100], (inset, magnetization versus temperature curve along [001]); (C)
polarization versus magnetic field at 5 K corresponding to M-H curve. Dashed lines are used to show the phase boundary in (B) and (C). Figure 1.3-5 Electric, transport, and magnetic behaviour of the lead zirconate titanate (PZT)/12 u.c. lanthanum strontium manganite oxide (LSMO) structure.

Figure 1.3-6 Schematic model of the spin configurations in LSMO at the PZT interface for the depletion and accumulation states, showing the changes in the Mn and O orbital states and the expected changes in the magnetic moment per layer.

Figure 1.3-7 (a) Polarization dependent oxygen K-edge XAS spectra at T = 10 K. Temperature dependent polarized XAS spectra with the polarization direction in-plane (b) and out-of-plane (c) for the specified bonding region of O 2p - Mn(Fe) 3d. (d) Temperature dependence of peak positions of interface orbitals.

Figure 1.3-8 (a) Schematic diagram of the interface electronic orbital reconstruction, with hybridization. (b) Proposed interface spin configuration and coupling mechanism with x^2-y^2 orbital ordering in the interfacial LSMO. (c) Schematic diagram of the origin of the interface magnetism.

Figure 1.3-9 Electric transport properties of BFO/LSMO: (a) temperature dependence of shear resistance, with the inset showing the temperature range from 0 to 300 K; (b) magnetic field dependence of normalized resistance after -1 T and 1 T cooling; (c) hysteresis behaviour of R_s vs. V_G; (d) hysteresis behaviour of H_c-V_G.

Figure 1.3-10 Periodical control of the exchange bias field, H_{EB}, with pulsed voltage.
Figure 1.3-11 (a) PFM image of BFO (red and green show opposite polarizations),
(b) XMCD–PEEM image of LSMO deposited on BFO, (c) images for different incoming light directions\textsuperscript{161}. .............................................................. 54
Figure 1.3-12 Schematic diagram showing mechanism of exchange bias mediated ME coupling in the LSMO/BFO system\textsuperscript{161} ....................................................... 54
Figure 1.3-13 Reversible control of main FM domain in LSMO film by external electric field applied on BFO\textsuperscript{161} ........................................................................ 55
Figure 1.3-14 Resistances and TMR in fields of 2 junctions for tunnel junction with ferroelectric interlayer\textsuperscript{162}. .................................................................................. 56
Figure 1.3-15 Reversible control of TMR in external electric field and magnetic field \textsuperscript{162}. BTO is bismuth titanium oxide. ........................................................... 56
Figure 2.1-1 (a) XRD refinement calculation results on DyMnO\textsubscript{3} with $\chi^2 = 1.7$ (star symbols: experimental data, and solid red line: fitted curve, using Rietveld structural refinement, respectively.) The mismatch between the measured and Rietveld refined spectra is plotted with a slight downshift for clarity. The short vertical solid lines are guides for the eyes to mark the corresponding Bragg positions. (b) Lattice parameter dependence on Fe content of DyMn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} samples .............................................................................................................. 75
Figure 2.1-2 Fe content dependence of Mn/Fe-O bond distances and Mn/Fe-O-Mn/Fe bond angles: interplane (a) and in-plane (b). ....................................................... 77
Figure 2.1-3 (a) Raman spectra of representative DyMn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} samples measured at room temperature, (b) the typical result of fitting DyMn\textsubscript{0.67}Fe\textsubscript{0.33}O\textsubscript{3} with a Voigt profile. ................................................................................................................ 79
Figure 2.1-4 Fe content dependence of the typical vibration modes (a) and their FWHMs (b). ............................................................................................................... 80
Figure 2.2-1 (a) XRD refinement calculation results on DyMn$_{0.8}$Fe$_{0.2}$O$_3$ with $R_p = 8.9\%$ (star symbols, experiment data; solid line, fitting data; short vertical solid lines, Bragg positions; fluctuation line at bottom, difference). Inset: Fe content dependence of Mn/Fe-O-Mn/Fe angles and Mn/Fe-O distances within $ab$-plane. (b) Lattice parameter dependence on Fe content. ................................. 89

Figure 2.2-2 (a) ZFC and FC M-T curves of DyMnO$_3$. Inset: Temperature dependence of normalized $d\chi/dT$ for $x \leq 0.5$. (b) / (c) temperature dependence of magnetic moment at low/high temperature range for $0.5 < x \leq 1$. (d) The Fe content dependence of the Néel temperatures ($T_N$) and spin reorientation temperatures ($T_r$). Speculated magnetic states are presented. ............................ 91

Figure 2.2-3 Heat capacity property of DyMnO$_3$ measured from 2K to 55K, showing two abnormalities around 6.5K and 39K, respectively. ................................. 92

Figure 2.2-4 (a-c) ZFC and FC temperature dependence of magnetic moment for samples with $x=0.2$, 0.33 and 0.5, respectively. ......................................................... 93

Figure 2.2-5 Curie-Weiss law fitting of DyMn$_{1-x}$Fe$_x$O$_3$, $x = 0.6$ to 1.0. .................. 94

Figure 2.2-6 (Colour online) Magnetic hysteresis loops at 5 K from -5 T to 5 T for samples with (a) $x \leq 0.5$ and (b) $0.5 < x \leq 1$. ................................................................. 98

Figure 3.1-1 (a) X-ray diffraction patterns of all samples, (b) $x$ dependence of lattice parameters. ........................................................................................................... 104

Figure 3.1-2 Temperature dependence of complex dielectric constants and loss for representative samples. ................................................................. 106

Figure 3.1-3 Frequency dependence of the real dielectric constant $\varepsilon'$ at various temperatures: scattered symbols, experimental data; lines, the output of fitting via the modified Debye equation. ......................................................... 107
Figure 3.1-4 Arrhenius Law fitting for all samples and corresponding activation energies at low temperature. .......................................................................................................................... 108

Figure 3.1-5 Fe content dependence of characteristic frequency $f_0$ and activation energy $E$ ............................................................................................................................. 109

Figure 3.2-1 XRD refinement result of DyMn$_{0.33}$Fe$_{0.67}$O$_3$ with $R_p = 9.9\%$ (star symbols, measured, and solid line, fitted). The difference between the measured and Rietveld refined spectra is plotted with a slight downshift for clarity. The short vertical solid lines are guides for the eyes to mark the corresponding Bragg positions. .................................................................................................................. 116

Figure 3.2-2 (a) Temperature dependence of magnetic moment from 10 K to 600 K (black closed triangles: standard mode, red closed circles: oven mode). Inset: magnetic hysteresis loop measured at 5 K. (b) Inverse DC susceptibility versus temperature as measured in an external field of 1000 Oe for the paramagnetic state of DyMn$_{0.33}$Fe$_{0.67}$O$_3$ above 450 K (dashed line: Curie-Weiss fit; triangles: the inverse curve from experimental data). ........................................................................ 118

Figure 3.2-3 Frequency dependence of dielectric constant, loss at 310 K, 285K and 250K, respectively............................................................................................................................. 119

Figure 3.2-4 Frequency dependence of magnetodielectric coupling constant (MDC) and dynamic magnetoloss (ML) at 310 K, 285K and 250K, respectively........ 120

Figure 3.2-5 Frequency dependence of dynamic magnetoresistance (MR) at 310 K, 285K and 250K, respectively.............................................................. 121

Figure 4.4-1 XRD patterns for Nd$_{1-x}$Er$_x$MnO$_3$ ......................................................................................................................... 129

Figure 4.4-2 Typical refinement results for Nd$_{0.67}$Er$_{0.33}$MnO$_3$ with $\chi^2 = 1.8$ .......... 130

Figure 4.4-3 Doping rate x dependence of lattice parameters ......................... 131

Figure 4.4-4 X dependence of theoretical tolerance factors and spontaneous stress 131
Figure 4.4-5 X dependence of Mn-O bond distances, Mn-O-Mn bond angles inter-plane and in-plane, and Nd/Er-Mn distances. ................................................................. 134

Figure 4.4-6 Field cooling temperature dependence of magnetic moment for NdMnO$_3$, (a) 20 and -20 Oe (cooling field); (b) 100 and -100 Oe. ....................... 135

Figure 4.4-7 Field cooling temperature dependence of magnetic moment: (a) $x = 0.1$, 500 Oe, and $x = 0.2$, 100 Oe; (b) $x = 0.33$, 100 Oe, and $x = 0.5$, 100 Oe. ...... 136

Figure 4.4-8 Magnetic hysteresis loops for $x = 0$ measured at (a) 30 K and 55 K, (b) 20 K and 35 K. .................................................................................. 138

Figure 4.4-9 Magnetic hysteresis loops for $x = 0.1$, 0.2 and 0.33 measured at 30 K ............................................................................................................. 139

Figure 4.4-10 Magnetic hysteresis loops for $x = 0.5$ measured at 30 K, showing a typical AFM behaviour .................................................................................... 139

Figure 4.4-11 Temperature dependence of magnetic moment in various magnetic fields ........................................................................................................ 140

Figure 4.4-12 Temperature dependence of $dM/dT$ under different cooling fields: (a) $x = 0$, 1 T; (b) $x = 0$, 5 T; (c) $x = 0.1$, 0.5 T; and (d) $x = 0.5$, 0.1 T. ............... 142

Figure 4.4-13 Curie-Weiss Law fitting of all samples ................................................................................................................................. 143

Figure 4.4-14 Proposed magnetic ordering of Mn$^{3+}$ sub-lattice at 0 T for (a) $x = 0$ at 55 K, (b-c) $x = 0.1$, 0.2, 0.33, and 0.5 at 30 K, respectively. ..................... 144

Figure 4.4-15 Low temperature magnetic hysteresis loops at 5 K ................. 145

Figure 5.4-1 Temperature dependence of $Cp/T$ for Nd$_{1-x}$Er$_x$MnO$_3$ for $x = 0$, 0.1, 0.2, 0.33, and 0.5. ................................................................. 152

Figure 5.4-2 (a) Phonon and electron contribution to specific heat (small red dotted line) is subtracted from experimental data (big blue dotted line) for the sample with $x = 0$; (b) temperature dependence of the residual magnetic contributions to
the antiferromagnetic transitions for all samples; (c) temperature dependence of integrated magnetic entropy for all samples calculated from (b). ............... 153

Figure 5.4-3 Energy level and ground state splitting scheme of (a) Nd$^{3+}$ $^4I_9/2$ and (b) Er$^{3+}$ $^4I_{15/2}$. ........................................................................................................... 154

Figure 5.4-4 (a) Low temperature specific heat fitting for sample with $x = 0$ (red dots: experimental data; solid black line: fitting result; green dashed dotted line: spin wave and lattice contribution; red dashed line: Schottky anomaly from ground state splitting of rare earth Nd$^{3+}$ ions); (b) low temperature specific heat fitting for sample with $x = 0.2$ (red dots: experimental data; solid black line: fitting result; blue dashed dotted line: spin wave and lattice contribution; red dashed dotted line: Schottky anomaly from ground state splitting of rare earth Nd$^{3+}$ ions; green dotted line: Schottky anomaly from ground state splitting of rare earth Er$^{3+}$ ions). ......................................................................................... 157

Figure 5.4-5 Low temperature specific heat fitting for samples with $x = 0.1, 0.33$ and 0.5 (red dots: experimental data; solid black line: fitting result; blue dashed dotted line: spin wave and lattice contribution; red dashed dotted line: Schottky anomaly from ground state splitting of rare earth Nd$^{3+}$ ions; green dotted line: Schottky anomaly from ground state splitting of rare earth Er$^{3+}$ ions). ............ 159

Figure 5.4-6 Doping rate dependence of the energy gap between two splitting Nd$^{3+}$ ground states ($E_1$). ....................................................................................................................... 160

Figure 5.4-7 Doping rate dependence of the energy gap between two splitting Er$^{3+}$ ground states ($E_2$). ....................................................................................................................... 161

Figure 5.4-8 Doping rate dependence of spin wave stiffness coefficient. ............... 163

Figure 6.1-1 XRD Rietveld refinement results for NdMnO$_3$, with $\chi^2 = 2.4$ (star symbols, experimental data, and solid red line, fitted pattern from Rietveld
structural refinement, respectively). The mismatch between the measured and Rietveld refined spectra is plotted with a slight downshift for clarity. The short vertical solid lines are guides for the eyes to mark the corresponding Bragg positions.

Figure 6.1-2 (a) Zero field cooling and 5000 Oe field cooling temperature dependence of magnetic moment; (b) Curie-Weiss law fitting for spin state calculation.

Figure 6.1-3 (a-d) Magnetic hysteresis loop measured at 30 K while the Nd$^{3+}$ is in the short range ordering state after cooling down from 150 K in various positive cooling fields: 0 T, 2 T, 5 T, and 10 T, respectively.

Figure 6.1-4 (a-d) Magnetic hysteresis loop measured at 8 K, at which temperature the Nd$^{3+}$ is in the long-range ordering state after cooling down from 150 K in various positive cooling fields: 0 T, 2 T, 5 T, and 10 T, respectively.

Figure 6.1-5 (a) Cooling field dependence of the exchange bias field at 30 K (red solid circles); (b) cooling field dependence at 8 K (pink triangles).

Figure 6.1-6 (a) Scheme of the spin arrangement when Nd$^{3+}$ is in the short-range ordering state at 30 K; (b) scheme of the spin arrangement when Nd$^{3+}$ is in the long-range ordering state at 8 K.

Figure 6.2-1 The cooling field temperature dependence of magnetic moment in cool-down mode; inset: Temperature dependence of $dM/dT$, which helps to display the two transitions clearly.

Figure 6.2-2 The magnetic hysteresis loops measured in zero cooling field at 295K (a), 130K (b) and 100K (c) from -2000 Oe to 2000 Oe.
Figure 6.2-3 The magnetic hysteresis loops measured at 130K (a) and 100K (b) after the sample was cooled down from 200K in the 3T external field, respectively
........................................................................................................................................ 189

Figure 6.2-4 The magnetic hysteresis loops measured at 30K (a), 20K (b) and 10K (c), after the sample was cooled down from 200K in the 0T external field, respectively; The magnetic hysteresis loops measured at 30K (d), 20K (e) and 10K (f), after the sample was cooled down from 200K in the 3T external field, respectively. ..................................................................................................... 190

Figure 6.2-5 The cooling field dependence of the exchange bias fields at 30K, 20K and 10K. ........................................................................................................................................ 191

Figure 7.4-1 X-ray diffraction of the SmFeO₃ film deposited on (001) Nb-STO single crystal substrate, lattice parameter: STO cₐ=3.905 and SFO cₐ=3.720. ............ 200

Figure 7.4-2 (a) The interface between the SmFeO₃ thin film and the STO substrate, on which the grain boundary of [010]₀ and [101]₀ is also shown. (b) the HRTEM image of the film/substrate interface, magnified the selected [010] growth area in (a). showing the epitaxial growth. (d) Selected area electron diffraction pattern, the high level diffraction spot shows the splitting, indicating of the different structures existing in the film......................................................... 201

Figure 7.4-3 (a) Electric hysteresis loop of SmFeO₃ films on Nb-STO at room temperature, (b) time dependence of applied voltage and corresponding current. ........................................................................................................................................ 203

Figure 7.4-4 Fatigue test result after 10⁶ cycles (10 data points every decade)....... 203

Figure 7.4-5 The time dependence of (a) applied voltage (ranging from -2V to 2V) and (b) consequent current measured by PUND mode........................................ 205
Figure 7.4-6 Nano-scale ferroelectric domain structure characterized by PFM: (a) amplitude image and (b) phase image; (c) PFM lithography, inset: the pre-set pattern and (d) amplitude distribution along the red line across the lithography pattern in (c).

Figure 7.4-7 (a) Temperature dependence of magnetic moment from 10K to 300K, and Magnetic hysteresis loop measured at 100K; (b) Antiferromagnetic interaction of Fe$^{3+}$ sublattice confirmed by Curie-Weiss law fitting with temperature range from 100-300K.
LIST OF TABLES

Table 1 the information on atomic positions, bond lengths, and bond angles .......... 133
Table 2 Spin state calculation based on the Curie-Weiss Law fitting results .......... 143
1 INTRODUCTION

Magnetic materials are widely used in our daily lives and in industry. One of these representative applications is data storage based on the magnetoresistance effect in some novel magnetic materials. In this chapter, I would like to briefly introduce the background of basic magnetic systems and review several significant physical phenomena which are regarded as the milestones and hot topics in the physics and materials fields.

To be simple, intrinsic magnetism can be induced by unpaired electrons whose spins produce net magnetic moments. This phenomenon can be observed in ionic states (for example, LaMnO$_3$ is a classic magnetic material as the element Mn is in an ionic state and carries unpaired electrons) and in normal atomic states as well (for example, CoPt is a typical magnetic material, as Co carries unpaired electrons, but not in an ionic state). We are familiar with Fe, as it is an important material used in various fields, such as steel in housing and buildings in general. It is also the structural material of cars. Fe itself can also be a magnetic material, and Fe rods are usually inserted into solenoids to enhance the output magnetic fields. Considering that there are many atoms or ions containing unpaired electrons, magnetism can exist in a large numbers of materials. On the other hand, a magnetic field can be produced by an electric current, as shown in any introductory physics textbook, but it is a non-intrinsic magnetism and different from what I am going to present in this thesis.

In the last several decades, magnetic materials have been of great interest in physics research. The following brief review will allow us to know some unique magnetic properties, such as the magnetoresistance effect, the exchange bias effect, the multiferroic property, and the magnetolectric effect.
1.1 Magnetoresistance effect

The relative change in the electric resistivity due to an external magnetic field in a magnetic material is called the magnetoresistance (MR) effect, in form of \((R_H - R_0)/R_0 \times 100\%\), where \(R_H\) and \(R_0\) refer to the resistance with and without magnetic field.. In common magnetic materials, the MR effect is small, but it is obvious in many perovskite manganese oxides, in which the effect can reach from several percent to several hundred percent.\(^1\) Previously, magnetic materials were usually used as magnets, but the MR effect has given the magnetic materials new life, especially based on the discovery of the giant and colossal magnetoresistance (GMR/CMR) effects. New types of memory devices, magnetic recording heads, and spin valve sensors\(^2\) were designed,\(^3\) and application in industry has also been achieved.\(^3, 4\) According to the value of the MR effect, it can be divided into three categories: common MR, GMR, and CMR.

The common MR effect prevails in most magnetic materials, but its value is quite small, so that we could miss observing it on occasion. Hence, it failed to attract the wide attention of physical scientists. However, the situation changed when people found that the MR effect can reach several percent in some magnetic multilayer systems, a phenomenon denoted as GMR effect. Initially, the GMR was observed in magnetic superlattices\(^5\), ferromagnetic multilayers\(^6\), heterogeneous alloys\(^7\), and some mixed-valence manganese oxides\(^8, 9\). Furthermore, the MR effect can exceed a hundred percent and even higher around the magnetic transitions in many pervoskite manganese oxides, a phenomenon which is called the CMR effect.\(^10-12\) Such large MR effects foreshadow possible applications in spintronic devices. In this section, I am going to concisely review the historical study of the GMR and CMR effects.
1.1.1 Giant magnetoresistance effect (GMR)

Early in 1988, M.N. Baibich et al. found that there is an obvious change in electric resistance on applying a magnetic field to Fe/Cr superlattices produced by molecular beam epitaxy. The study is regarded as symbolic of the giant magnetoresistive effect era. In their work, the GMR effect in a (Fe 3 nm/ Cr 0.9 nm) sample could reach 45% at 4.2 K when the magnetic field was 2 T, as shown in Figure 1.1-1. The tremendous difference in the electric resistance can be explained by a two-current model. The physical explanation can be based on the two-current model and the spin-dependent scattering of conduction electrons on the interface: the spin-down electrons have different scattering scales from the spin-up electrons due to the density difference in the empty states at the Fermi level, which will produce a smaller resistance in the ferromagnetic configuration than that in the antiferromagnetic configuration.

![Figure 1.1-1 The GMR effect reported by M.N. Baibich et al. in Fe/Cr superlattices.](image)

---

13 In their work, the GMR effect in a (Fe 3 nm/ Cr 0.9 nm) sample could reach 45% at 4.2 K when the magnetic field was 2 T, as shown in Figure 1.1-1. The tremendous difference in the electric resistance can be explained by a two-current model. The physical explanation can be based on the two-current model and the spin-dependent scattering of conduction electrons on the interface: the spin-down electrons have different scattering scales from the spin-up electrons due to the density difference in the empty states at the Fermi level, which will produce a smaller resistance in the ferromagnetic configuration than that in the antiferromagnetic configuration.
They also studied the thickness dependence of the non-magnetic Cr layer, where the saturation magnetic field, $H_s$, decreased and the GMR effect also decreased with increasing thickness. This thickness dependence was also investigated in detail and found to be a non-linear behaviour with an oscillatory period, which will be discussed later.

According to this basic model, it is not difficult for researchers to design other new GMR systems if the relative configurations of two adjacent magnetic layers can be adjusted by the external magnetic field.

(1) Antiferromagnetic multilayers

Just as mentioned above, the GMR in Fe/Cr multilayers is a typical antiferromagnetic multilayer system. A simple way to achieve GMR is by using another non-magnetic layer to replace the Cr layer, such as a Cu layer. As the structure of Fe is close to that of Cr, it is easy to obtain epitaxial growth, and this will help to reduce parasitic scattering and allow higher electronic conduction. This situation is totally changed when the non-magnetic layer consists of Cu. Because the structure of the Cu layer is different from that of the Fe, the interface parasitic scattering is quite strong, and this weakens the spin scattering effect. Hence, the final MR effect is much weaker compared with that in the Fe/Cr system. If the Cr layer is kept as the non-magnetic layer, the Fe layers can be replaced by Co or NiFe alloy.

What is interesting is that the GMR effect and the saturation magnetic field have a non-linear dependent on the thickness of the non-magnetic layers. They show oscillatory dependence with a certain repeat period. One example is the non-linear behaviour of the GMR effect in a Fe/Cr superlattice reported by S.S.P. Parkin et al.
as shown in Figure 1.1-2.\textsuperscript{17} This behaviour also indicates the oscillatory interaction between the ferromagnetic layers.\textsuperscript{18-21}

![Figure 1.1-2](image)

Figure 1.1-2 Oscillatory dependence of the GMR effect (top) and saturation field (bottom) on the thickness of the non-magnetic layer in Fe/Cr superlattices, with the insets showing enlargements for higher thicknesses.\textsuperscript{17}

(2) Ferromagnetic-Non-magnetic-Ferromagnetic multilayers

Is it possible to achieve the GMR effect in a ferromagnetic configuration? To allow the change in electronic resistance, two different magnetic configurations (parallel
and antiparallel arrangements) need to be achieved by the external magnetic field. Apart from the spontaneous antiferromagnetic arrangement, the initial magnetic state can also exist in a spontaneous ferromagnetic arrangement in some unique multilayer systems. Taking the Ni$_{80}$Fe$_{20}$/Cu/Co multilayer for example, the coercive fields of ferromagnetic Ni$_{80}$Fe$_{20}$ and Co are different, so it is possible to apply a moderate magnetic field that can only switch one of them while the other remains the same. In fact, this idea is feasible and was reported by T. Shinjo et al. in 1990. In their work, magnetic hysteresis loops ranging from -1 kOe to 1 kOe were measured, while the MR effect was also detected in the same magnetic field range, which is consistent with the magnetic states in different magnetic fields. When the magnetic field is applied along the initial ferromagnetic vector, the resistance is low and becomes higher when one of the magnetic layers is switched by the scanning magnetic field. The same idea also applies to other systems, such as soft ferromagnetic sandwiches NiFe/Cu/NiFe/FeMn, Fe/Ag/Co, and NiFe/Cu/NiCo.

![Figure 1.1-3 Magnetic hysteresis loop and GMR effect in NiFe/Cu/NiCo](image)

Figure 1.1-3 Magnetic hysteresis loop and GMR effect in NiFe/Cu/NiCo.  

26
To better understand the GMR effect in this kind of sandwich, Figure 1.1-3 shows the results for NiFe/Cu/NiCo reported by B. Dieny et al.\textsuperscript{23}. As the coercive fields of these three systems are very low, the field for switching one layer is just around 50 Oe or even lower, and the GMR effect can reach several percentages. For the NiFe/Cu/NiFe/FeMn structure, the authors introduced an FeMn layer to apply an extra pinning force on the cohesive NiFe layer and achieved a higher coercive field than that in the NiFe layer which was deposited on the non-magnetic Cu layer.\textsuperscript{23} This kind of design allows the possibility that a moderate magnetic field can only switch the spins in the NiFe layer with a low coercive field. It is also possible to produce two ferromagnetic layers with different coercive fields by controlling their thickness if the coercive field is dependent on the thickness.

(3) Non-multilayer materials

The representative works on the GMR effect in bulk materials were done by J.Q. Xiao et al.\textsuperscript{24} and A.E. Berkowita et al.\textsuperscript{7}. Their works were both based on magnetic alloys. According to their results, the GMR effect can only occur when there is a phase separation state in which small ferromagnetic clusters are embedded in a non-magnetic matrix. On the contrary, there is no GMR effect in homogeneous bulk alloys. Co\textsubscript{16}Cu\textsubscript{84} alloys can display a 9\% GMR effect at 5 K, as shown in Figure 1.1-4. If the granular particle size is a little smaller, the GMR can increase to 11.5\%.\textsuperscript{24} This phenomenon disappears in homogeneous Co\textsubscript{80}Cu\textsubscript{20} alloys. The GMR effect can also be observed in phase separated Fe\textsubscript{30}Cu\textsubscript{70}. They also studied the magnetic rare earth alloy Gd\textsubscript{25}Ti\textsubscript{75}, which is also in a phase separation state. No GMR effect can be found in this alloy thin film, however. Hence, the spins contributed by the 3d orbitals are critical and necessary to achieve the GMR effect because the electrons in 3d orbitals in Co or other magnetic transition metals are also
responsible for the conductivity, while Gd is just a ferromagnetic atom without itinerant electrons. The magnetic field cannot affect the conductivity where there are localized spins, and this is why the GMR effect is absent in Gd_{25}Ti_{75}.

![Figure 1.1-4](image)

Figure 1.1-4 The GMR effect (top) and magnetic hysteresis loop at 5 K (bottom) in phase separation state of Co_{16}Cu_{84} alloy thin film. 24

In other alloy systems, such as Ag-Co 25, FeNi-Au 26, Cu-Fe-Ni 27, and FeRh 28, GMR effects have also been reported. This kind of material is easy to synthesize with a tuneable GMR effect, as the particle size can be controlled, which is helpful for material processing in device engineering.

1.1.2 Colossal magnetoresistance effect (CMR)

A different sort of MR effect that is found in bulk manganese oxides with perovskite or similar structures is extremely big around the paramagnetic-ferromagnetic phase transition, and is named the colossal magnetoresistance (CMR) effect. The
representative material is $La_{0.67}Ca_{0.33}MnO_3$. The resistivity is reduced when the manganese oxide enters into the ferromagnetic state from the paramagnetic state, as was revealed early in 1950. Much more interesting, the resistivity could drop further when a magnetic field was applied in this kind of material. As displayed in Figure 1.1-5, the resistivity in $Sm_{1-x}Sr_xMnO_3$ and $Nd_{1-x}Sr_xMnO_3$ (x = 0.45) shows relatively high values in zero magnetic field around the ferromagnetic transition, while the resistivity decreases significantly in magnetic fields. This CMR effect is almost 100%. The magnetic transition here corresponds to the insulator-metal transition. As the $Sr^{2+}$ doping introduces the mixed $Mn^{3+}/Mn^{4+}$ state, the interaction between $Mn^{3+}$ and $Mn^{4+}$ is dominated by the double-exchange interaction, which requires electron hopping. Above the ferromagnetic transition temperature, the spins are in a highly disordered state, and the materials show insulating behaviour, while the materials show metal conductive behaviour below the Curie temperature, $T_C$, due to the local alignment of spins. When the magnetic field is applied, the spins in the materials are aligned at long range, which further reduces the scattering and enhances the electronic hopping. In this case, a significant drop in the electrical resistivity can be observed. In fact, the MR effect already occurs above $T_C$, which suggests that the mechanism is much more complicated. To explain this “anomaly”, the spin-lattice coupling is introduced, also named the spin-phonon coupling. The spin-phonon coupling stems from the lattice deformation or Jahn-Teller effect around the magnetic transition, during which the energy level of the 3$d$ orbital decreases though the distortion of the $MnO_6$ octahedra. This deformation is a dynamical process and allows for itinerate electrons. Above the magnetic transition, the dynamical Jahn-Teller distortion could produce polarons, which are temperature and magnetic field
dependent\textsuperscript{31, 33, 34}. Hence, the CMR effect can occur from temperatures above the ferromagnetic transition temperature.\textsuperscript{1}

Figure 1.1-5 Magnetic field effect on the resistivity in Sm\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} and Nd\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}\textsuperscript{1}.

The mechanism may quite different in different CMR systems (with some systems having charge ordering or a phase separation state), and there are many works reported in the literature based on both experimental measurements and theoretical calculations.\textsuperscript{1, 12, 35, 36}
1.2 Exchange bias effect

An anisotropy can be induced by the coupling between a ferromagnetic and an antiferromagnetic interface when the temperature is lower than their transition temperatures.\textsuperscript{37, 38} Such anisotropy may favour an asymmetric magnetic hysteresis loop with different coercive fields in the ferromagnetic component, which is termed the exchange bias effect. Generally, the exchange bias effect can be observed in antiferromagnetic and ferromagnetic bilayers, antiferromagnetic-ferrimagnetic interfaces, and ferromagnetic-ferromagnetic interfaces.\textsuperscript{39, 40} Because of the relatively easy control of bilayer systems, the exchange bias effects in such systems have been widely studied. On the other hand, the exchange bias effect can also occur in single phase bulk materials. Here, I am going to review the exchange bias effects in bilayers and bulk materials.

1.2.1 Exchange bias effect in bilayers

(1) Classic exchange bias bilayer systems

The magnetic transition metals and their oxides can form the classic exchange bias systems, such as Co-CoO\textsuperscript{41-44}, Fe-FeO\textsuperscript{45, 46}, and Ni-NiO\textsuperscript{47}. This system can be effectively modified and characterized. The training effect and temperature dependence have been demonstrated by several groups.\textsuperscript{48, 49} Meanwhile, this kind of system is sensitive to the synthesis process and the temperature. By adequate heat treatment, the exchange bias effect can be enhanced.\textsuperscript{44} There are also theoretical models and experimental explanations for such bilayer systems.\textsuperscript{40, 42, 50} One of the most accepted explanations is the uncompensated spins on the antiferromagnetic layer. Such spins offer a pinning force on the ferromagnetic layer and induce the asymmetric exchange interaction and consequent anisotropy, i.e., the exchange bias
effect.\textsuperscript{39} This explanation is based on the assumption that the spins in antiferromagnetic and ferromagnetic layers are in-plane. On the contrary, there is another explanation based on the assumption that there are some out-of-plane spins. If considering the practical case, certain factors, such as the roughness and interface impurities, make the effect much more complicated to understand. Hence, achieving an understanding of the exchange bias effects is still an ongoing project.

(2) New exchange bias bilayer systems

![Graph](image)

Figure 1.2-1 Exchange bias effect observed in LaNiO$_3$-LaMnO$_3$ superlattice interface\textsuperscript{51}.

Recently, artificial interfaces have allowed researchers to find some unique physical properties, such as superconductivity\textsuperscript{52, 53} and magnetoelectric coupling (which will be discussed later). In addition to these interesting interface effects, magnetism can also be found in some non-magnetic interfaces, as reported by A. Brinkman et al.\textsuperscript{54}. Furthermore, two different groups claim the non-existence of magnetism and two-dimensional superconductivity in LaAlO$_3$/SrTiO$_3$ heterostructures.\textsuperscript{55, 56} These ideas
are also intriguing for the observation of the exchange bias effect at the LaNiO$_3$-LaMnO$_3$ interface, as shown in Figure 1.2-1.$^{51}$ As LaNiO$_3$ is paramagnetic material while LaMnO$_3$ is an antiferromagnetic material, the exchange bias effect should not occur in such systems. The interface effect induces a possible ferromagnetic layer in LaNiO$_3$, however, and produces the exchange bias effect as a consequence. This work provides the experimental guidance towards achieving exchange bias effects in some other similar or even totally different systems in which we never think about the possibility of such unique effects.

1.2.2 Exchange bias effect in bulk materials

(1) Alloy

As magnetism can exist in atomic states, the alloys containing magnetic atoms can show magnetism as well. If there are more than one magnetic phase, such as with the coexistence of ferromagnetism and antiferromagnetism, the exchange bias effect may occur. This assumption has already been proved by the exchange bias in UMn$_2$ as early as 1957 by S.T. Lin and A.R. Kaufmann.$^{57}$ After that, more such Laves phase intermetallic alloys were found to allow the exchange bias effect, such as Sm$_{0.975}$Gd$_{0.025}$Cu$_4$Pd$^{58}$, Nd$_{60}$Fe$_{30}$Al$_{10}$$^{59}$, and Nd$_{0.75}$Ho$_{0.25}$Al$_2$$^{60}$. The interaction between different magnetic orderings or secondary phases in these complex magnetic states is responsible for the exchange bias effect.

Apart from the above materials, exchange bias effects are also observed in other families, such as some Heusler alloys and binary alloys.$^{61}$ Binary alloys are easy to obtain and modify and some representative alloys with the exchange bias effect are listed here: Ni-Mn$^{62}$, Co-Mn$^{63}$, and Fe-Mn$^{64}$. Representative Heusler alloys with the exchange bias effect are the Ni-Mn-X (X = Sb, In, Sn)$^{65-71}$ family and Cu-Mn-Al
alloy. In Ni-Mn-Sn, Z. Li et al. studied the temperature dependent exchange bias field, and the exchange bias effect is ascribed to the coexistence of antiferromagnetic and ferromagnetic ordering in the martensitic state. Sometimes, the magnetic competition may induce a frustrated state, such as spin-glass-like behaviour, and such state can allow an exchange bias effect if a ferromagnetic ordering is also present.

(2) Metal oxides

Analogous to the exchange bias effects obtained in alloys, it is also possible to achieve exchange bias effects in magnetic metal oxides, so long as there is coexistence of antiferromagnetism or a spin glass like state and ferromagnetism in the same compound. A typical oxide compound is Pr$_{1/3}$Ca$_{2/3}$MnO$_3$, as reported by D. Niebieskikwiat and M.B. Salamon in 2005. Charge ordering exists due to the mixture Mn$^{3+}$ and Mn$^{4+}$ states in this material, which may allow the coexistence of ferromagnetic clusters and antiferromagnetic ordering, a situation that is generally named phase separation. This ‘rule’ seems to apply to other phase separation systems, such as La$_{1-x}$Ca$_x$MnO$_3$ and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$, in which exchange bias effects have also been demonstrated.

On the other hand, magnetic rare earth elements have a strong interaction with the transition metal in some ABO$_3$ compounds. In such system, there are two magnetic sublattices, in which the coercive fields may be different. Based on this assumption, the exchange bias effects may be achieved if only one set of magnetic sublattice is adjustable by external magnetic field, while the other remains substantially the same. Recently, two groups reported exchange bias effects in La$_{1-x}$Pr$_x$CrO$_3$ and Sr$_2$YbRuO$_6$ (or SrYb$_{0.5}$Ru$_{0.5}$O$_3$). In their work, the polarity of the
exchange bias effect can be changed at high cooling field, due to the flipping of one magnetic sublattice which should remain unchanged in a low cooling field.

Here, another magnetic metal oxide compound, LaMn$_{0.7}$Fe$_{0.3}$O$_3$, should be mentioned, as its complex magnetic configuration consists of both a ferromagnetic cluster glass state and a spin glass state. On the interface of the different glass states, the anisotropy can be induced due to the freezing effect, and the exchange bias effect can be produced in various external cooling fields.$^{81, 82}$

1.3 Multiferroics and the magnetoelectric coupling effect

Multiferroics are materials that possess more than one “ferro-type” property (ferroelectric, ferromagnetic, ferroelastic). Among some of multiferroic materials, one “ferro” property is associated with the other. When the electric properties are correlated with the magnetic properties, magnetoelectric coupling arises (generally, it is called ME effect). Traditionally, electric properties can be affected by an external magnetic field, a common phenomenon in multiferroic materials with the ME effect. Recently, more effort has been focused on the inverse effect: electric field controlled magnetic properties, which is called the inverse ME effect. Because of the advantages of multiferroic materials, allowing more operation of degree of freedoms, they are expected to be innovative material for use in electronic devices, such as memory devices.$^{83}$

1.3.1 Representative multiferroic materials

(1) BiFeO$_3$

BiFeO$_3$ has been strongly investigated during the past several years, for it is the only single phase material which has both electric and magnetic ordering above room temperature.$^{84, 85}$ It has a rhombohedral structure at room temperature with point
As the temperature is increased, a high temperature phase occurs with a volume contraction around 1098 K, at which the ferroelectric-paraelectric transition occurs. The structure of BiFeO₃ at high temperature has been studied by many groups because of its complex properties. In most cases, it is accepted that BiFeO₃ has an orthorhombic structure at high temperature. There are also many reports claiming monoclinic, (pseudo)tetragonal, or rhombohedral structures. It is believed that there is another cubic phase at higher temperature.

Room temperature ferroelectric properties have been investigated based on the polycrystalline, single crystal, and thin film BiFeO₃ samples. In the single crystal, the remnant polarization $P_r$ can reach 60 $\mu$C/cm² normal to (001), which corresponds to 100 $\mu$C/cm² along the [111] direction in pseudocubic form. Theoretical calculation shows that the ferroelectric polarization in bulk BiFeO₃ can reach 90-100 $\mu$C/cm² and is sensitive to artificial stress. The strain effects on the polarization have been examined by a few groups. Considering the leakage of BiFeO₃, element doping was used to improve the ferroelectric properties.

The magnetism of BiFeO₃ stems from the Fe sublattice. The basic spin configuration is a G-type antiferromagnetic state starting from 643 K. At the same time, there is an extra long-range superstructure in form of an incommensurate spin cycloid with a 62 nm period. Additional evidence, however, shows that there are two extra transitions at low temperature. One is around 140 K, while the other transition occurs around 200K. Furthermore, ferromagnetic behaviour could be observed from the magnetic hysteresis loop at low temperature. These phenomena are consistent with each other and indicate that there is strong competition between antiferromagnetic and ferromagnetic interactions at low temperature. This competition could induce a spin-glass-like intermediate state.
Based on these considerations, it is not difficult to find that the origins of the magnetic and ferroelectric interactions are different, considering their different phase transition temperatures. The main contribution of polarization comes from the classic atomic displacement of Bi. Therefore, to observe the magnetoelectric coupling in BiFeO$_3$ is no easy task, as the coupling is very weak. In spite of this difficulty, it is still possible to combine BiFeO$_3$ with other magnetic materials and achieve magnetoelectric coupling at the interfaces, which will be discussed later.

Meanwhile, we should also have an idea in mind that only direct coupling between magnetic and ferroelectric ordering could produce strong magnetoelectric coupling. To explore such materials, one possibility is that special magnetic ordering could induce the simultaneous occurrence of ferroelectric ordering. The following sections show just this kind of phenomenon.

(2) RMnO$_3$ (R = Dy, Tb, Gd, Y, Ho)

The listed rare earth manganese oxides are in the orthorhombic structure except for YMnO$_3$ and HoMnO$_3$. For YMnO$_3$ and HoMnO$_3$, the orthorhombic structure can only be stabilized under high pressure during the synthesis process.

In fact, YMnO$_3$ and HoMnO$_3$ show the ferroelectric property below their ferroelectric transition temperature at 920 K when they are in the normal hexagonal structure.$^{114, 115}$ Considering the trimmer structure, the Mn spins cannot arrange themselves in the normal collinear antiferromagnetic state or even the canted antiferromagnetic state because of magnetic structure frustration. The detailed magnetic structure was revealed by several groups, and there is an antiferromagnetic transition around 70-80 K.$^{116-119}$ A dielectric anomaly was observed around the
antiferromagnetic transition, suggesting coupling between the magnetic and the ferroelectric ordering.\textsuperscript{120} This is also confirmed by domain studies.\textsuperscript{121, 122}

On the other hand, orthorhombic YMnO\textsubscript{3} and HoMnO\textsubscript{3} have also been studied in form of bulk materials and thin films.\textsuperscript{114, 123, 124} To synthesize orthorhombic YMnO\textsubscript{3} and HoMnO\textsubscript{3}, high strain should be applied. Therefore, it is easy to deposit thin films rather than prepare single phase bulk materials. Contrary to the situation in the hexagonal structure, the magnetic phase transition is quite different in the orthorhombic structure. The Mn sublattice enters into an incommensurate antiferromagnetic ordering around 42 K, and there is an extra lock-in transition into a temperature independent wave vector at the lower Néel temperature, $T_{N2}$.\textsuperscript{123, 125, 126} These two transitions are hard to identify just based on physical properties magnetic system (PPMS) magnetic measurement, due to the subtle change in the magnetic moment during the transitions, but they can be determined by the optical and dielectric methods.\textsuperscript{127} This kind of magnetic phase transition prevails in another three compounds (DyMnO\textsubscript{3}, TbMnO\textsubscript{3}, GdMnO\textsubscript{3}). Because of the change in the structure and symmetry, the previous high temperature ferroelectric transition disappears and is replaced by a low temperature ferroelectric transition induced by the special magnetic ordering.\textsuperscript{127} The polarization in orthorhombic YMnO\textsubscript{3} is also very small, only 0.2 $\mu$C/cm\textsuperscript{2},\textsuperscript{127} compared with that in the hexagonal structure, in which the polarization can reach 5.5 $\mu$C/cm\textsuperscript{2}.\textsuperscript{128} Although the polarization is small, a clear dielectric anomaly can be observed below $T_{N2}$, suggesting obvious magnetoelectric coupling.\textsuperscript{127}

For DyMnO\textsubscript{3}, TbMnO\textsubscript{3}, and GdMnO\textsubscript{3}, the structures are very close to each other. Early in 2005, T. Kimura and Y. Tokura et al. reported their multiferroic properties and carried out a magnetoelectric coupling study.\textsuperscript{129} Generally, these compounds
exist in the orthorhombic structure and experience an incommensurate antiferromagnetic transition around 40-45 K. As the temperature goes even lower, a long-wavelength, nearly lock-in, antiferromagnetic (spiral) ordering appears with different propagation vectors. Such a superstructure could induce an improper ferroelectric ordering according to the spin current model. Meanwhile, the dielectric measurements shows that there is an anomaly when the sample enters into the spiral ordering, suggesting magnetoelectric coupling.\textsuperscript{129, 130} The magnetoelectric diagram in various magnetic field was presented, and it was found that the magnetic field along a certain direction could induce the flipping of the spiral propagation vector and the consequent ferroelectric polarization vector.\textsuperscript{129} This phenomenon was further investigated by another group.\textsuperscript{131}

Based on these results, many groups have attempted to adjust the magnetic and ferroelectric properties by applying stress to thin films and by A site and B site element doping in the bulk ABO\textsubscript{3} structure.\textsuperscript{132-135}

(3) CaMn\textsubscript{7}O\textsubscript{12}

A charge ordering state was found around 440 K in CaMn\textsubscript{7}O\textsubscript{12}, and there is a strong dielectric response at room temperature which is attributed to the presence of charge ordering and the Maxwell-Wagner effect.\textsuperscript{136-138} In contrast to the orthorhombic RMnO\textsubscript{3}, CaMn\textsubscript{7}O\textsubscript{12} belongs to the quadruple (AC\textsubscript{3})B\textsubscript{4}O\textsubscript{12} perovskite structure, while the Mn on the C site is Mn\textsuperscript{3+} and the Mn on the B site is Mn\textsuperscript{3.25+} (mixed state of Mn\textsuperscript{3+} and Mn\textsuperscript{4+}).\textsuperscript{139} Hence, the charge ordering forms in the Mn sublattice on the B sites.\textsuperscript{140} At high temperature above 440 K, the material is in cubic structure, and the Mn\textsuperscript{3+} and Mn\textsuperscript{4+} at the B sites are in a disordered state. On decreasing the
temperature, the symmetry becomes lower, and the compound is in the rhombohedral phase.\textsuperscript{139}

The magnetic transition had been studied by several groups, but the results are not well consistent with each other.\textsuperscript{141-143} Detailed investigation by more accurate magnetic measurements and the thermodynamic method confirms that there are two obvious magnetic transitions: one is located around 90 K and the other takes place at 50 K. The higher temperature magnetic transition is a typical antiferromagnetic transition from the paramagnetic state to a complex non-collinear antiferromagnetic state.\textsuperscript{144} The second transition around 50 K still lacks study, and the magnetic properties cannot be exactly determined.

Ferroelectricity was first observed by G.Z. Zhang et al.\textsuperscript{140}. The ferroelectric transition was found to start from 90 K, which is the same as with the magnetic transition, suggesting a magnetic origin, and the low temperature polarization is about 0.045 \( \mu \text{C/cm}^2 \). Therefore, the ferroelectric property of CaMn\(_7\)O\(_{12}\) shares the same mechanism with that of DyMnO\(_3\). The work done by G.Z. Zhang et al. also shows that magnetic field will suppress the polarization, further confirming the magnetic mechanism and magneto-electric coupling. Another similar work was also carried out by R.D. Johnson et al., and their results show a larger polarization, reaching 0.28 \( \mu \text{C/cm}^2 \), in single crystal.\textsuperscript{144} Therefore, their work sheds light on exploring new multiferroic materials in the quadruple family.

(3) CuB\(_2\) (B = Br, Cl)

Beyond manganese oxide, the attempt to find new and simple multiferroic compounds is still ongoing. The multiferroic property of CuCl\(_2\) was first proposed by M.G. Banks et al.\textsuperscript{145} CuCl\(_2\) just contains two elements, and it crystallizes with a
monoclinic structure with $C2/m$ symmetry. A systematic magnetic study was conducted based on neutron diffraction, heat capacity, and common magnetic measurements. Their results show that there is strong lattice/structure change and magnetic diffraction near 24 K, based on their neutron diffraction experiment, which corresponds to a long-range incommensurate antiferromagnetic transition with a propagation vector $(1, 0.225, 0.5)$. According to the spin current model, this kind of magnetic ordering may allow ferroelectric polarization. The ferroelectric property was revealed by the experimental results from the Y. Tokura group. Detailed polarization analysis was carried out by them, such as temperature dependence, direction dependence, and magnetic field dependence. A clear polarization – electric field (P-E) hysteresis loop was obtained at low temperature, and magnetic field could induce direction flipping of spiral spin ordering and suppress the polarization, indicating the magnetic-field-induced ferroelectric polarization and strong magnetoelectric coupling.

Following the above results, L. Zhao et al. reported that they observed ferroelectric polarization in antiferromagnetic CuBr$_2$, while another group explained the phenomenon based on theoretical calculations. Compared with CuCl$_2$, CuBr$_2$ has a much higher magnetic/ferroelectric transition temperature, which can reach 73.5 K, but similar ferroelectric polarization. Furthermore, external magnetic field could help to enhance the polarization, suggesting the complex magnetic competition and a positive magnetoelectric coupling.

Therefore, the simple multiferroic compounds may attract the attention of more researchers to achieve multiferroic phases in other possible compounds and improve the ferroelectric transition temperature.
1.3.2 Magnetoelectric coupling

The magnetoelectric coupling becomes extremely interesting because it allows the possible operation of extra degrees of spin freedom beyond the general electric freedom, which can achieve much higher data storage density. Just as mentioned above, many groups have observed the coupling between magnetic and electric orderings by means of dielectric methods and the application of external magnetic field. Apart from the above materials, researchers have also found many other alternative materials which show tremendous potential for application in electronic devices.

1.3.2.1 Non-centrosymmetric (Cu, Ni)B$_2$O$_4$

M. Saito et al. employed a non-centrosymmetric insulating magnet, (Cu, Ni)B$_2$O$_4$, to achieve the periodic rotation of the magnetization by an electric field$^{152}$. Previously, a material with magnetostriction or ferro-elasticity could be regarded as a good candidate to achieve ME coupling though structural change when an external magnetic or electric field is added. The structural change is not suitable for fast repeatable rotation control of the magnetization direction, however, for this process will cost significant energy and be accompanied by fatigue. Based on this demand, a material with small magnetic anisotropy can be a good replacement and works continuously with subtle structural modification.
The symmetry is reduced when CuB$_2$O$_4$ changes into the ferromagnetic phase. If an external H field is applied along the [110] axis, the point group becomes $mm\overline{2}$ instead of $-42m$, and the electric polarization $P_0$ can exist along the $c$ axis. A two-fold rotation about the $a$ or $b$ axis can induce the opposite electric polarization $-P_0$ because of the [1-10] oriented magnetization. From the reciprocity theorem, an electric field along the $c$ axis should induce in-plane magnetic anisotropy with the easy axis along a diagonal axis, and the opposite field can rotate the magnetic easy axis by 90° in the $ab$ plane.

Ni doped into CuB$_2$O$_4$ can increase magnetic permeability, solving the problem of suppressed magnetic permeability while using a 30 mT field to fully align the magnetic domains of CuB$_2$O$_4$, allowing a lower magnetic field to align the domains. They observed magnetic moment rotation under external electric field by the magneto-optical Kerr effect (MOKE) technique, as shown in Figure 1.3-1. Firstly, a small magnetic field along the $a$ axis is applied to induce saturation of the moment. After this, an electric field normal to the $ab$ plane is applied along the $c$ axis. By
changing the value of electric field, moment rotation can be achieved. This phenomenon indicates that the electric field induces a moment along the [110] or [1-10] direction, and a rotation is the cooperative effect of this moment and the moment along the $a$ axis. Therefore, the rotation $\Delta \theta$ cannot exceed $45^\circ$. When applying a small magnetic field and a suitable electric field, obvious rotation can be observed. When the magnetic field is large, such as 20 or 50 mT, this field will prevent the rotation induced by the electric field. In this case, higher electric field is needed to produce the same rotation as the case of small magnetic field.

Figure 1.3-2 Dependence of $\Delta \theta$ on the magnetic field in various electric fields.  

A multidomain state should exist when the magnetic field along the $a$ axis is small, as shown in Figure 1.3-2. Increasing this magnetic field can suppress the formation of domains, and the crystal becomes single domain under large external magnetic field, so that the electric field cannot rotate this domain easily.

Therefore, a non-centrosymmetric magnet sheds great light on the potential control of magnetization by electric field at higher temperature, especially at room temperature.
1.3.2.2 Spiral Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$

Early in 2008, Tokura’s group in the University of Tokyo found that they could control the electric polarization through a low magnetic field, only 30 mT, in a helimagnetic single crystal of Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$. They also achieved the periodical switching of polarization with a controlling magnetic field. As shown in Figure 1.3-3, Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$ has a complex structure, which is ferrimagnetic below 553 K and a proper screw spin structure with $k0$ along the $c$ axis below 195 K. At the same time, the material shows a spin reorientation transition to a longitudinal conical orientation at about 50 K, which shows the spontaneous magnetization along the $c$ axis. The fine magnetic states can be well resolved through M-H measurement, with $H$ on the $x$-axis in a base 10 logarithmic form. At 5 K, it is in the FE1 state with transverse conical magnetic order, while $B$ is from 0 to 60 mT, in the FE2 state with unknown magnetic order from 60 mT to 0.12 T, in the FE3 state with non-collinear ferrimagnetic order from 0.12 T to 3.8 T, and in the paraelectric (PE) state with collinear ferrimagnetism above 3.8 T.
Figure 1.3-3 Structure and spin arrangement in single crystal $\text{Ba}_2\text{Mg}_2\text{Fe}_{12}\text{O}_{22}$. (A) the schematic crystal structure with alternative L (brown) and S (green) blocks; (B) proper screw spin structure at zero field (from 50-195 K); (C) longitudinal conical spin structure at zero field for $T < 50$ K; (D) slanted conical spin structure when the field is 30 mT below 195 K.\textsuperscript{153}
Figure 1.3-4 (A) Magnetoelectric phase diagram in magnetic field; (B) magnetization versus magnetic field curve at 5 K when the magnetic field is applied along [100], (inset, magnetization versus temperature curve along [001]); (C) polarization versus magnetic field at 5 K corresponding to M-H curve. Dashed lines are used to show the phase boundary in (B) and (C). 153

The four fine states can be clearly seen from Figure 1.3-4(B). Otherwise, polarization increases with increasing magnetic field up to 2T, but reaches a plateau when the magnetic field is from 2 T to 10 T. Above 10 T, the polarization begins to drop sharply. The magnetic moment, however, is still increasing in a large field such as 10 T, indicating that the ferrimagnetic order changes to ferromagnetic order. In this case, the polarization state is broken. During the process of increasing the magnetic
field, the magnetic moment value experiences four stages, which can match well with the phase diagram in Figure 1.3-4(A).

The polarization is the integrated value of the spin current induced by external magnetic field. Polarization reaches its maximum when the spin current experiences a zero–zero process (always positive or negative). The spin current reaches its maximum when magnetic field begins to be reversed. Therefore, the maximum value of polarization arrives nearly simultaneously with the maximum value of magnetic field. Similar work has been done in other systems.\textsuperscript{154-157} The electric control of magnetic properties has not been achieved, but is worth to doing.

1.3.2.3 Thin films

Because the ME effect cannot be easily obtained in single phase bulk materials, it has been proved that a more obvious ME effect could be observed on lowering the dimensions from 3D to 2D. Only in materials with ME coupling can we achieve electric control of spin. A break in time reversal and spatial symmetry can occur at the interface of two different phases. Here, some results are listed according to their different mechanisms of ME coupling.

1.3.2.3.1 Spin configuration or orbital reconstruction

A.A.F. Vaz et al. in Yale University found a large ME coupling in Pb(Zr\textsubscript{0.2}Ti\textsubscript{0.8})O\textsubscript{3}/La\textsubscript{0.8}Sr\textsubscript{0.2}MnO\textsubscript{3} bilayer.\textsuperscript{158} Aided by near edge X-ray absorption spectroscopy (as a function of $P$), they obtained the electronic valence state. The change in valence induced by charge carrier modulation caused a temperature independent shift of the Mn absorption edge, showing the electronic origin of the ME effect.
The resistivity state. It is correlated changes +0.3 eV between Mn polarization indicating switching.

The main finding is the energy shift by +0.3 eV when switching from depletion to accumulation. To confirm the correlation between Mn valence change and charge carrier modulation induced by switching the polarization, X-ray absorption spectroscopy (XAS) was conducted at different electric fields with the same photon energy value. A mimic loop can be found, indicating the Mn valence change contains the information on the polarization switching. The charge induced moment change estimated through previous work cannot be responsible for the actual change in moment. Therefore, they think there must be some other mechanism. A spin exchange coupling model is proposed, as presented in Figure 1.3-6. Spin exchange coupling is modified from the ferromagnetic (FM) depletion state to the antiferromagnetic (AFM) accumulation state.

Figure 1.3-5 Electric, transport, and magnetic behaviour of the lead zirconate titanate (PZT)/12 u.c. lanthanum strontium manganite oxide (LSMO) structure. 158

The electric and magnetic behaviour is displayed in Figure 1.3-5. The peak in resistivity is in accordance with the transition between the metallic and the insulating state. It is clear that the saturated moment is higher in the depletion state, which is correlated with the electronic state of the Mn. Their results show that the Mn valence changes at two different polarization states. The main finding is the energy shift by +0.3 eV when switching from depletion to accumulation. To confirm the correlation between Mn valence change and charge carrier modulation induced by switching the polarization, X-ray absorption spectroscopy (XAS) was conducted at different electric fields with the same photon energy value. A mimic loop can be found, indicating the Mn valence change contains the information on the polarization switching. The charge induced moment change estimated through previous work cannot be responsible for the actual change in moment. Therefore, they think there must be some other mechanism. A spin exchange coupling model is proposed, as presented in Figure 1.3-6. Spin exchange coupling is modified from the ferromagnetic (FM) depletion state to the antiferromagnetic (AFM) accumulation state.
According to the proposed scheme and first-principles calculations done previously, the interface layer in the accumulation state consists of strongly depopulated antibonding, e.g., $3z^2-r^2$, states, which decrease the double-exchange interaction at these orbitals, and then the antiferromagnetic order can form at the interface layer. In this case, the change in spin reconfiguration can be used to explain the observed large change in the moment value between the two polarization states.

So their results pave the way to control the spin by electric field, due to magnetic order reconstruction caused by charge accumulation.

1.3.2.3.2 Electric control of exchange bias

P. Yu et al. in Ramesh’s group reported that orbital reconstruction at the interface of a BiFeO$_3$-La$_{0.7}$Sr$_{0.3}$MnO$_3$ heterostructure is the origin of ferromagnetism in AFM BiFeO$_3$, which couples with the AFM lanthanum strontium manganese oxide (LSMO) and causes the onset of exchange bias, as proved by the X-ray magnetic circular dichroism (XMCD) of Mn and Fe L$_{2,3}$ edges. The result is confirmed by linearly polarized X-ray absorption measurements at the oxygen K edge. Based on
In this report, it has become possible to control the exchange bias through an external electric field, which can adjust the orbital reconstruction.

The red shift of \( P2c \) at oxygen K-edges and the blue shift of \( P1a \) and \( P2a \) in Figure 1.3-7 confirms the hybridization between \( e_g \) orbitals of \( \text{Mn}^{3+} \) and \( \text{Fe}^{3+} \), which affects the XAS behaviour of oxygen. A schematic diagram of the possible mechanism is shown in Figure 1.3-8.

![Diagram showing XAS spectra and hybridization](image)

Figure 1.3-7 (a) Polarization dependent oxygen K-edge XAS spectra at \( T = 10 \) K. Temperature dependent polarized XAS spectra with the polarization direction in-plane (b) and out-of-plane (c) for the specified bonding region of O 2p - Mn(Fe) 3d. (d) Temperature dependence of peak positions of interface orbitals. 159
Figure 1.3-8 (a) Schematic diagram of the interface electronic orbital reconstruction, with hybridization. (b) Proposed interface spin configuration and coupling mechanism with $x^2-y^2$ orbital ordering in the interfacial LSMO. (c) Schematic diagram of the origin of the interface magnetism.\textsuperscript{159}

Based on this work, Ramesh’s group conducted another experiment: controlling the exchange bias at the BiFeO$_3$ (BFO)/LSMO interface by external voltage pulse.\textsuperscript{160}

Figure 1.3-9 presents the voltage dependence of the shear resistance ($R_s$) and the coercive field, both showing hysteresis behaviour, meaning that a high voltage such as 60 V can induce two states instantly without relaxation. In this case, periodical reversible control of the exchange bias can be achieved, as shown in Figure 1.3-10.

Figure 1.3-9 Electric transport properties of BFO/LSMO: (a) temperature dependence of shear resistance, with the inset showing the temperature range from 0 to 300 K; (b) magnetic field dependence of normalized resistance after -1 T and 1 T cooling; (c) hysteresis behaviour of $R_s$ vs. $V_G$; (d) hysteresis behaviour of $H_c$-$V_G$.\textsuperscript{160}
1.3.2.3.3 Electric control of FM mediated by exchange bias effect

Early in 2008, Ying Hao Chu and R. Ramesh used a Co$_{0.9}$Fe$_{0.1}$/BiFeO$_3$ heterostructure to achieve electric field control of local ferromagnetism based on the exchange bias effect. 161 The polarization of BFO was characterized by piezoresponse force microscopy (PFM), as shown in Figure 1.3-11. There are two opposite polarizations, corresponding to polarization at 71° and 109°. After depositing LSMO, the XMCD – photoelectron emission microscope (PEEM) image identifies the ferromagnetic domain, which is identical to in-plane projection of the polarization. The contrast suggests that the white strip is the upwards domain. The blank one is the left-oriented domain, as confirmed by rotation of the sample. The
possible mechanism is shown in Figure 1.3-12, that the antiferromagnetic vector of BFO is strongly coupled with the ferromagnetic vector of LSMO. The direction of the ferromagnetic vector can be changed via external electric field, as shown in Figure 1.3-13. Hence, the different polarization directions will determine the directions of the ferromagnetic vector of LSMO via the exchange bias effect.

Figure 1.3-11 (a) PFM image of BFO (red and green show opposite polarizations), (b) XMCD–PEEM image of LSMO deposited on BFO, (c) images for different incoming light directions\textsuperscript{161}.

Figure 1.3-12 Schematic diagram showing mechanism of exchange bias mediated ME coupling in the LSMO/BFO system\textsuperscript{161}.
Figure 1.3-13 Reversible control of main FM domain in LSMO film by external electric field applied on BFO$^{161}$. 

1.3.2.3.4 Tunnel junctions

V. Garcia et al. reported that they prepared a tunnel junction with a ferroelectric interlayer. When the interlayer is poled, there are two possible directions (up or down in a direction normal to the film plane). The measured tunnelling magnetoresistance (TMR) values of these two different situations are quite different, indicating that the interlayer plays a role in controlling the spin current. This work has further proved that the magnetic tunnel junction is an important structure, based on which, people can design ferroelectric random access memory (RAM)$^{162}$. 

Polarizations along different directions can induce two different TMR. For the two different junctions, similar TMR effects can be observed despite the different values presented in Figure 1.3-14. The variation of resistance for different polarization directions is due to piezoelectric related tunnelling electroresistance (TER) effect. The sensitivity of electric field controlled TMR can be defined by the term TEMR = (TMR$_{VP+}$ − TMR$_{VP-}$)/TMR$_{VP-}$, which is about 450% for junction #1 and 140% for
junction #2. More importantly, the TMR can be reversed when applying an alternative electric field, as shown in Figure 1.3-15.

Figure 1.3-14 Resistances and TMR in fields of 2 junctions for tunnel junction with ferroelectric interlayer$^{162}$.  

Figure 1.3-15 Reversible control of TMR in external electric field and magnetic field$^{162}$. BTO is bismuth titanium oxide.

1.4 My motivation and projects for this thesis work

a) Structure, magnetic, heat capacity, and dielectric behavior in DyMn$_{1-x}$Fe$_x$O$_3$
DyMnO$_3$ possesses an incommensurate antiferromagnetic ordering at low temperature due to the magnetic interaction competition, which can also be regarded as a frustrated magnetic state. This special ordering produces a ferroelectric ordering according to the spin current model. To study the magnetic competition behavior, we replace the Mn$^{3+}$ by partial Fe$^{3+}$, considering that Fe$^{3+}$ has 5 electrons on its 3d orbital while Mn$^{3+}$ only has 4 electrons on that orbital. This work will help in understanding the stability of spiral ordering and provide experimental evidence to demonstrate the possibility of modifying the magnetic ordering in the frustrated state.

b) Structure and magnetic properties in Nd$_{1-x}$Er$_x$MnO$_3$

The rare earth manganese oxides have interesting physics, such as the orbital ordering in LaMnO$_3$. As mentioned above, DyMnO$_3$ shows multiferroic properties. The different physical behavior is strongly dependent on the rare earth element. In this work, we chose to study the Er$^{3+}$ doping effect on the magnetic behavior in NdMnO$_3$, considering that both Er$^{3+}$ and Nd$^{3+}$ are magnetic ions. This study will help in understanding the interaction between magnetic rare earth ions and transition metal ions, and the competition between two different magnetic rare earth ions.

c) Heat capacity in Nd$_{1-x}$Er$_x$MnO$_3$

This work is based on a thermodynamic study. The heat capacity can reveal the low temperature behavior, such as an anomaly in the magnetic entropy and the ground state splitting of rare earth ions. Combined with the result from b), we can explain the competition between the crystal field (dependent on structure) and the exchange field (dependent on the magnetic interaction).

d) Exchange bias in NdMnO$_3$ and Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$
The exchange bias effect is usually observed in bilayer systems. For bulk materials, the exchange bias effect has not been investigated widely. In this work, we have studied the simple perovskite NdMnO$_3$ and the magnetocaloric Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ alloy. The exchange bias field in NdMnO$_3$ can reach -2400 Oe and 1800 Oe in various cooling fields. This work will help in exploring more single phase materials with an exchange bias effect. This foreshadows the possibility of a room temperature exchange bias effect in other similar or different alloys.

e) Interface structure and ferroelectricity in SmFeO$_3$ thin film

Artificial stress engineering can modify the physical behavior in bulk materials. It is also possible to achieve a relatively strong ferroelectric state in some nonferroelectric or weak ferroelectric materials. In this work, we intended to confirm this assumption and study epitaxial SmFeO$_3$ on Nd-SrTiO$_3$ substrate based on structure characterization and electric/magnetic measurements. This work will stimulate interest in interface ferroelectric behavior.

1.5 References


2 THE STRUCTURAL AND MAGNETIC PROPERTIES IN DYMN$_{1-x}$FE$_x$O$_3$

2.1 Fe doping induced Jahn-Teller orbital ordering instability in DyMn$_{1-x}$Fe$_x$O$_3$ at room temperature

2.1.1 Abstract

The perovskite DyMn$_{1-x}$Fe$_x$O$_3$ system was studied by detailed structural analysis based on X-ray diffraction pattern refinement and Raman spectroscopy at room temperature. The lattice parameters show that static orbital ordering exists in the samples with $x \leq 0.2$, while phonon modes of Raman spectra show clear hardening or softening and are strongly dependent on Fe content. Abnormal changes in these phonon modes are observed at $x \approx 0.3$, corresponding to the appearance of dynamic orbital ordering instead of static orbital ordering. When $x$ is bigger than 0.5, strong softening of several phonon modes can be identified, indicating the collapse of the dynamic orbital ordering. The FWHM change around $x = 0.6$ shows that strong disorder vibration exists when dynamic orbital ordering disappears.

2.1.2 Introduction

Perovskite rare earth titanates, vanadates, and manganites with the ABO$_3$ structure are of great interest because of their complex magnetic phase transitions and unique properties. In some ABO$_3$ perovskite materials, Jahn-Teller distortion of octahedral BO$_6$ plays an important role, which may determine the magnetic ordering types and/or affect the magnetic transition temperatures. LaTiO$_3$ experiences an antiferromagnetic transition at around 146 K because of an $\alpha < 90^\circ$ O-Ti-O site distortion, while YTiO$_3$ experiences an ferromagnetic transition around 30 K because of an $\alpha = 90^\circ$ O-Ti-O site distortion. In the Y$_{1-x}$La$_x$VO$_3$ system, La doping can
cause changes in the ionic radius on the A site, which consequently induces change in the VO$_6$ distortion, the antiferromagnetic magnetic transition temperature ($T_N$), and the orbital ordering temperature ($T_{OO}$). In the region of $0 \leq x \leq 0.18$, both $T_{OO}$ and $T_N$ decrease as the La doping content increases. When $x$ is bigger than 0.2, $T_N$ suddenly increases, and the increase continues until $x = 1$, but no obvious orbital ordering could be observed. A heat capacity study of samples with $x = 0.40, 0.738,$ and 0.858 has shown that the magnetic transition temperature becomes difficult to exactly identify because of significant fluctuation around the transition, which could originate from the competition and/or coupling between short-range orbital ordering and spin ordering. LaMnO$_3$ is the parent material of a family in which the giant magnetoresistance effect can be observed after doping with alkali metal ions. It experiences an orbital ordering transition at 780 K and an A-type antiferromagnetic transition at 140 K, as confirmed by resonant X-ray scattering. The orbital ordering will become unstable and even disappear under pressure, which favours stronger ferromagnetic interaction, and LaMnO$_3$ undergoes a transition from its original insulating state to the metallic state. Hence, the study of orbital ordering will help us to understand the mechanisms behind the complex magnetic states found in these ABO$_3$ perovskites.

Multiferroic manganites have been intensively studied recently due to their potential application in memory devices. This kind of material includes TbMnO$_3$, GdMnO$_3$, DyMnO$_3$, YMnO$_3$, and HoMnO$_3$. In terms of the study and modification of multiferroic properties, there are a few studies on doping effects on magnetic and ferroelectric properties in some of these manganites, such as Eu$_{1-x}$Y$_x$MnO$_3$ and DyMn$_{1-x}$Fe$_x$O$_3$. Although their magnetic properties have been investigated systematically and it is expected that Jahn-Teller distortion plays an important role
when the magnetic state changes, knowledge of the structure is still insufficient to establish a close relationship with the magnetic properties. Therefore, in this work, we report Fe doping induced Jahn-Teller orbital ordering instability in the DyMn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} system, based on X-ray diffraction and Raman spectroscopy, which shows the detailed changes in bond lengths, bond angles, and vibration modes as Fe doping content varies. This work will present a clear picture to show how the structure changes after doping and will help us to understand the consequent changes in the magnetic properties.

2.1.3 Experimental

Polycrystalline samples of DyMn\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} (x = 0, 0.2, 0.33, 0.5, 0.6, 0.67, 0.8, 0.9, and 1.0) were made by the traditional solid state reaction method from Dy\textsubscript{2}O\textsubscript{3} (99.9%), MnCO\textsubscript{3} (99.9%), and Fe\textsubscript{2}O\textsubscript{3} (99.9%) powder bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, followed by pressing into pellets 15 mm in diameter at 20 MPa. Samples were calcined at 950 °C for 10 hours and sintered at 1440 °C for 6 hours. The crystal structures of the samples were examined by X-ray diffraction (XRD, model: GBC MMA), using Cu K\textalpha radiation at $\lambda = 1.54056$ Å. The Rietveld refinement calculations were conducted via FULLPROF software. Raman scattering measurements were performed with a Raman spectrometer (HR320; HORIBA Jobin Yvon, He-Ne laser 632.8 nm) at room temperature from 200 to 800 cm\textsuperscript{-1}. Origin software was employed to fit the Raman spectra with a Voigt profile.
2.1.4 Results and Discussion

![XRD refinement calculation results on DyMnO$_3$](image)

Figure 2.1-1 (a) XRD refinement calculation results on DyMnO$_3$ with $\chi^2 = 1.7$ (star symbols: experimental data, and solid red line: fitted curve, using Rietveld structural refinement, respectively.) The mismatch between the measured and Rietveld refined spectra is plotted with a slight downshift for clarity. The short vertical solid lines are
guides for the eyes to mark the corresponding Bragg positions. (b) Lattice parameter dependence on Fe content of DyMn$_{1-x}$Fe$_x$O$_3$ samples.

The results of structural characterization of the representative sample with $x = 0$ by XRD are presented in Figure 2.1-1(a). We employed Rietveld analysis to refine the diffraction patterns. All XRD patterns of the samples, regardless of doping level, can be assigned to the single phase orthorhombic structure with space group $Pbnnm$, and no detectable impurity phase is present. The lattice parameter dependence on the Fe content, derived from the Rietveld refinement, is shown in Figure 2.1-1 (b). Good linear relationships in the Fe content dependence of the three lattice parameters can be observed when $x$ is no more than 0.5, but the lattice parameters fluctuate slightly when $x$ exceeds 0.5. With increasing Fe content, the $b$-axis parameter of the unit cell becomes monotonically shorter, the $c$-axis parameter becomes longer in a linear way, and the $a$-axis parameter only increases slightly. Consistent with our previous work\textsuperscript{15}, the relation $b > a > c/\sqrt{2}$ is found in samples with $x < 0.33$, showing a static Jahn-Teller (JT) distortion (cooperative antiferroic JT orbital ordering) superimposed on the high temperature O-type (i.e., not JT distorted) orthorhombic structure\textsuperscript{14, 17}. With $x > 0.33$, $a < c/\sqrt{2}$ is found. According to the reported work, the static orbital ordering is expected to be absent and replaced by weaker and weaker dynamic orbital ordering when $x$ varies from 0.33 to 0.5, and the orbital ordering probably disappears in samples with $x > 0.5$.

However, the Fe content dependence of the lattice parameters can only show the total change in the crystal structure. To determine what happens in the internal structure, we obtained the bond information based on the results from the refinement. The Fe content dependence of average Mn/Fe-O bonding distances and the Mn/Fe-
O-Mn/Fe angles both interplane and in-plane are given in Figure 2.1-2(a) and (b), respectively.

Figure 2.1-2 Fe content dependence of Mn/Fe-O bond distances and Mn/Fe-O-Mn/Fe bond angles: interplane (a) and in-plane (b).
Bond distances and bond angles don’t show monotonic change when the Fe content varies. On the contrary, there are three obvious transitions. The first transition is around x = 0.28, the second is around x = 0.55, and the third is around x = 0.75. From the interplane bond information that is shown in Figure 2.1-2(a), the Mn/Fe-O bond distance decreases slightly when x is 0.1, and then increases until x = 0.5. When x is higher than 0.5, the bond distance decreases again until x = 0.75, after which the bond distance increases. Meanwhile, the Mn/Fe-O-Mn/Fe bond angles show an opposite trend to that of the Mn/Fe-O bond distance.

On the other hand, as presented in Figure 2.1-2(b), the trend in the bond distances and bond angles in-plane is different from those interplane. In a single octahedral MO$_6$ unit, the two Mn/Fe-O bond distances are asymmetric in the $ab$-plane, and they show opposite dependence trends on the Fe content. The three transitions can still be observed at the same doping rates. Considering the average distance, it first decreases until x = 0.5, and then increases until x = 0.75, after which it decreases again. The bond angles show an opposite trend to that of the average bond distance, which is similar to the interplane case.

The transition at x = 0.28 suggests the occurrence of dynamic orbital ordering instead of the previous static orbital ordering. The significant change around x = 0.5 represents the disappearance of dynamic orbital ordering. This is consistent with the results from lattice parameter comparison. In the region between x = 0.5 and x = 0.75, the structure seems to be somewhat unstable or is in a state with relatively high disorder. The relative changes in the interplane and in-plane bond distances and bond angles also precede the change in the antiferromagnetic interaction when x increases. According to our previous work, $T_N$ increases as x increases. In this case, the enhanced in-plane antiferromagnetic interaction dominates the interplane
antiferromagnetic interaction except in the region of $0.5 < x < 0.75$. For the case of $0.5 < x < 0.75$, the interplane antiferromagnetic interaction is enhanced with increasing $x$ and dominates the relatively reduced in-plane antiferromagnetic interaction.

![Raman spectra](image)

Figure 2.1-3 (a) Raman spectra of representative DyMn$_{1-x}$Fe$_x$O$_3$ samples measured at room temperature, (b) the typical result of fitting DyMn$_{0.67}$Fe$_{0.33}$O$_3$ with a Voigt profile.
To better characterize the dynamic distortion and orbital ordering instability, Raman spectroscopy was employed at room temperature. The Raman spectra of the as-grown samples are presented in Figure 2.1-3(a).

![Raman spectra of the as-grown samples](a)

![Fe content dependence of the typical vibration modes](b)

Figure 2.1-4 Fe content dependence of the typical vibration modes (a) and their FWHMs (b).
Clear Raman shifts can be observed in several vibration modes, but they seem not to shift linearly against the Fe content. The Raman spectra were fitted by Voigt profiles with reasonable peak numbers. A representative fitting result for \( x = 0.2 \) is given in Figure 2.1-3(b), in which the good coverage of the experimental data suggests a very high quality of fitting. The typical vibration modes were assigned according to previous Raman studies on DyMnO\(_3\), DyFeO\(_3\), and other rare earth manganites or ferrites.\(^{18-21}\)

Figure 2.1-4 (a) shows selected characteristic Raman vibration modes from the fitting results, while Figure 2.1-4 (b) presents the full width at half maximum (FWHM) of the \( B_{2g}(1) \), \( A_g(1) \), and \( B_{1g}(3) \) modes. \( B_{2g}(1) \) and \( A_g(1) \) represent in-phase stretching in the \( ab \)-plane, which is dominated by the Mn/Fe-O interaction in-plane. The \( A_g(3) \), \( B_{1g}(3) \) and \( B_{2g}(3) \) modes are an out-of-phase bending mode, the out-of-phase \( c \)-rotation mode, and another out-of-phase bending mode (opposite to \( A_g(3) \)), respectively. All of these modes become harder and harder when the Fe content increases until \( x = 0.5 \). However, there is an increasing rate of change of these modes between \( x = 0.2 \) and \( x = 0.33 \), which suggests the occurrence of dynamic orbital ordering instead of static orbital ordering. Above \( x = 0.5 \), a significant increase is found in the \( B_{2g}(1) \) mode, and an obvious decrease is found in the other four modes. This anomaly suggests the disappearance of the dynamic orbital ordering, in line with the results based on the analysis of interplane and in-plane bond distances and bond angles. On the other hand, another vibration mode is assigned to the \( B_{2g} \) mixed mode, which shows decreasing dependence on Fe content until \( x = 0.5 \). At the same time, it shows a relatively obvious jump between \( x = 0.2 \) and \( x = 0.33 \), opposite to the trend in the other five modes presented in Figure 2.1-4(a). The change in the \( B_{2g} \) mixed mode further confirms the Fe doping induced orbital ordering instability.
similar unstable or transition region can also be found at $0.5 < x < 0.75$, in and after which, the change trends of all modes become discontinuous. The FWHM values of three selected modes are shown in Figure 2.1-4(b) and provide additional evidence to show the changes mentioned above. Around $x = 0.28$, the Fe content dependence of the FWHM changes suddenly, indicative of the occurrence of dynamic orbital ordering instead of the previous static orbital ordering. At $x = 0.6$, the average FWHM reaches its maximum, suggesting a highly disordered state or an intermediate state.

Therefore, combining studies of the lattice parameters, bond distances, bond angles, and vibration modes can give a clear picture to show what happens after Fe doping in this system, which will help us to understand the magnetic interactions and the magnetic phase transition.

2.1.5 Conclusion

The structure of polycrystalline DyMn$_{1-x}$Fe$_x$O$_3$ samples has been systematically investigated by X-ray diffraction and Raman spectroscopy at room temperature. Rietveld refinement indicates that all samples are single phase with $Pbnm$ symmetry. By comparing the lattice parameters, static orbital ordering is expected to exist in samples with $x < \sim 0.28$, which will be replaced by dynamic orbital ordering when the Fe content is in the range of $\sim 0.28$ to $\sim 0.55$. Above $x = 0.55$, the dynamic orbital ordering will disappear. The results obtained from the analysis based on internal bond relationships are well consistent with those from the Raman vibration modes. Three transition regions can be found, which confirms the results from the lattice parameter comparison. According to the bond information, the in-plane antiferromagnetic interaction dominates the interplane antiferromagnetic interaction
over the whole doping range, except for the region of $0.55 < x < 0.75$, in which the interplane antiferromagnetic interaction dominates. The FWHM at $x = 0.6$ reaches its maximum, indicative of a state with relatively high disorder or an intermediate state. This work presents a clear picture of the Jahn-Teller orbital ordering instability after Fe doping and its effect on magnetic properties.

2.1.6 Reference


2.2 Spin reorientation, and magnetic competition in the DyMn\(_{1-x}\)Fe\(_x\)O\(_3\) system

2.2.1 Abstract

Long-range cooperative Jahn-Teller orbital ordering exists, according to the lattice parameter relation, but becomes progressively less stable as x increases from 0 to 0.5. At the composition x > 0.5, Jahn-Teller orbital ordering starts to disappear, and spin reorientation starts to appear, which is confirmed by the temperature dependence of the magnetic moment. For the samples with x < 0.5, the antiferromagnetic transition temperature increases as x increases, as indentified by the temperature dependence of modified d\(\chi\)/dT. For samples with x > 0.5, the spin reorientation temperature (T\(_r\)) and the antiferromagnetic Néel temperature (T\(_N\)) gradually separate and widen the temperature range of the magnetic metastable state between T\(_r\) and T\(_N\), reaching T\(_r\) = 65 K and T\(_N\) = 680 K for x = 1. The change of the antiferromagnetic transition temperature is due to the stronger antiferromagnetic interaction induced by Fe\(^{3+}\) ion substitution, with its e\(_g\) orbital half-occupied, for the Mn\(^{3+}\) ion, with its e\(_g\) orbital quarter-occupied. The spin reorientation is modified by the competition between the Fe\(^{3+}\)-Fe\(^{3+}\) interaction and the Dy\(^{3+}\)-Fe\(^{3+}\) interaction.

2.2.2 Introduction

Multiferroic materials are potential functional materials for future spintronic application.\(^1\)\(^-\)\(^2\) A great amount of work has been done to explore mutual control of the electric and magnetic degrees of freedoms, the so-called magnetoelectric (ME) coupling.\(^3\)\(^-\)\(^5\) Meanwhile, the abundant phase transitions that occur in some multiferroic systems have inspired great interest\(^6\)\(^-\)\(^7\). The dielectric property changes around the magnetic phase transition can offer a way to achieve magnetodielectric coupling. One can modify the magnetic transition and the dielectric property by an
external magnetic field.\textsuperscript{8-11} Magnetic competition in some rare earth manganites, such as orthorhombic TbMnO\textsubscript{3}\textsuperscript{7} and GdMnO\textsubscript{3}\textsuperscript{7}, as well as DyMnO\textsubscript{3}\textsuperscript{7, 12, 13}, could induce magnetic frustration and complex spin states. Cross-coupling between ferroelectricity and magnetism can be realized in these manganites because of the broken spatial inversion and time-reversal symmetries.\textsuperscript{14} DyMnO\textsubscript{3} experiences its antiferromagnetic (AFM) transition at \( \sim 39 \) K. When temperature is between 39 K and 18 K, Mn\textsuperscript{3+} spins are expected to firstly order along \( b \) axis in an incommensurate magnetic (ICM) sinusoidal arrangement. Below 18 K, an additional component of the Mn\textsuperscript{3+} magnetic moment along \( c \) axis gives rise to a spiral magnetic ordering and breaks the inversion symmetry, leading to the observation of \( Ps \) reflection along \( c \) axis.\textsuperscript{7, 13} Exchange striction working between Mn\textsuperscript{3+} ions is probably responsible for this spin configuration change. Dy\textsuperscript{3+} itself orders antiferromagnetically around 6.5 K.\textsuperscript{15}

In rare earth orthoferrites and some ferromagnetic films, a special magnetic phase transition occurs, called spin reorientation. During this process, the easy axis of magnetism varies from one direction to another without any obvious structural change. A representative example of this kind of material is DyFeO\textsubscript{3}\textsuperscript{8, 16, 17}. DyFeO\textsubscript{3} is a typical orthoferrite and shows weak ferromagnetism below its antiferromagnetic transition temperature. In addition, it is the only rare-earth orthoferrite to show Morin transition, where the Fe\textsuperscript{3+} system spins in single crystal reorient from \( \Gamma_4 \) (antiferromagnetic configuration along \( a \) axis with weak ferromagnetic component along \( c \) axis) to \( \Gamma_1 \) (simple un-canted antiferromagnetism along \( b \) axis) around 35 K.\textsuperscript{18} The spin reorientation is decided by several factors, and Fe\textsuperscript{3+}-Fe\textsuperscript{3+} interaction combined with magnetic anisotropy plays an important role. Much more interesting, Y. Tokunaga and Y. Tokura \textit{et al.} found that magnetic field along \( c \) axis of DyFeO\textsubscript{3}
single crystal ($Pbnm$) can induce a gigantic ME effect$^{19}$. In addition, A. V. Kimel et al. reported that they had achieved spin reorientation in TmFeO$_3$ via ultra-short laser pulses.$^{20}$ Rare earth orthoferrites have strong temperature-depandant anisotropy. Optical excitation can cause electron-phonon relaxation and phonon-phonon interaction to occur, which then changes the anisotropy axis in subpicosecond. This kind of magnetic phase control may be a good technique to produce optical switches and magnetic sensors. Spin reorientation can also occur in other systems, such as epitaxial La$_{0.5}$Sr$_{0.5}$CoO$_3$ films$^{21}$ and CoFe$_2$O$_4$ films$^{22}$. Considering the possible control of magnetic anisotropy by lattice strain, these film and bulk systems are possible choices to achieve ME coupling by external magnetic and electric fields, when they are combined with ferroelectric materials.

At present, spintronic application has to meet many challenges, and one may be finding strong ME coupling at room temperature in multiferroic materials. The core of this challenge is modification of magnetic and electric polarization phases. Therefore, phase transition research becomes extremely important and can give us theoretical and experimental guidance in the search for multiferroic materials and in achieving practical applications. There are two prospective ways, which should be considered first, to obtain the phases demanded for ME coupling. One is to force spin arrangements frustrated by doping, especially spiral spins. Electric polarization can be achieved through inverse Dzyaloshinsky-Moriya (DM) interaction in spiral spin materials.$^{23}$ The other is to control interfacial ME coupling in film systems in certain temperature ranges. No matter which method we use, phase transitions should be studied urgently. In this paper, we study systematically the spin reorientation and antiferromagnetic transition in the distorted perovskite DyMn$_{1-x}$Fe$_x$O$_3$ system and illustrate how the interactions among rare earth ions and transition metal ions affect
these transitions. The results show something of interest and suggest a possible way to achieve ME coupling and modify multiferroic properties in this type of material.

2.2.3 Experimental

Polycrystalline samples of DyMn$_{1-x}$Fe$_x$O$_3$ (x = 0, 0.2, 0.33, 0.5, 0.6, 0.67, 0.8, 0.95, and 1.0) were made by the solid state reaction method. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, followed by pressing into pellets 15 mm in diameter at 20 MPa. Samples were calcined at 950 °C for 10 hours and sintered at 1440 °C for 6 hours. The crystal structures of the samples were examined by x-ray diffraction (XRD, model: GBC MMA) at room temperature. The magnetic measurements and the heat capacity were carried out using a 14 T physical properties measurement system (PPMS).

2.2.4 Results and Discussion

Figure 2.2-1 (a) shows the typical results of Rietveld structural refinement of DyMn$_{0.8}$Fe$_{0.2}$O$_3$ with Rp value of 8.9%. All diffraction patterns can be assigned to the single phase orthorhombic structure with space group $Pbnm$. The Fe content dependence of average Mn/Fe-O bonding distances and Mn/Fe-O-Mn/Fe angles within $ab$-plane are given in the inset. There are two transitions at x=0.5 and x=0.67, may suggesting two magnetic transitions. The lattice parameter dependence on the Fe content is shown in Figure 2.2-1 (b). With increasing x, both $a$ axis and $c$ axis become longer monotonously while $b$ axis decreases linearly but shows weak fluctuation above x=0.5.
Figure 2.2-1 (a) XRD refinement calculation results on DyMn$_{0.8}$Fe$_{0.2}$O$_3$ with R$_p$ = 8.9\% (star symbols, experiment data; solid line, fitting data; short vertical solid lines, Bragg positions; fluctuation line at bottom, difference). Inset: Fe content dependence of Mn/Fe-O-Mn/Fe angles and Mn/Fe-O distances within $ab$-plane. (b) Lattice parameter dependence on Fe content.

The measurement of the field and zero-field cooling (FC and ZFC) temperature dependence of the magnetic moment was carried out for samples with $0 \leq x \leq 0.5$. The results are presented in Figure 2.2-2. DyMnO$_3$ shows a typical paramagnetic-like state over the whole temperature range, as seen in Figure 2.2-2(a). It was reported
that DyMnO\(_3\) changes to an AFM state around 39 K.\(^7,\)\(^13\) Because of the strongly paramagnetic Dy\(^{3+}\), the transition from PM state to AFM state is masked. However, the heat capacity measurement confirmed this magnetic phase transition and Dy\(^{3+}\) ordering around 6.5 K, shown in Figure 2.2-3).
Figure 2.2-2 (a) ZFC and FC M-T curves of DyMnO$_3$. Inset: Temperature dependence of normalized $d\chi/dT$ for $x \leq 0.5$. (b) / (c) temperature dependence of magnetic moment at low/high temperature range for $0.5 < x \leq 1$. (d) The Fe content dependence of the Néel temperatures ($T_N$) and spin reorientation temperatures ($T_r$). Speculated magnetic states are presented.
Figure 2.2-3 Heat capacity property of DyMnO$_3$ measured from 2K to 55K, showing two abnormalities around 6.5K and 39K, respectively.

When the Fe content increases, the ZFC and FC curves separate from each other at higher temperature, suggesting a possible magnetic phase transition, shown in Figure 2.2-4. To remove the Dy$^{3+}$ moment contribution and determine the exact phase transition temperature, we plot the normalized $d\chi/dT-T$ curves (shifted by proper interval), as shown in the inset of Figure 2.2-4(a). Clear peaks can be observed and the magnetic phase transition temperature increases when the Fe content increases. Low temperature and high temperature FC magnetic properties for samples with 0.5 $< x \leq 1$ were measured on heating in a field of 1000 Oe, as shown in Figure 2.2-4(b) and (c), respectively. There are two transitions which correspond to the sudden change of magnetic moment.
Figure 2.2-4 (a-c) ZFC and FC temperature dependence of magnetic moment for samples with $x=0.2$, 0.33 and 0.5, respectively.
Figure 2.2-5 Curie-Weiss law fitting of DyMn$_{1-x}$Fe$_x$O$_3$, x =0.6 to 1.0.

The spin state of Fe$^{3+}$ and Mn$^{3+}$ can be obtained by Curie Weiss Law fitting and the results are presented in Figure 2.2-5. For the rare earth metal ion Dy$^{3+}$, its maximum effective moment is 9.9µB/atom found in the oxide state. Fitting results show that all values of the Dy$^{3+}$ effective moment are above 9.5µB/atom, if Fe$^{3+}$ and Mn$^{3+}$ are in high spin state (Fe$^{3+}$: S=5/2, 5.9µB/atom and Mn$^{3+}$: S=2, 4.9µB/atom), indicating that Fe$^{3+}$ and Mn$^{3+}$ must always be in high spin state no matter what the Fe content. In addition, all Curie Weiss Law fittings give negative Curie-Weiss temperatures. Negative Curie Weiss temperatures indicate that the transitions at high temperature
range are AFM transitions. The high spin states of Mn$^{3+}$ and Fe$^{3+}$ further confirm that they are AFM transitions rather than ferromagnetic (FM) transitions. The increasing moment below this transition indicates that the AFM states are not pure but with weak ferromagnetic (WFM) component. The existence of FM clusters can be easily excluded because the magnetic hysteresis loop measured at 5K shows typical PM/AFM behaviour presented in Figure 2.2-6(b). Hence, the high temperature transitions are transitions from PM states to canted AFM states. The sudden decrease of magnetic moment at low temperature in Figure 2.2-2(b) should be the result of disappearance of WFM component. Hence, the transition at low temperature range is assigned to spin reorientation from canted AFM state to collinear AFM state. The spin reorientation temperature shifts to lower temperature with increasing Fe content while $T_N$ increases. The Fe content dependence of all transition temperatures is presented in Figure 2.2-2(d). Hence, the two transitions of bonding distances and angles within $ab$-plane just reflect the Fe doping induced magnetic transitions from paramagnetic state ($0 \leq x \leq 0.5$) to collinear antiferromagnetic state ($x=0.6$) to canted antiferromagnetic state ($0.67 \leq x \leq 1$) at room temperature.

In distorted perovskite ABO$_3$ type compounds with orthorhombic structure, such as LaMnO$_3$ and YbMnO$_3$, the cooperative rotation of corner-sharing BO$_6$ octahedra can bias the cooperative Jahn-Teller orbital ordering. In-plane magnetic interaction of BO$_6$ octahedra is decided by the competition between the FM interaction of $e_g$ electrons ($\sigma$-bond component) and the AFM interaction of $t_{2g}$ electrons ($\pi$-bond component). The interplane magnetic interaction can be divided into two major parts, according to the different contributions from electrons in different 3d sub-orbitals. One is the AFM interaction between half-filled $t_{2g}$ orbitals of transition metal B ions via O$^{2-}$ ions. The other is the AFM and FM competition interaction among $e_g$ orbitals.
(e.g., $3z^2-r^2$ and $x^2-y^2$). Generally, the interplane AFM interaction of $t_{2g}$ plays a dominating role, resulting in an AFM spin configuration along $c$ axis. For LaMnO$_3$, there is A-type antiferromagnetic order due to the dominating FM interaction of $e_g$ in-plane.$^{24}$ Here, DyMnO$_3$ shows an incommensurate antiferromagnetic configuration with a wave number of 0.72 at $T_N$. Our experiment shows that the AFM transition temperatures of DyMn$_{1-x}$Fe$_x$O$_3$ are modified by Fe doping, which stems from subtle structural change. For DyMnO$_3$ and low Fe doping samples with $x \leq 0.2$, a relation $b > a > c/\sqrt{2}$ is found, suggesting a static Jahn-Teller orbital ordering. Therefore, for $x \leq 0.5$, the Fe doping can affect the magnetic exchange interaction in the following way: because $e_g$ orbital of Fe$^{3+}$ ion is half occupied and that of Mn$^{3+}$ ion is quarter occupied, such an occupied electronic state enhances the AFM exchange interaction of the whole system, both in-plane and interplane, according to the Hund rule. In addition, Fe doping also promotes the increase in $c/\sqrt{2}$ relative to $a$, the orbital ordering becomes less stable, and stronger AFM interaction of $e_g^2$-O-$e_g^2$ (Fe-O-Fe) emerges. The increasing Mn/Fe-O-Mn/Fe angles within $ab$-plane confirm the enhancement of AFM interaction according to the Goodenough-Kanamori (GK) rule.$^{26-28}$ For $x > 0.5$, the magnetic interaction should be considered in a quite different way. Similar to Yb(Mn$_{1-x}$Fe$_x$)O$_3$,$^{25}$ despite the disappearance of the static Jahn-Teller distortion and long range orbital order, the dynamic Jahn-Teller site transformation still remains. The AFM interaction totally overwhelms the weak FM interaction of electrons in the Mn$^{3+}$ $e_g$ orbital and favours the G-type spin configuration. Moreover, this AFM interaction becomes much stronger in samples with higher Fe doping level so that $T_N$ shifts significantly. In G-type antiferromagnetic order, a weak FM component could be induced along $c$ axis because of Dzyaloshinsky-Moriya (DM) interaction, if spins are normal to $b$ axis in
As for spin reorientation, there are a few factors that affect this transition: magnetic anisotropy, single ion anisotropy, the DM interaction, and exchange interaction. In our case, Dy$^{3+}$-Fe$^{3+}$/Mn$^{3+}$ ion exchange interaction seems to play an important role. In a pure DyFeO$_3$ sample, the spin reorientation takes place at a relatively low temperature, ~65K ($T_r$), when the strong Dy$^{3+}$-Fe$^{3+}$ interaction dominates the Fe$^{3+}$-Fe$^{3+}$ interaction along one axis over other axis. For samples with lower Fe content, the Fe$^{3+}$-Fe$^{3+}$ interaction in the whole system becomes weaker because of Mn$^{3+}$ substitution. Hence, even at higher temperature, the Dy$^{3+}$-Fe$^{3+}$ interaction can overwhelm thermal disturbance and the Fe$^{3+}$-Fe$^{3+}$ interaction, forcing spin reorientation to occur.

The M-H loops at 5 K of all samples are plotted in Figure 2.2-6. For $x \leq 0.5$, M-H loops are shown in Figure 2.2-6(a) individually and the saturation magnetic moments are nearly the same, but obvious remnant moments can be observed except DyMnO$_3$. Remnant moments decrease when $x$ increases. DyMnO$_3$ is neither the standard PM loop nor an AFM loop which should be attributed to the spiral magnetic configuration below 20 K. This indicates that Fe doping not only enhances antiferromagnetic interaction, but also induces stronger or weaker spin frustration compared with non-doped spiral DyMnO$_3$, especially at low doping rates. The local DM interaction among these frustrated spins may be responsible for the weak ferromagnetic component at low temperature. For $x > 0.5$, it is clear that the saturation magnetic moments increase when $x$ increases and there are no remnant moments, shown in Figure 2.2-6(b), meaning that it is collinear antiferromagnetism after spin reorientation.
Figure 2.2-6 (Colour online) Magnetic hysteresis loops at 5 K from -5 T to 5 T for samples with (a) \(x \leq 0.5\) and (b) \(0.5 < x \leq 1\).

2.2.5 Conclusion

In summary, we have studied polycrystalline perovskite DyMn\(_{1-x}\)Fe\(_x\)O\(_3\) samples by means of structural and magnetic measurements. In samples with \(x \leq 0.2\), strong Jahn-Teller distortion favours static orbital orderings, which become less stable in samples with \(x \leq 0.5\) and probably disappears in samples with \(x > 0.5\), according to the analysis of structure and magnetic property. Because of the introduction of Fe\(^{3+}\),
which is half-occupied in e_g orbital, the AFM transition temperatures become very sensitive to Fe content and shift to higher temperatures from 39 K to 680 K. When x exceeds 0.5, spin reorientations take place at certain temperatures which show an opposite shifting tendency to T_N.

2.2.6 References


25 Y. H. Huang, M. Karppinen, N. Imamura, H. Yamauchi, and J. B.


3 DIELECTRIC PROPERTY STUDY IN DYMN_{1-x}FE_{x}O_{3} SYSTEM

3.1 Dielectric Relaxation in the DyMn_{1-x}Fe_{x}O_{3} System

3.1.1 Abstract

The dielectric constant and loss of perovskite DyMn_{1-x}Fe_{x}O_{3} samples show strong dispersion in various frequencies, which is indicative of relaxation. The activation energies were obtained through Arrhenius law fitting and range from 0.213 eV to 0.385 eV. The Fe content dependence of the characteristic frequency $f_0$ and the activation energy $E_\alpha$ shows two transitions which are well consistent with the change in orbital ordering. Meanwhile, different magnetic orderings could affect the relaxation and induce the change in $E_\alpha$.

3.1.2 Introduction

The giant magnetoresistance effect has aroused great interest in physics during the past several years and has been widely used in electronic memory storage\(^1,^2\). The next generation memory and computation devices are expected to be based on multiferroic materials, in which the spin degree of freedom can be controlled apart from the charge degree of freedom\(^3^6\). A great amount of work has been done to explore mutual control of these two degrees of freedoms, the so-called magnetoelectric (ME) coupling\(^7^9\). On the other hand, the dielectric property changes around the magnetic phase transition can offer a way to achieve magnetodielectric coupling,\(^10^13\) which also provides an alternative way to achieve more operation of degrees of freedoms. Magnetic field induced dielectric constant changes are observed in metastable orthorhombic HoMnO\(_3\) and YMnO\(_3\) below their incommensurate antiferromagnetic (AFM) transition temperature of 42 K\(^14\). To achieve real
applications based on spin related dielectric properties, it seems to be necessary to study their frequency and temperature dependence. Recently, dielectric relaxation was studied in La$_2$MgMnO$_6$\textsuperscript{15} and La$_2$NiMnO$_6$\textsuperscript{16,17} with double perovskite structure. However, up to now, there have been few systematic studies on dielectric relaxation in a magnetic system, and there are few reports on the relation between dielectric relaxation and subtle structural change and magnetic ordering. In the multiferroic DyMn$_{1-x}$Fe$_x$O$_3$ system, there is continuous structural and magnetic evolution\textsuperscript{18} The static Jahn-Teller orbital ordering becomes unstable and is replaced by dynamic orbital ordering as x increases from 0 to 0.5, while the collinear AFM transition temperature shifts to higher temperature. Orbital ordering disappears in the samples with x > 0.5, and the samples show canted AFM ordering and experience spin reorientation from canted AFM to collinear AFM at relatively low temperature. Hence, this is a good magnetic system for spin and structure related dielectric study.

In this letter, we report the dielectric relaxation in the DyMn$_{1-x}$Fe$_x$O$_3$ system at low temperature over a wide frequency range. There are two transitions of x dependent activation energies, which are found to be consistent with the transitions of orbital ordering, and magnetic ordering as well. This indicates that there are probably strong correlations between dielectric relaxation, and structural and magnetic properties.

3.1.3 Experimental

Polycrystalline samples of DyMn$_{1-x}$Fe$_x$O$_3$ (x = 0, 0.1, 0.2, 0.33, 0.5, 0.6, 0.67, 0.9) were made by the traditional solid state reaction method from Dy$_2$O$_3$ (99.9%), MnCO$_3$ (99.9%), and Fe$_2$O$_3$ (99.9%) powder bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, followed by pressing into pellets 15 mm in diameter at 20 MPa.
Samples were calcined at 950 °C for 10 hours and sintered at 1440 °C for 6 hours. The crystal structures of the samples were examined by x-ray diffraction (XRD, Model: GBC MMA), using Cu Kα radiation at $\lambda = 1.54056$ Å. The Rietveld refinement calculations were conducted via FULLPROF software. An Agilent 4294A precise impedance analyser was employed for dielectric property measurements, scanning from 1 kHz to 1 MHz.

3.1.4 Results and discussion

3.1.4.1 Structure

The results of structural characterization of all samples by XRD are given in Figure 3.1-1 (a). We employed Rietveld analysis to refine the diffraction patterns. All XRD patterns can be assigned to the single phase orthorhombic structure with space group $Pbnm$, and no detectable impurity phase is present. The lattice parameter dependence on the Fe content, derived from the Rietveld refinement, is shown in Figure 3.1-1 (b).

![Figure 3.1-1](#)

Figure 3.1-1 (a) X-ray diffraction patterns of all samples, (b) x dependence of lattice parameters.
With increasing Fe content, the $b$-axis parameter of the unit cell becomes monotonically shorter, the $c$-axis parameter becomes longer in a linear way, and the $a$-axis parameter only increases slightly. Consistent with our previous work\textsuperscript{18}, the relation $b > a > c/\sqrt{2}$ is found in samples with $x < 0.33$, showing a static Jahn-Teller (JT) distortion (cooperative antiferroic JT orbital ordering) superimposed on high temperature O-type (i.e., not JT distorted) orthorhombic structure\textsuperscript{19,20}. As $x > 0.33$, $a > c/\sqrt{2}$ is found. According to the reported work, the static orbital ordering is expected to be absent and replaced by weaker and weaker dynamic orbital ordering when $x$ varies from 0.33 to 0.5, and the orbital ordering probably disappears in samples with $x > 0.5$.

3.1.4.2 Dielectric relaxation

The temperature dependence of the dielectric constant and loss at different frequencies is shown in Figure 3.1-2 for representative samples with $x = 0.2$ (shown in Figure 3.1-2 (a) and (c)) and 0.9 (shown in Figure 3.1-2 (b) and (d)). Strong relaxation of the dielectric constant and loss is observed in the investigated frequency range, where the temperatures of dielectric constant/loss peaks shift to higher temperature with increasing frequency. Comparing the relaxation processes between $x=0.2$ and $x=0.9$, it is clear that loss peak at a certain frequency also shifts strongly. This indicates that Fe doping can introduce significant change into the relaxation processes.
To calculate the activation energy of the relaxation process, we employ the modified Debye relaxation model, as shown in equation (1), to fit the experimental data for the sample with $x = 0$. This is because the loss peak information is difficult to extract from the loss-frequency curves.

\[
\varepsilon_r = \varepsilon' + i \varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \tag{1}
\]

where $\varepsilon_0$ / $\varepsilon_\infty$ is the static/very high frequency permittivity, $\omega$ is the angular frequency, $\tau$ is the relaxation time, and $\alpha$ is a parameter to describe the degree of difference from standard Debye relaxation. The data were only collected below the temperature of the loss peak in 1 kHz. The fitting results are shown in Figure 3.1-3.
Figure 3.1-3 Frequency dependence of the real dielectric constant $\varepsilon'$ at various temperatures: scattered symbols, experimental data; lines, the output of fitting via the modified Debye equation.

A series of relaxation times $\tau$ were obtained, and it is found that they follow the Arrhenius Law:

$$\tau = \tau_0 \exp\left(\frac{E_\alpha}{k_B T}\right)$$  \hspace{1cm} (2),

where $\tau_0$ is the relaxation time at infinite temperature (pre-exponential factor), $E_\alpha$ is the relaxation activation energy, $k_B$ is the Boltzmann constant, and $T$ is the temperature. The Arrhenius Law fitting results are given in Figure 3.1-4 (a) with $E_\alpha = 0.213$ eV and $\tau_0 = 6.43 \times 10^{-12}$ s. Considering the relaxation $\tau_0 \times f_0 = 1$, where $f_0$ is the characteristic frequency at infinite temperature, we can obtain an $f_0$ of $1.55 \times 10^{11}$ Hz for the sample with $x = 0$. 


Figure 3.1-4 Arrhenius Law fitting for all samples and corresponding activation energies at low temperature.

For all the other samples, the dielectric loss peak can be well indentified. The frequencies and temperatures of loss peaks follow the Arrhenius Law:

\[ f = f_0 \exp\left(\frac{E_a}{k_B T}\right) \]  \hspace{1cm} (3)

while the Arrhenius Law fitting results are given in Figure 3.1-4 (b-h).

The Fe content dependence of the characteristic frequency \( f_0 \) and activation energy \( E_a \) is shown in Figure 3.1-5. The characteristic frequency \( f_0 \) decreases sharply from \( 1.55 \times 10^{11} \) Hz for \( x = 0 \) to \( 3.8 \times 10^9 \) Hz for \( x = 0.2 \), increases dramatically from \( x = 0.33 \) to \( x = 0.6 \), and then drop rapidly again when \( x \) further increases. The activation energy \( E_a \) increases slowly when \( x \) varies from 0 to 0.2 and then goes up significantly until \( x = 0.6 \), after which it declines quickly. Therefore, two obvious transitions of \( f_0 \) and \( E_a \) that are dependent on Fe content can be identified clearly, and they are well matched to each other.
Figure 3.1-5 Fe content dependence of characteristic frequency $f_0$ and activation energy $E_a$.

3.1.4.3 Discussion

It is interesting that these two transitions correspond to structural and magnetic transitions in this system. The first transition between $x = 0.2$ and $x = 0.33$ is consistent with the structural change where static orbital ordering disappears and is replaced by weaker dynamic orbital ordering due to weaker Jahn-Teller distortion.
The transition between \( x = 0.5 \) and \( x = 0.6 \) is found to correspond to the disappearance of dynamic orbital ordering and the appearance of spin reorientation. These two transitions are also consistent with the result reported by Chiang\(^{21}\) \textit{etc}. In their work, the static orbital ordering becomes unstable in the sample with \( x \) around 0.3 shown in Figure 1 (b) and begins to disappear in the sample with \( x \) around 0.5 shown in Figure 4 (a) in Ref.\(^{21}\). Therefore, the structural variation is probably responsible for the variation in the characteristic frequency \( f_0 \) and the activation energy \( E_{a} \). Otherwise, the magnetic orderings seem to affect the relaxation as well. With \( x \) increasing from 0, the \( E_{a} \) increases until \( x = 0.6 \), during which the AFM transition temperature increases from 39 K to 400 K.\(^{18}\) The enhanced superexchange interaction restricts the electron transfer and consequently introduces higher \( E_{a} \). For \( x \geq 0.6 \), spin reorientation (SR, from the canted AFM state to the collinear AFM state in this system) appears, and the transition temperature of SR decreases with increasing \( x \).\(^{18}\) The relaxation process becomes easier because the canted AFM states allow a higher chance for electron transfer, compared with the collinear AFM state, and this effect introduces a smaller \( E_{a} \). The small amounts of Mn\(^{4+}/Mn^{2+}\) and Fe\(^{2+}\), due to the inevitable presence of oxygen defects, which occur often in manganites\(^{22}\) and ferrites\(^{23}\), are likely to be responsible for the relaxation process. The electron can hop in an external AC electric field between mixed-valence ions. Due to the different ionic radii of the ions with different valences, the hopping consequently induces lattice deformation and introduces polaronic distortion.

3.1.5 Conclusion

In conclusion, we prepared perovskite DyMn\(_{1-x}\)Fe\(_{x}\)O\(_{3}\) samples by solid state reaction. All samples are pure phase and show orthorhombic structure. Strong Jahn-Teller
distortion is expected to favor orbital ordering in the samples with $x = 0 - 0.2$. However, orbital ordering becomes weaker with increasing $x$ and disappears in the samples with $x > 0.5$. The dielectric constant and loss show strong dielectric dispersion in various frequencies, which is indicative of the relaxation. The frequencies and temperatures of the loss peaks follow the Arrhenius law, and the activation energies have been obtained, ranging from 0.23 eV to 0.36 eV. The Fe content dependence of the characteristic frequencies and activation energies shows a similar trend, which is well consistent with the change in the orbital ordering. In the light of this, dielectric and magnetic properties may be modified simultaneously by the variation in the structure because the magnetic properties of this system are also strongly related with the structure.

3.1.6 References


113


3.2 Temperature and Frequency Dependent Giant Magnetodielectric Coupling in DyMn$_{0.33}$Fe$_{0.67}$O$_3$

3.2.1 Abstract

Perovskite DyMn$_{0.33}$Fe$_{0.67}$O$_3$ experiences a paramagnetism-antiferromagnetism transition at 450 K and spin reorientation at 290 K. Magnetodielectric properties were studied around the spin reorientation transition. Both giant positive and giant negative magnetodielectric coupling (MDC) were observed near room temperature. The MDC shows strong temperature and frequency dependence, and the sign changes from positive to negative when magnetic state transits from a canted antiferromagnetic state to a collinear antiferromagnetic state. Possible mechanisms are proposed based on the Maxwell-Wagner model, phase transition, the magnetoresistance effect, and spin-phonon coupling.

3.2.2 Introduction

Dielectric materials are common materials which have wide applications in energy storage, electronic switches, sensors, and actuators. To develop next generation multifunctional devices, effective control of more degrees of freedom beyond electric charge should be given a priority. Considerable work has been done to control the dielectric property by magnetic methods$^{1-4}$, the so-called magnetodielectric coupling (MDC) effect. Most MDC effects appear around the magnetic phase transition temperature, at which dielectric abnormality can be observed and modified by external magnetic fields. These effects are notably found in some manganites. In BiMnO$_3$, the dielectric constant is suppressed around 100 K, where ferromagnetic ordering occurs$^5$ and a giant negative MDC effect could be induced. For spin frustrated perovskite TbMnO$_3$ (Pbnm space group)$^6$, an obvious peak in the
temperature dependence of the \( c \)-axis dielectric constant is found at 27 K, where the sinusoidal antiferromagnetic (AFM) magnetic modulation wave vector is locked at a constant value. Magnetic field can shift the dielectric peak slightly around 27 K and induce an extra dielectric peak at lower temperature. In metastable orthorhombic \( \text{HoMnO}_3 \) and \( \text{YMnO}_3 \), the MDC effect occurs below their incommensurate AFM transition temperature of 42 K. Apart from these manganites, the MDC effect can be found in other systems, such as \( \text{SeCuO}_3 \), \( \text{TeCuO}_3 \), \( \text{MCr}_2\text{O}_4 \) (\( \text{M} = \text{Mn}, \text{Co}, \text{and} \text{Ni} \)) and \( \text{Bi}_2\text{Mn}_{4/3}\text{Ni}_{2/3}\text{O}_6 \), although their MDC values are very small. Colossal magnetoresistance materials, such as \( \text{EuNbO}_2\text{N} \) and \( \text{HgCr}_2\text{S}_4 \), also show significant magnetodielectric response at low temperature. To achieve practical applications, it would be ideal to find materials with MDC effects near room temperature. In addition, the MDC effect should be strong. Here, we present both giant positive and giant negative MDC in perovskite \( \text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3 \) near room temperature, 290 K, at which spin reorientation occurs.

3.2.3 Experimental

Polycrystalline sample of \( \text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3 \) was made by the traditional solid state reaction method with \( \text{Dy}_2\text{O}_3 \) (99.9%), \( \text{MnCO}_3 \) (99.9%), and \( \text{Fe}_2\text{O}_3 \) (99.9%) powder bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, followed by pressing into pellets 15 mm in diameter at 20 MPa. Samples were calcined at 950 °C for 10 hours and sintered at 1440 °C for 6 hours. The crystal structure of the sample was examined by X-ray diffraction (XRD, Model: GBC MMA), using \( \text{Cu K}\alpha \) radiation at \( \lambda = 1.54056 \) Å. The Rietveld refinement calculations were conducted via FULLPROF software. The magnetic measurements were carried out using a 14 T physical properties
measurement system (PPMS), equipped with a vibrating sample magnetometer (VSM), in magnetic fields up to 5 T, over a wide temperature range from 5 to 340 K in standard mode, and from 310 K to 750 K in oven mode. Pt electrodes were deposited on both sides of the thin pellet by magnetic scattering coating for dielectric measurement. An Agilent 4294A impedance analyser was employed for dielectric property measurements, scanning from 1 kHz to 1MHz, while the temperature and applied magnetic fields were controlled by PPMS. A room temperature resistance measurement was carried out with a multimeter, and it showed resistivity of $\sim 10^7 \ \Omega\text{cm}$.

3.2.4 Results and discussion

Figure 3.2-1 shows the X-ray powder diffraction pattern and Rietveld refinement results at room temperature. All diffraction peaks can be assigned to the single phase orthorhombic structure with space group $Pnma$, and no detectable impurity phase is present. The quality of refinement is determined by refinement parameter $R_p = 10.2\%$ and variance $\chi^2 = 1.9$. The calculated lattice parameters are $a = 5.6237(10) \ \text{Å}$, $b = 7.5602(13) \ \text{Å}$, $c = 5.2912(9) \ \text{Å}$.

![Intensity vs. 2θ plot](image)

Figure 3.2-1 XRD refinement result of DyMn$_{0.33}$Fe$_{0.67}$O$_3$ with $R_p = 9.9\%$ (star symbols, measured, and solid line, fitted). The difference between the measured and
Rietveld refined spectra is plotted with a slight downshift for clarity. The short vertical solid lines are guides for the eyes to mark the corresponding Bragg positions. The temperature dependence of the magnetic moment of DyMn$_{0.33}$Fe$_{0.67}$O$_3$ is shown in Figure 3.2-2 (a). There are two transitions that can be clearly indentified. One is the transition from paramagnetism (PM) to canted antiferromagnetism (AFM), with a weak ferromagnetic component (WFM) around 450 K, while the other is the transition from a canted AFM (WFM) to a collinear AFM around 290 K as the temperature decreases. Curie-Weiss fitting was conducted above 450 K, as displayed in Figure 3.2-2 (b), where the sample shows intrinsic paramagnetic features, giving a Curie-Weiss temperature of $-79$ K, Curie constant of 15.6, and effective moment of 11.2 $\mu_B$. The negative Curie-Weiss temperature suggests the antiferromagnetic transition around 450 K. The theoretical value of maximum moment for DyMn$_{0.33}$Fe$_{0.67}$O$_3$ is 11.4 $\mu_B$ if all ions are in the high spin state (4.9 $\mu_B$/Mn$^{3+}$, 5.9 $\mu_B$/Fe$^{3+}$, and 9.9 $\mu_B$/Dy$^{3+}$). The close values of the theoretical and the experimental moments indicate that all magnetic ions are in the high spin state.
Figure 3.2-2 (a) Temperature dependence of magnetic moment from 10 K to 600 K (black closed triangles: standard mode, red closed circles: oven mode). Inset: magnetic hysteresis loop measured at 5 K. (b) Inverse DC susceptibility versus temperature as measured in an external field of 1000 Oe for the paramagnetic state of DyMn$_{0.33}$Fe$_{0.67}$O$_3$ above 450 K (dashed line: Curie-Weiss fit; triangles: the inverse curve from experimental data).

The increasing moment below this transition indicates that the antiferromagnetism is not pure but has a weak ferromagnetic component. Generally, in G-type antiferromagnetic order, a WFM component could be induced along the $c$ axis because of the Dzyaloshinsky-Moriya interaction, if spins are normal to $b$ axis in the $ab$ plane$^{13}$. The possibility of ferromagnetic (FM) clusters can be easily excluded because the magnetic hysteresis loop measured at 5 K shows typical paramagnetic/antiferromagnetic behaviour. A similar antiferromagnetic transition can also be observed in DyFeO$_3$$^{14}$. The sudden decrease in the magnetic moment at 290 K is likely to be the result of the disappearance of the WFM component. Below it, the sample is in the pure AFM state, as confirmed by the magnetic hysteresis loop at 5 K. Hence, this transition is a spin reorientation caused by the change in the
highly temperature sensitive magnetic anisotropy, which is similar to the case of DyFeO$_3$\textsuperscript{14}. The continuous increase in the magnetic moment at low temperature is due to paramagnetic behaviour of Dy$^{3+}$. The magnetic property is consistent with the previous work.\textsuperscript{15}

Figure 3.2-3 Frequency dependence of dielectric constant, loss at 310 K, 285K and 250K, respectively.

To investigate coupling between the magnetic field and the dielectric property, dielectric constants and loss were collected in different magnetic fields at 310 K, 285 K and 250 K respectively, as shown in Figure 3.2-3 (a, b, c). Obvious up/down shifts in the dielectric constant can be observed in the frequency dependence of the dielectric constants when measurements were carried out in various magnetic fields, indicating the occurrence of magnetodielectric coupling.
Figure 3.2-4 Frequency dependence of magnetodielectric coupling constant (MDC) and dynamic magnetoloss (ML) at 310 K, 285K and 250K, respectively.

The strength of magnetodielectric coupling is determined by the MDC constant in the form of \((\varepsilon_{H} - \varepsilon_{H=0})/\varepsilon_{H=0}\), which is calculated and given in Figure 3.2-4(a, b, c). It is clear that the MDC is extremely significant, especially in high magnetic field. At 310 K, we found a positive MDC constant as large as 53% (0.53) around \(2\times10^4\)Hz. At the low frequency range, the MDC constant approaches zero when the frequency decreases, indicating that mobile charge doesn’t contribute to the MDC effect too much. Just below the spin reorientation temperature, at 285 K, an opposite MDC effect occurs, giving a large value of -35% around \(1\times10^4\)Hz. The MDC constant also approaches zero when the frequency is close to 0 Hz, confirming the negligible effect of mobile charge on MDC. Maximum MDC can be observed at the conductivity cut-off frequency \(1/RC\) (where R and C are the resistance and capacitance of the equal circle, respectively). When the temperature cools down from the spin reorientation temperature, this negative MDC effect becomes much stronger, reaching -70% around \(5\times10^3\)Hz at 250 K, as shown in Figure 3.2-4(c). Hence, the MDC effect is strongly temperature dependent. On the other hand, clear frequency dependence of MDC can be well observed.
Figure 3.2-5 Frequency dependence of dynamic magnetoresistance (MR) at 310 K, 285K and 250K, respectively.

Up to now, there are three proposed mechanisms to explain the MDC effect. One is based on intrinsic multiferroic relaxor behaviour\textsuperscript{17}, one is based on the Maxwell-Wagner model\textsuperscript{16} and one is based on spin-phonon interaction. Although DyMnO\textsubscript{3} and DyFeO\textsubscript{3} also show multiferroic features, their multiferroic properties can only appear at very low temperature, below 18 K\textsuperscript{18} and 3.5 K\textsuperscript{19}, because of the inverse Dzyaloshinsky-Moriya interaction and exchange striction, respectively. Hence, near room temperature, the multiferroic relaxor based mechanism is not appropriate for our result. However, the giant MDC can be tentatively explained by the Maxwell-Wagner model at low frequency range below the cut-off frequency 1/ RC. To better understand these unique phenomena, we present the frequency dependence of the dynamic magnetolos (ML), ML = (Loss\textsubscript{H}-Loss\textsubscript{H=0})/Loss\textsubscript{H=0}, as shown in Figure 3.2-4(a, b, c). The significant change of ML can be observed as increasing frequency, and the ML shows the opposite tendency to that of MDC. Considering the ML effect and the result in Ref. [16], we could assign this MDC effect to the MR related MDC effects. Above the spin reorientation temperature of 290 K, such as at 310 K, the material shows WFM, but the applied magnetic field suppresses the spin fluctuation in the WFM state\textsuperscript{20, 21}. This results in a negative magnetoresistance (MR) and favours a positive MDC effect according to the Maxwell-Wagner model, similar to
the positive MDC effect that occurs in EuNbO$_2$N below the ferromagnetic transition temperature$^{11}$. During our experiment measurement, dynamic frequency dependent resistances were obtained. Figure 3.2-5 presents the dynamic magnetoresistance in form of \( MR = \frac{R_{H}-R_{H=0}}{R_{H=0}} \). A negative MR effect is observed at 310K as shown in Figure 3.2-5 (a). The result confirms our assumption. On the contrary, when the temperature is 285 K or 250 K, the material experiences a magnetic phase transition from WFM to AFM. The MDC may be contributed by the following possible factors: first, MR effect induced by spin polarized tunnelling between charge depleted grain boundaries$^{20}$; second, the intrinsic magnetoelectric effect due to magnetostriction$^{22}$; third, the spin pair correlation, as explained in the phenomenal model$^{23}$. In our case, the magnetostriction effect should be very small and negligible, as the sample is not a typical magnetostriction material. In addition, the spin pair correlation cannot induce such a giant MDC effect. Hence, the most likely factor is the contribution by MR effect induced by spin polarized tunnelling, despite the AFM property. This is proved by the positive MR effects are observed at 280 K and 250 K as shown in Figure 3.2-5 (b) and (c), which could induce a negative MDC according to the Maxwell-Wagner model. In the light of this, the MDC at low frequency range below the cut-off frequency $1/RC$ is related to space charge effect, which can be further confirmed by the strong frequency dependence and MR effect. For the case at high frequency range above the cut-off frequency $1/RC$, the MDC effect becomes weaker, which should due to the absence of space charge effect. Different magnetic states will affect the strength and mode of spin-phonon interaction and dielectric constant is consequently modified$^{8, 24}$. Similar effect is observed in Mn$_3$O$_4$, in which opposite MDC effects happen above and below magnetic transition temperature$^{25}$. Hence, spin-phonon interaction is supposed to be responsible for the MDC at high frequency
3.2.5 Conclusion

In summary, we have studied the phase transitions and MDC effect in DyMn$_{0.33}$Fe$_{0.67}$O$_3$. Two magnetic phase transitions are found at 290 K and 450 K, corresponding to spin reorientation and the antiferromagnetism-paramagnetism transition, respectively. MDC show strong temperature and frequency dependence. Giant positive and negative MDC effects are observed in the vicinity of the spin reorientation temperature. Magnetoresistance based Maxwell-Wagner model is employed to explain the MDC at low frequency range below the cut-off frequency $1/RC$ and spin-phonon interaction is responsible for the MDC at high frequency range above the cut-off frequency $1/RC$. These effects make it promising to produce multifunctional devices based on such kinds of materials.

3.2.6 References

4 STRONG 4F ELECTRON INTERACTION AND MAGNETIC ORDERING MODIFICATION IN Nd_{1-x}Er_xMnO_3 (0 \leq x \leq 0.5)

4.1 Abstract

The structural properties, magnetic properties, and heat capacity have been systematically studied in perovskite Nd_{1-x}Er_xMnO_3 (0 \leq x \leq 0.5). Er^{3+} doping enhances the Jahn-Teller distortion, strongly affects the Nd^{3+}-Mn^{3+} interaction, destroys the intermediate state below the antiferromagnetic transition temperature in NdMnO_3, and breaks the antiparallel arrangement between Nd^{3+} and Mn^{3+} spin ordering. In spite of the high compression of the lattice along the c axis, the spin states of Mn^{3+} are stable and are always high spin states. For x < 0.5, both the Mn^{3+} antiferromagnetic transition temperatures and the Nd^{3+} ferromagnetic transition temperatures decrease after Er^{3+} doping. For x = 0.5, Mn^{3+} probably enters a pure A-type antiferromagnetic (AFM) state at lower temperature, which is different from the canted A-type AFM state found in other samples, and there is no Nd^{3+} ordering observed above 5 K. The decreasing ferromagnetic component in magnetic hysteresis loops at 30 K indicates that the canted angles vary with x. Otherwise, the coincidence between the magnetic entropy abnormality and the structural change suggests that the magnetic transition may accompany structural change. These results offer strong evidence for the interaction between rare earth ions and transition metal ions, and competition among rare earth ions as well.

4.2 Introduction

The manganites have aroused great interest during the past several years because of the magnetoresistance effect\(^1,2\). During these years, more attention has been paid to some manganites due to their unique multiferroic properties\(^3,4\). For ABO_3-type
perovskite manganites, the structures evolve gradually from orthorhombic to hexagonal when the A site ion varies from lanthanum to lutetium, and the magnetic behaviour becomes quite different. Abundant magnetic phase transitions are observed in these manganites. LaMnO$_3$ shows typical A-type antiferromagnetism (AFM) at 140 K because of the orbital ordering arising from the distorted perovskite structure$^5$. A-type AFM still exist in SmMnO$_3$, in which Sm$^{3+}$ has a smaller ionic radius than La$^{3+}$, but it is canted A-type AFM with a weak ferromagnetic component$^6$. The magnetic properties become much more complicated in orthorhombic DyMnO$_3$, which experiences a sinusoidal incommensurate AFM transition at 39 K and a spiral spin ordering below 18 K, after which ferroelectric polarization can be observed because of an inverse Dzyaloshinsky-Moriya (DM) interaction$^3$. A similar magnetic phase transition can also be found in TbMnO$_3$$^3$.

When La$^{3+}$ is replaced by much smaller atoms, such as Er$^{3+}$, the orthorhombic structure will be disturbed, and the hexagonal structure becomes stable, so that ErMnO$_3$ has a frustrated triangular spin arrangement on the Mn$^{3+}$ sublattice$^7,8$.

To well understand the mechanisms behind the different magnetic properties in these manganites, it is necessary to illustrate the interaction between the rare earth ions and Mn$^{3+}$, based on some reports that have been focused on the doping effects of rare earth ions. In the Er$_{1-x}$Y$_x$MnO$_3$ system$^9$, the strong geometrical frustration effect in YMnO$_3$ becomes weaker and weaker as the Er$^{3+}$ content increases, but the ordered moments are very stable without strong doping dependence, which suggests that there is strong coupling between Er$^{3+}$ and Mn$^{3+}$. Gd$^{3+}$ with 4f electrons has been introduced to replace La$^{3+}$ in LaMnO$_3$, and spin canting of Mn$^{3+}$ can polarize the 4f spins in Gd$^{3+}$. $^{10}$
Considering the different magnetic phases in orthorhombic and hexagonal manganites, it is of interest to study the structural variation and consequent evolution of magnetic properties by combining two such manganites together. In the Eu$_{1-x}$Y$_x$MnO$_3$ system$^{11,12}$, the rare earth ions are both non-magnetic, and ferroelectric polarization is observed below the antiferromagnetic transition temperature in samples with $x \geq 0.3$, presumably due to the emergence of spiral spin ordering, although only on the Mn$^{3+}$ sub-lattice. When $x$ is around 0.2, weak ferroelectric polarization and weak ferromagnetism coexist and show the multiferroic property, probably due to a cone-like spin ordering.

In this work, we study the structural and magnetic properties in the Nd$_{1-x}$Er$_x$MnO$_3$ system. Both Nd$^{3+}$ and Er$^{3+}$ are magnetic rare earth ions with 4f electrons, but with quite different moments. From the experiments, we observe an intermediate state in NdMnO$_3$, although it disappears in other samples after Er$^{3+}$ doping. Meanwhile, the antiferromagnetic coupling between the ferromagnetic (FM) components of Nd$^{3+}$ and Mn$^{3+}$ that is found in NdMnO$_3$ is also totally destroyed by Er$^{3+}$ doping. It is proposed that the canted angle of the Mn$^{3+}$ sub-lattice is rotated by doping and disappears in the sample with $x = 0.5$. Otherwise, there is a coincidence between the structural change at room temperature and the magnetic entropy abnormality, suggesting that the magnetic transition may accompany subtle structural change.

4.3 Experimental

Polycrystalline samples of Nd$_{1-x}$Er$_x$MnO$_3$ ($x = 0, 0.1, 0.2, 0.33, 0.5, \text{ and } 1.0$) were made by the traditional solid state reaction method. Stoichiometric amounts of raw oxide powder were weighed and then mixed in an agate mortar, which was followed by pressing into pellets 15 mm in diameter at 20 MPa. Samples were calcined at 950
°C for 10 hours and sintered at 1450 °C for 48 hours. The crystal structures of the samples were examined by X-ray diffraction at room temperature (XRD, model: GBC MMA), using Cu Kα radiation at λ = 1.54056 Å. The Rietveld refinement calculations were conducted via FULLPROF software to obtain the lattice parameters and bond information. The magnetic measurements were carried out using a 14 T physical properties measurement system (PPMS).

4.4 Results and discussion

4.4.1 Structural properties

The crystalline structures of all samples were examined by X-ray diffraction. The results are given in Figure 4.4-1. The two end samples, NdMnO₃ and ErMnO₃, are in the orthorhombic and hexagonal structure, respectively. When NdMnO₃ is doped with Er, the samples with x ≤ 0.5 always exhibit the orthorhombic structure with regularly shifting diffraction peaks. For the sample with x > 0.5, both orthorhombic phase and hexagonal phase can be clearly identified (not shown).

![Figure 4.4-1 XRD patterns for Nd₁₋ₓErₓMnO₃.](image)
We employed FULLPROF software to refine the diffraction patterns to enable the lattice parameters to be obtained. A typical result of Rietveld structural refinement of Nd$_{0.67}$Er$_{0.33}$MnO$_3$ is given in Figure 4.4-2 with $\chi^2 = 1.8$. All diffraction patterns can be assigned to the single phase orthorhombic structure with space group $Pbnm$, and no detectable impurity phase is present.

![Diffraction pattern and refinement results](image)

**Figure 4.4-2** Typical refinement results for Nd$_{0.67}$Er$_{0.33}$MnO$_3$ with $\chi^2 = 1.8$

The Er content dependence of the lattice parameters is given in Figure 4.4-3. It is clear that 10% Er doping affects the lattice parameters significantly. The relation $b > a > c/\sqrt{2}$ can be found for each sample and suggests a static Jahn-Teller orbital ordering\textsuperscript{10}. The bigger and bigger difference between the $b$ axis and $a$ axis parameters with increasing Er content is due to the replacement of Nd$^{3+}$ by the smaller Er$^{3+}$ ion. This can induce stronger Jahn-Teller distortion, which favours stronger in-plane ferromagnetic double exchange. Theoretical tolerance factors were calculated in form of $t = (R_A + R_O^2)/\sqrt{2} (R_{\text{Mn}^{3+}} + R_O^2)$ shown in Figure 4.4-4, where $R_A = (1-x)R_{\text{Nd}^{3+}} + xR_{\text{Er}^{3+}}$. On increasing the Er doping level, the structure diverges.
further from the ideal structure. This is confirmed by the increasing spontaneous stress\textsuperscript{13} calculated in form of \(2(b - a)/(b + a)\), as shown in Figure 4.4-4. A significant change is also observed at \(x = 0.1\).

Figure 4.4-3  Doping rate \(x\) dependence of lattice parameters

Figure 4.4-4 X dependence of theoretical tolerance factors and spontaneous stress
To understand how Er\(^{3+}\) doping affects the structure in detail, the Mn-O bond lengths and Mn-O-Mn bond angles both in-plane and inter-plane, and the Nd/Er-Mn distances were extracted based on the results of refinement. The information on atomic positions, bond lengths, and bond angles is presented in Table 1. It is clear that the atomic positions, bond lengths, and bond angles do not show any regular change with increasing \(x\), which may be due to the quite different atomic radii of Nd\(^{3+}\) and Er\(^{3+}\). Meanwhile, Nd\(^{3+}\) and Er\(^{3+}\) are magnetic rare earth ions with different moments, which may also be responsible for the complex spatial atomic arrangements. The Er content dependence of bond distances and bond angles inter-plane and in-plane, and the Nd/Er-Mn distances are shown in Figure 4.4-5. When the doping rate is 0.1, significant changes in the bond distance and bond angle are observed. The bond distance and bond angle in the sample with \(x = 0.5\) also show relatively big changes compared with the other samples (\(x = 0, 0.2, \) and 0.33) in which the bond distances and bond angles remain very close. Meanwhile, the changes in the bond distances and bond angles in-plane seem to show the opposite trend to those of the bond distances and bond angles inter-plane. This means that there is strong competition in terms of structural stability inter-plane and in-plane, which also suggests that there would be strong magnetic competition between the inter-plane and in-plane moments.
<table>
<thead>
<tr>
<th>x atom site x</th>
<th>y</th>
<th>z</th>
<th>x atom site x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd 4c 0.0623(6)</td>
<td>0.25</td>
<td>0.9872(10)</td>
<td>Mn 4b 0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>O1 4e 0.477(6)</td>
<td>0.25</td>
<td>0.098(5)</td>
<td>O2 8d 0.184(4)</td>
<td>0.555(4)</td>
<td>0.231(6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd 4c 0.0631(11)</td>
<td>0.25</td>
<td>0.9881(19)</td>
<td>Er 4c 0.0631(11)</td>
<td>0.25</td>
<td>0.9881(19)</td>
</tr>
<tr>
<td>Mn 4b 0</td>
<td>0.5</td>
<td>O1 4e 0.398(11)</td>
<td>0.25</td>
<td>0.096(10)</td>
<td></td>
</tr>
<tr>
<td>O2 8d 0.168(9)</td>
<td>0.468(9)</td>
<td>0.323(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd 4c 0.0739(5)</td>
<td>0.25</td>
<td>0.9866(9)</td>
<td>Er 4c 0.0739(5)</td>
<td>0.25</td>
<td>0.9866(9)</td>
</tr>
<tr>
<td>Mn 4b 0</td>
<td>0.5</td>
<td>O1 4e 0.499(5)</td>
<td>0.25</td>
<td>0.099(5)</td>
<td></td>
</tr>
<tr>
<td>O2 8d 0.286(4)</td>
<td>0.452(3)</td>
<td>0.289(5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd 4c 0.0776(7)</td>
<td>0.25</td>
<td>0.9876(13)</td>
<td>Er 4c 0.0776(7)</td>
<td>0.25</td>
<td>0.9876(13)</td>
</tr>
<tr>
<td>Mn 4b 0</td>
<td>0.5</td>
<td>O1 4e 0.477(7)</td>
<td>0.25</td>
<td>0.096(7)</td>
<td></td>
</tr>
<tr>
<td>O2 8d 0.278(6)</td>
<td>0.457(4)</td>
<td>0.295(5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd 4c 0.0769(8)</td>
<td>0.25</td>
<td>0.9888(15)</td>
<td>Er 4c 0.0769(8)</td>
<td>0.25</td>
<td>0.9888(15)</td>
</tr>
<tr>
<td>Mn 4b 0</td>
<td>0.5</td>
<td>O1 4e 0.486(8)</td>
<td>0.25</td>
<td>0.105(8)</td>
<td></td>
</tr>
<tr>
<td>O2 8d 0.321(6)</td>
<td>0.444(4)</td>
<td>0.264(8)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: the information on atomic positions, bond lengths, and bond angles.
Figure 4.4-5 X dependence of Mn-O bond distances, Mn-O-Mn bond angles inter-plane and in-plane, and Nd/Er-Mn distances.

4.4.2 Magnetic properties

As shown in Figure 4.4-6, the field cooling (FC) temperature dependence of the magnetic moment was measured in various fields. Figure 4.4-6(a) shows the M-T curves of NdMnO$_3$ in 20 Oe and -20 Oe, while Figure 4.4-6(b) shows the M-T curves in 100 Oe and -100 Oe. In these figures, we can always observe a transition at 79 K. In addition, another transition can also be observed around 15 K, where negative (positive) moments change to positive (negative) moments. The transition at high temperature showing the weak ferromagnetic (WFM) property is assigned to the canted A-type antiferromagnetic (AFM) transition of Mn$^{3+}$, which has been well studied$^6$, $^{14}$. The low temperature transition is assigned to ferromagnetic (FM) ordering of Nd$^{3+}$. Considering the sign change in the moment at low temperature, we can claim that the magnetic vector of Nd$^{3+}$ ordering is opposite to the magnetic
vector of Mn$^{3+}$ ordering, meaning that Nd$^{3+}$ couples with Mn$^{3+}$ antiferromagnetically, which can also been confirmed by the neutron result. The asymmetric values of moments in opposite applied fields at 5 K further confirm this spin configuration. Similar spin arrangements between rare earth ions and transition metal ions are also found in SmMnO$_3$ and GdMnO$_3$.

Figure 4.4-6 Field cooling temperature dependence of magnetic moment for NdMnO$_3$, (a) 20 and -20 Oe (cooling field); (b) 100 and -100 Oe.
Figure 4.4-7 Field cooling temperature dependence of magnetic moment: (a) $x = 0.1$, 500 Oe, and $x = 0.2$, 100 Oe; (b) $x = 0.33$, 100 Oe, and $x = 0.5$, 100 Oe.

The FC temperature dependence of the magnetic moment was examined for the other four samples, as shown in Figure 4.4-7(a) and (b). For $x < 0.5$, the magnetic moments suddenly increase at certain temperatures, which become lower and lower with increasing $x$, suggesting a shift in the magnetic phase transition temperature.
This increase is due to the ferromagnetic component in the canted A-type AFM ordering of Mn$^{3+}$, similar to what occurs in NdMnO$_3$. The downshift in the Néel temperature ($T_N$) is due to enhanced Jahn-Teller distortion, which has been well studied in other systems\textsuperscript{16}. For $x = 0.5$, such a sudden increase in moment cannot be observed in the M-T curve, which is probably due to the disappearance of the ferromagnetic component.

The ferromagnetic-like behaviour for $x < 0.5$ is confirmed by the magnetic hysteresis loops measured at temperatures below $T_N$, as shown in Figure 4.4-8(a-b) and Figure 4.4-9(a-b). The M-H loop of the sample with $x = 0.5$ measured at 30 K in Figure 4.4-10 shows typical paramagnetic/antiferromagnetic behaviour, confirming the disappearance of the ferromagnetic component. In contrast to NdMnO$_3$, the moment shows no sign change in the M-T curves in the low temperature range for the other four samples, in spite of reduced Nd/Er-Mn distances. This indicates that the orderings in NdMnO$_3$ are severely disturbed by Er$^{3+}$ doping, which favours general orderings (Mn$^{3+}$ and Nd$^{3+}$ ordering in the same or a similar direction).
Figure 4.4-8 Magnetic hysteresis loops for $x = 0$ measured at (a) 30 K and 55 K, (b) 20 K and 35 K.
The unique M-H loop of NdMnO$_3$ at 30 K is probably attributable to variation in the intermediate state at high fields. To confirm the existence of this intermediate state
and study its origin, another M-H loop was collected at 20 K, which also shows abnormal behaviour. However, this state disappears at 35 K, as proved by the M-H loop at that temperature. Meanwhile, the temperature dependence of the magnetic moment was measured at different magnetic fields, as shown in Figure 4.4-11.

![Figure 4.4-11 Temperature dependence of magnetic moment in various magnetic fields](image)

Figure 4.4-11 Temperature dependence of magnetic moment in various magnetic fields

To extract the detailed information from M-T curves, Figure 4.4-12 presents the temperature dependence of dM/dT for x = 0, 0.1, and 0.5 under different cooling fields. For x = 0, a clear peak can be identified at 79 K at 1 T (shown in Figure 4.4-12(a)), and it shifts to 88.1 K at 5 T (shown in Figure 4.4-12(b)), which corresponds to the antiferromagnetic transition. Meanwhile, an intermediate state transition is observed at ~33.5 K at 1 T with a sharp increase in dM/dT, which is consistent with the results from M-H loops at 30 K and 35 K. The intermediate state transition can also be found at 5 T in Figure 4.4-12(b). Hence, both the M-H loop at
20 K and dM/dT for NdMnO$_3$ further confirm the existence of an intermediate state at 30 K. The intermediate state should be ascribed to the coexistence state of short range Nd$^{3+}$ ordering and long range Mn$^{3+}$ ordering. We propose the spin configuration shown with the M-H loop at 20 K in Figure 4.4-8(b), which also applies to the M-H loop at 30 K. At high magnetic field, the FM vectors of the Mn$^{3+}$ spins have the same spin direction as the Nd$^{3+}$ spins. When the field sweeps from ~7000 Oe to ~7000 Oe (or from ~7000 Oe to ~7000 Oe), the spin direction of Mn$^{3+}$ doesn’t change, but the Nd$^{3+}$ spins gradually flip. On further increasing the field, the Mn$^{3+}$ spins flip, and their FM vectors show the same direction as Nd$^{3+}$ again. The difference between the M-H loops at 20 K and 30 K is due to the different amounts of Nd$^{3+}$ short range ordering. The negative remnant moment sweeping from A to B (positive from C to D) in the M-H loop at 20 K is due to the bigger total moment of Nd$^{3+}$ compared to Mn$^{3+}$. To determine the actual spin configuration, further study is needed based on neutron diffraction. However, this intermediate state is not observed in the other samples, as confirmed by Figure 4.4-12(c) and (d). The disappearance of the intermediate state further confirms that Er$^{3+}$ doping severely affects the interactions among Mn$^{3+}$ and Nd$^{3+}$ ions.

The magnetic hysteresis loops at 30 K also reflect the subtle magnetic evolution. The coercive field and remnant moment increase when the Er$^{3+}$ doping rate x is 0.1, as compared with the behaviour of NdMnO$_3$, and then decrease gradually with increasing x. No obvious coercive field is observed in the sample with x = 0.5. The coercive field and remnant moment should be determined by the magnitude of the ferromagnetic component, which is dominated by the canted angle of ferromagnetic Mn$^{3+}$ spin ordering in the $ab$-plane.
Figure 4.4-12 Temperature dependence of dM/dT under different cooling fields: (a) $x = 0$, 1 T; (b) $x = 0$, 5 T; (c) $x = 0.1$, 0.5 T; and (d) $x = 0.5$, 0.1 T.

The spin states were deduced from Curie-Weiss Law fitting. In Figure 4.4-13, $1/\chi - T$ shows a linear relation above the AFM transition temperature for all samples. For $x = 0$-0.2, Curie-Weiss Law fitting gives positive Curie temperatures, which are likely to be due to the strong canted AFM ordering with an obvious FM component. For $x > 0.2$, the Curie temperatures are negative due to AFM ordering with weak FM and without FM components. Curie constants were obtained, and experimental theoretical effective magnetic moments have been calculated, as can be seen in Table 2. Theoretical effective magnetic moments were also calculated (Nd$^{3+}$: 3.62 $\mu_B$, Er$^{3+}$: 9.59 $\mu_B$, Mn$^{3+}$: low spin state, 2.828 $\mu_B$, and high spin state, 4.9 $\mu_B$). It is clear that the experimental effective moments are close to the theoretical effective moments in which Mn$^{3+}$ is in the high spin state. Therefore, in this system, the spin state is very
stable, although higher distortion is induced and samples become highly compressed along the $c$ axis after Er$^{3+}$ doping.

![Figure 4.4-13 Curie-Weiss Law fitting of all samples](image)

**Table 2 Spin state calculation based on the Curie-Weiss Law fitting results**

<table>
<thead>
<tr>
<th>$x$</th>
<th>Curie constant</th>
<th>Experimental effective moment</th>
<th>Theoretical effective moment</th>
<th>Nd$^{3+}$</th>
<th>Er$^{3+}$</th>
<th>Mn$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Low spin state</td>
<td>High spin state</td>
<td></td>
<td>Low spin state</td>
<td>High spin state</td>
</tr>
<tr>
<td>0</td>
<td>5.00</td>
<td>6.00</td>
<td>4.59</td>
<td>6.09</td>
<td>3.62</td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>7.88</td>
<td>6.86</td>
<td>5.38</td>
<td>6.71</td>
<td>3.62</td>
<td>9.59</td>
</tr>
<tr>
<td>0.2</td>
<td>6.45</td>
<td>7.18</td>
<td>6.07</td>
<td>7.27</td>
<td>3.62</td>
<td>9.59</td>
</tr>
<tr>
<td>0.33</td>
<td>1.23</td>
<td>8.11</td>
<td>6.86</td>
<td>7.95</td>
<td>3.62</td>
<td>9.59</td>
</tr>
<tr>
<td>0.5</td>
<td>10.38</td>
<td>9.11</td>
<td>7.78</td>
<td>8.75</td>
<td>3.62</td>
<td>9.59</td>
</tr>
</tbody>
</table>

Hence, according to the changes discussed above, the proposed magnetic ordering of Mn$^{3+}$ with no applied magnetic field is presented in Figure 4.4-14, which shows the variation in the canted angle of Mn$^{3+}$ spins in the $ab$-plane. The canted angle increases as $x$ changes from 0 to 0.1, as can be seen in Figure 4.4-14(a) and (b), corresponding to the increasing remanent moment found in the sample with $x = 0.1$ compared with that with $x = 0$. Then, the angle decreases continuously with increasing $x$, as illustrated in Figure 4.4-14(c) and (d), which corresponds to the
decreasing remanent moment. In the sample with $x = 0.5$, the spins are arranged in collinear AFM, as illustrated in Figure 4.4-14(e), corresponding to the typical A-type AFM hysteresis loop shown in Figure 4.4-10.

![Diagram of magnetic ordering](image)

Figure 4.4-14 Proposed magnetic ordering of Mn$^{3+}$ sub-lattice at 0 T for (a) $x = 0$ at 55 K, (b-e) $x = 0.1, 0.2, 0.33$, and 0.5 at 30 K, respectively.

Low temperature magnetic hysteresis loops at 5 K are also presented in Figure 4.4-15. Clear ferromagnetic behaviour can be observed in samples with $x < 0.5$. When $x = 0.5$, the sample presents typical paramagnetic/antiferromagnetic properties, indicating that Nd$^{3+}$ ordering is absent above 5 K, and the ferromagnetic component of Mn$^{3+}$ ordering disappears, which is in accordance with the analysis of the M-T curve and M-H loop at 30 K.
Figure 4.4-15 Low temperature magnetic hysteresis loops at 5 K.

4.5 Conclusion

In conclusion, perovskite Nd$_{1-x}$Er$_x$MnO$_3$ compounds with magnetic rare earth ions have been studied based on structural and magnetic properties. Stronger distortion is induced after Er$^{3+}$ doping, which is responsible for the decreasing $T_N$. The intermediate state and the antiparallel arrangement between Nd$^{3+}$ FM ordering and Mn$^{3+}$ WFM ordering in NdMnO$_3$ are destroyed by Er$^{3+}$ doping. Meanwhile, the canted angles of Mn$^{3+}$ ordering vectors probably rotate and disappear with varying $x$. These results show that there are strong interactions between Nd$^{3+}$/Er$^{3+}$ and Mn$^{3+}$, and competition between Nd$^{3+}$ and Er$^{3+}$.

4.6 References


5 COMPETITION BETWEEN THE CRYSTAL FIELD AND THE EXCHANGE FIELD IN ER\textsuperscript{3+} DOPED NDMINO\textsubscript{3}

5.1 Abstract

The specific heat of Nd\textsubscript{1-x}Er\textsubscript{x}MnO\textsubscript{3} has been systematically studied. Anomalies of the magnetic entropy, contributed by the antiferromagnetic transition, and the spin wave stiffness coefficient are found in the sample with x = 0.1 due to a stronger ferromagnetic component, which is consistent with previous magnetic measurements and analysis. The careful investigation of specific heat in the low temperature range below 25 K shows that the ground state splitting of Nd\textsuperscript{3+} has been modified by the Er\textsuperscript{3+} doping, which shows a nonlinear dependence on the Er\textsuperscript{3+} doping rate, due to the competition between the crystal field and the exchange field. On the other hand, the ground state splitting of Er\textsuperscript{3+} has a linear dependence on the doping rate, which is attributed to the dominance of the crystal field over the exchange field. Hence, the competition between the crystal field and the exchange field must be considered for the low temperature study of rare earth ions when they are comparable in other similar systems. The spin wave coefficients decline linearly with increasing Er\textsuperscript{3+} doping content, except in the case of x = 0.1, in line with the weaker antiferromagnetic interaction.

5.2 Introduction

The pervoskite LaMnO\textsubscript{3} is a classic manganite, a good study subject and the object of great physical interest, in which the Jahn-Teller distortion and the orbital ordering play an critical role in determining the antiferromagnetic interaction.\textsuperscript{1} It shows typical A-type antiferromagnetism (AFM) at 140 K because of the orbital ordering.\textsuperscript{2} When divalent ions are doped into the La\textsuperscript{3+} sites, the manganese ions will be in the
forms of both Mn$^{3+}$ and Mn$^{4+}$, as in the La$_{1-x}$Ca$_x$MnO$_3$ system for example$^3$, allowing the magnetoresistance effect to occur.$^4$, $^5$ Current memory devices are mainly designed based on the giant magnetoresistance effect found in such materials. On the other hand, when the La$^{3+}$ site is totally replaced by other rare earth ions, unique physical properties can be observed. A-type AFM still exists in SmMnO$_3$, in which Sm$^{3+}$ has a smaller ionic radius than La$^{3+}$, but it is a canted A-type AFM with a weak ferromagnetic (FM) component.$^6$ The complex magnetic phase diagram and multiferroic properties have been well studied in DyMnO$_3$ and TbMnO$_3$.$^7$, $^8$ The inverse Dzyaloshinsky-Moriya (DM) interaction is employed to explain the improper ferroelectric polarization found in such spiral spin ordering systems.$^7$ When La$^{3+}$ is replaced by much smaller atoms, such as Er$^{3+}$, extremely strong distortion will be introduced, and the orthorhombic structure is no longer stable. This strong distortion favours the hexagonal structure, so that ErMnO$_3$ has a frustrated triangular spin arrangement on the Mn$^{3+}$ sublattice.$^9$, $^{10}$ It seems that the magnetic rare earth ions do not affect the antiferromagnetic interaction of the Mn$^{3+}$ sublattice too much beyond the distortion effect. On the contrary, the low temperature behaviour of magnetic rare earth ions is to some extent modified by the Mn$^{3+}$ ordering. When Gd$^{3+}$ with 4f electrons is introduced to replace La$^{3+}$ in LaMnO$_3$$^{11}$, the spin canting of Mn$^{3+}$ can polarize the 4f spins in Gd$^{3+}$. A similar interaction between magnetic rare earth ions and manganese ions is also reported in SmMnO$_3$.$^{12}$ It is found that the canted A-type antiferromagnetic ordering of Mn$^{3+}$ has a strong effect on Sm$^{3+}$ and induces a specific heat anomaly at low temperature, due to splitting of Sm$^{3+}$ ground state doublets in the exchange field, crystal field, and external magnetic field.$^{12}$ Systematic study of single crystal PrMnO$_3$ and NdMnO$_3$ have also indicated that the isotropic and anisotropic exchange fields play a critical role in determining the
splitting of rare earth ground states. The Pr\(^{3+}\) ground state splitting is dominated by the crystal field due to the absence of a ferromagnetic component, while the Nd\(^{3+}\) ground state splitting is dominated by the exchange field.\(^\text{13}\) Therefore, the low temperature behaviour of magnetic rare earth ions is strongly dependent on the exchange field. At the same time, the exchange field and the crystal field may compete or cooperate with each other. To elucidate this complex behaviour, we studied the specific heat in the Nd\(_{1-x}\)Er\(_x\)MnO\(_3\) system. Considering that the Er\(^{3+}\) ion size is a little smaller than that of Nd\(^{3+}\), the crystal field could be modified slightly by Er\(^{3+}\) doping. In addition, our previous work shows that the interaction between Nd\(^{3+}\) and Mn\(^{3+}\) is significantly disturbed by Er\(^{3+}\) doping, and the canted angle of Mn\(^{3+}\) antiferromagnetic ordering is also consequently modified, which indicates variation in the exchange field. In this case, this is an ideal system to study the relationship between the crystal field and the exchange field. The results show that the Nd\(^{3+}\) ground state splitting energy shows a nonlinear dependence on the Er\(^{3+}\) doping rate, while the Mn\(^{3+}\) spin wave stiffness coefficient obeys a linear dependence with a negative slope. The splitting energies of the Nd\(^{3+}\) ground state first decrease and then increase when the doping rate is as high as 50%. The nonlinear relationship is well fitted by a parabolic profile, which suggests that the crystal field and exchange field compete with each other. On the other hand, a linear relation is found in the Er\(^{3+}\) doping rate dependent ground state splitting of Er\(^{3+}\), and this behaviour is likely to be due to the dominance of the crystal field over the exchange field. The differences between Nd\(^{3+}\) and Er\(^{3+}\) ground state splitting indicate that the competition between the crystal field and the exchange field must be considered for the low temperature behaviour of magnetic rare earth ions when the exchange interaction between rare
earth ions and Mn$^{3+}$ ions is strong and comparable to that of the crystal field in other similar systems.

### 5.3 Experimental

Polycrystalline samples of Nd$_{1-x}$Er$_x$MnO$_3$ (x = 0, 0.1, 0.2, 0.33, 0.5) were made by the traditional solid state reaction method, with Nd$_2$O$_3$ (99.9%), Er$_2$O$_3$ (99.9%), and MnCO$_3$ (99.9%) powder bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, followed by pressing into pellets 15 mm in diameter at 20 MPa. Samples were calcined at 950 °C for 10 hours and sintered at 1450 °C for 48 hours. The specific heat was measured using the thermal relaxation technique with a 14 T physical properties measurement system (PPMS).

### 5.4 Results and Discussion

#### 5.4.1 Specific heat around antiferromagnetic transition

Specific heat measurements were conducted from 2 K to certain temperatures above the magnetic transition temperature. The temperature dependence of $C_p/T$ for samples with $x \leq 0.5$ is presented in Figure 5.4-1.
Figure 5.4-1 Temperature dependence of $C_p/T$ for Nd$_{1-x}$Er$_x$MnO$_3$ for $x = 0$, 0.1, 0.2, 0.33, and 0.5.

The peak at higher temperature is assigned to the AFM ordering of Mn$^{3+}$. To calculate the magnetic contribution to the antiferromagnetic transition, a third order polynomial background is subtracted from the experimental data to exclude the contribution from phonons and electrons. A fitting example is presented in Figure 5.4-2(a) for the sample with $x = 0$, and the residual magnetic contributions of all samples are shown in Figure 5.4-2(b).
Figure 5.4-2 (a) Phonon and electron contribution to specific heat (small red dotted line) is subtracted from experimental data (big blue dotted line) for the sample with x = 0; (b) temperature dependence of the residual magnetic contributions to the antiferromagnetic transitions for all samples; (c) temperature dependence of integrated magnetic entropy for all samples calculated from (b).

It is obvious that the specific heat peaks shift to lower temperature when x increases, which agrees with the temperature downshift identified by the sudden increase in the field cooling (FC) temperature dependence of the magnetic moment. The downshift in the transition temperature is the result of an enhanced Jahn-Teller effect, which has been discussed in connection with many rare earth manganites. The magnetic entropy of magnetic ordering is shown in Figure 5.4-2(c), calculated in the form of

\[ \Delta S_{Mag} = \int_{T_1}^{T_2} \frac{\Delta C_P}{T} dT. \]  

\[ (1) \]
The magnetic entropy decreases slightly when \( x \) varies from 0 to 0.2 to 0.33. The sample with \( x = 0.1 \) has the biggest magnetic entropy compared with the others, nearly twice the magnetic entropy of the sample with \( x = 0.33 \). This obviously different entropy change is in accordance with the significantly different bond length and bond angle in the sample with \( x = 0.1 \).\(^{14}\) The sample with \( x = 0.5 \) shows the smallest magnetic entropy, no more than half of the entropy in the sample with \( x = 0.33 \), probably due to the different magnetic ordering or the disappearance of the ferromagnetic component, which is also in accordance with the relatively big change in the bond length and the bond angle in-plane.\(^{14}\) Otherwise, the coincidence between the magnetic entropy abnormality and the structural change suggests that the magnetic transition may accompany structural change, which has been observed in other materials.\(^{16}\)

5.4.2 Specific heat in the low temperature range

![Energy level and ground state splitting scheme](image)

Figure 5.4-3 Energy level and ground state splitting scheme of (a) Nd\(^{3+}\) \( ^4I_{9/2} \) and (b) Er\(^{3+}\) \( ^4I_{15/2} \).
Below 25 K, there is another \( \lambda \)-shaped peak ascribed to the Schottky anomaly from the ground state doublet splitting of \( \text{Nd}^{3+} \) and/or \( \text{Er}^{3+} \). The energy splitting scheme is presented in Figure 5.4-3, which is plotted based on previous works.\(^{17-19}\) For \( \text{NdMnO}_3 \), the long range ordering temperature of \( \text{Nd}^{3+} \) is around 13 K according to the reported result\(^{14,20}\), which seems to contribute to the specific heat. However, short range ordering of \( \text{Nd}^{3+} \) is also found to exist above 13 K due to the strong \( \text{Nd}^{3+}-\text{Mn}^{3+} \) interaction\(^{14,21}\), similar to the case of \( \text{SmMnO}_3 \).\(^{12}\) In \( \text{NdNiO}_3 \)\(^{19}\) and \( \text{SmMnO}_3 \)\(^{12}\), the low temperature shoulders of the specific heat are both supposed to be related to the Schottky anomaly. According to the specific heat study on \( \text{Nd}_{0.67}\text{Sr}_{0.33}\text{MnO}_3 \), the entropy from the Schottky anomaly is only \( \sim 85\% \) of the expected entropy of normal \( \text{Nd}^{3+} \) ordering, suggesting an effective molecular-field mechanism because of the much stronger \( \text{Nd}^{3+}-\text{Mn}^{3+} \) interaction compared to the \( \text{Nd}^{3+}-\text{Nd}^{3+} \) interaction.\(^{22}\) On the other hand, in \( \text{ErMnO}_3 \) and \( \text{YMnO}_3 \), the small shoulder peaks at low temperature are also only attributed to the intrinsic \( \text{Mn}^{3+} \) ordering, but they are modified by the interaction between \( \text{Er}^{3+}/\text{Y}^{3+} \) and \( \text{Mn}^{3+} \) to some extent.\(^{23}\) Hence, it is reasonable to assign the peaks of specific heat at low temperature mainly to the Schottky anomaly in \( \text{Nd}_{1-x}\text{Er}_x\text{MnO}_3 \). At the same time, there is also a magnetic contribution from \( \text{Mn}^{3+} \) ordering. After doping with \( \text{Er}^{3+} \), the shoulders shift toward lower temperature, indicating change in the exchange field or interaction between rare earth ions and transition metal ions. To clarify the contribution from the Schottky anomaly and magnetic ordering, specific heat fitting was carried out. Generally, the total specific heat is made up of four distinct contributions: lattice, electron, hyperfine, and magnetic ordering, which can be described as below:

\[
C = C_{\text{lat}} + C_{\text{elec}} + C_{\text{hyp}} + C_{\text{mag}}. \tag{2}
\]
The lattice contribution can be written as $C_{\text{lat}} = \beta_3 T^3 + \beta_5 T^5$. In most cases, the contribution of $\beta_5 T^5$ is not considered, as it is too small. For a typical antiferromagnetic insulating material, the conductive electron contribution, $C_{\text{elec}} = \gamma T$, can be ignored.\textsuperscript{12} Likewise, the hyperfine contribution, $C_{\text{hyp}} = \alpha T^2$, is very small above 2 K and can also be ignored.\textsuperscript{22} LaMnO$_3$ is known as a typical A-type antiferromagnet, and the spin wave excitations could lead to an extra contribution to specific heat and give a $T^2$ term.\textsuperscript{24} The contribution can also be understood to originate from the ferromagnetic and antiferromagnetic spin fluctuations.\textsuperscript{25}

According to the report of Woodfield et al., an A-type antiferromagnetic spin wave excitation will contributed to specific heat in the form of $C_{\text{mag}} = 0.058k_B^3 T^2 / DpDz$, where $DpDz$ is the spin wave stiffness coefficient.\textsuperscript{24} In our study, this $T^2$ term contribution should be considered because Nd$_{1-x}$Er$_x$MnO$_3$ is also an A-type antiferromagnetic system. Therefore, the specific heat can be written in a simple way

$$C = C_{\text{lat}} + C_{\text{mag}}. \quad (3)$$

Considering the Schottky anomaly at low temperature, the final specific heat should be in the form of

$$C = C_{\text{lat}} + C_{\text{mag}} + C_{\text{Sch}}. \quad (4)$$

The Schottky anomaly comes from the ground state splitting of the rare earth ions Nd$^{3+}$ and/or Er$^{3+}$, and the corresponding specific heat contribution follows the expression:

$$C_{\text{Sch}} = R* (E/k_B T)^2 * \exp(E/k_B T) / [1 + \exp(E/k_B T)]^2,$$ \quad (5)

where $R$ is the ideal gas constant, $E$ is the splitting energy of ground state doublets, and $k_B$ is the Boltzmann constant.
Figure 5.4-4 (a) Low temperature specific heat fitting for sample with $x = 0$ (red dots: experimental data; solid black line: fitting result; green dashed dotted line: spin wave and lattice contribution; red dashed line: Schottky anomaly from ground state splitting of rare earth Nd$^{3+}$ ions); (b) low temperature specific heat fitting for sample with $x = 0.2$ (red dots: experimental data; solid black line: fitting result; blue dashed dotted line: spin wave and lattice contribution; red dashed dotted line: Schottky
anomaly from ground state splitting of rare earth Nd$^{3+}$ ions; green dotted line: Schottky anomaly from ground state splitting of rare earth Er$^{3+}$ ions).

Figure 5.4-4 presents the fitting results of representative samples with $x = 0$ and 0.2. The fitting curves well match the experimental data, which is indicative of good fitting quality. The fitting results for other samples are displayed in Figure 5.4-5.

It is found that the lattice and spin wave dominate the contributions to the specific heat at relatively higher temperatures. However, the Schottky anomaly plays a more important role at low temperature, especially below 15 K. The Nd$^{3+}$ ground state splitting of the sample with $x = 0$ is found to be $27.8 \, k_B$, which is close to the Nd$^{3+}$ ground state splitting energy of $27.15 \, k_B$ in powder NdCrO$_3$. However, this splitting is bigger than that found in single crystal NdMnO$_3$, in which the splitting is about $20 \, k_B$. The difference is probably due to the size effect. The grain size of the single crystal is much larger than that of a powder or polycrystalline sample. This sort of size effect has also been observed in Yb$_2$Ti$_2$O$_7$ and Gd$^{3+}$ doped SrCl$_2$, and can affect the crystal field. A sharp specific heat anomaly is found at low temperature in powder Yb$_2$Ti$_2$O$_7$, but this anomaly is not observed in the single crystal sample.

An electron paramagnetic resonant investigation of SrCl$_2$: Gd$^{3+}$ showed that the spectrum of Gd$^{3+}$ in small particle form is significantly different from those for the single crystal and large grain samples, suggesting change in the crystal field. The splitting of the Nd$^{3+}$ ground state doublets decreases to $23.25 \, k_B$ when $x$ is 0.2, and to $26.1 \, k_B$ when $x$ is 0.5.
Figure 5.4-5 Low temperature specific heat fitting for samples with $x = 0.1$, $0.33$ and $0.5$ (red dots: experimental data; solid black line: fitting result; blue dashed dotted line: spin wave and lattice contribution; red dashed dotted line: Schottky anomaly.
from ground state splitting of rare earth Nd\(^{3+}\) ions; green dotted line: Schottky anomaly from ground state splitting of rare earth Er\(^{3+}\) ions).

The doping rate dependence of the Nd\(^{3+}\) ground state splitting energy, \(E_1\), is plotted in Figure 5.4-6, where it shows nonlinear behaviour. It is clear that the splitting energies are reduced after doping, which suggests a weaker molecular field or a weaker Nd\(^{3+}\)-Mn\(^{3+}\) interaction, even if the distance between Nd\(^{3+}\) and Mn\(^{3+}\) ions becomes shorter.\(^{14}\) We tentatively use a parabolic profile to fit the splitting energy curve, except for the data point of the sample with \(x = 0.1\) in Figure 5.4-6, and get an empirical formula

\[
E_1 = 28 - 44.4x + 79.8x^2
\]  

(6)

\[
\begin{array}{c|c|c|c|c|c|c}
  x & 0.0 & 0.1 & 0.2 & 0.3 & 0.4 & 0.5 \\
  \hline
  E_1/k_B (K) & 30 & 28 & 26 & 24 & 26 & 30 \\
\end{array}
\]

Figure 5.4-6 Doping rate dependence of the energy gap between two splitting Nd\(^{3+}\) ground states (\(E_1\)).

For the sample with \(x = 0.1\), the anomalous splitting possibly stems from the significant lattice change compared with \(x = 0.2\) and 0.33. The spontaneous stress also shows an anomaly at \(x = 0.1\),\(^{14}\) which further confirms this assumption. On the
contrary, the enhanced ferromagnetic component of the Mn\(^{3+}\) sublattice in the sample with x = 0.1 fails to induce stronger Nd\(^{3+}\) ground state doublet splitting, which is probably due to the effect of the competition between the lattice anomaly and the molecular field provided by the Mn\(^{3+}\) sublattice. After doping with Er\(^{3+}\), the static Jahn-Teller distortion becomes stronger, which could induce a change in the crystal field. Meanwhile, the interaction between Nd\(^{3+}\) and Mn\(^{3+}\) ions is significantly disturbed, and the molecular field is consequently reduced. These two factors determine the nonlinear behaviour of the doping rate dependence of the splitting energies. The parabolic behaviour suggests that there is strong competition between the molecular field and the crystal field.

Figure 5.4-7 Doping rate dependence of the energy gap between two splitting Er\(^{3+}\) ground states (E\(_2\)).

As for Er\(^{3+}\), the ground state doublet splitting energies shown as E\(_2\) in Figure 5.4-7 are all quite close, around 10 \(k_B\). One of possible factors is that the Schottky anomaly
of Er\(^{3+}\) may be much less sensitive to the competitive or cooperative effects of the crystal field and the molecular field. A linear relation can be found

\[ E_2 = 8.5 + 4.5x \]  

(7)

Considering the competition behaviour between the molecular field and the crystal field found at the Nd\(^{3+}\) sites and assuming that a very similar crystal field applies to the Er\(^{3+}\), this linear behaviour is then mainly dominated by a possible linear change in the crystal field rather than the molecular field. In this case, the interaction between Er\(^{3+}\) and Mn\(^{3+}\) should be much weaker compared with that between Nd\(^{3+}\) and Mn\(^{3+}\). On the other hand, if the interaction between Er\(^{3+}\) and Mn\(^{3+}\) is comparable to that between Nd\(^{3+}\) and Mn\(^{3+}\) or even stronger, then the linear behaviour may suggest that the crystal field should be stronger on Er\(^{3+}\) than on Nd\(^{3+}\). In this case, the crystal field difference suggests that the Nd\(^{3+}\) and Er\(^{3+}\) ions could be interacting with each other, considering that only the same crystal field is offered by the Mn\(^{3+}\) sublattice. Further study is required to elucidate this complex mechanism.

The spin wave stiffness coefficients at low temperature were also obtained and the results are presented in Figure 5.4-8. Apart from the sample with x = 0.1, the spin wave contributions of the other four samples follow a linear dependence on the doping rate with a negative slope. This behaviour can be fitted by an empirical formula

\[ DpDz = (-4.23x+4.10)k_B^3 \]  

(8)

The weakening behaviour of the spin wave coefficient with increasing Er doping is due to the weaker antiferromagnetic interaction of the Mn\(^{3+}\) sublattice, which is consistent with the decreasing transition temperatures confirmed by the results given in Figure 5.4-1 and Figure 5.4-2(b). In addition, the weakening behaviour of the spin
wave coefficient is also in line with the weaker ground state doublet splitting of Nd$^{3+}$. The anomaly in the spin wave stiffness coefficient for the sample with $x = 0.1$ is probably due to an enhanced ferromagnetic component induced by the Dzyaloshinsky-Moriya interaction. This anomaly is also the consequent result of the anomaly found in the magnetic entropy at $x = 0.1$.

![Graph](image)

Figure 5.4-8 Doping rate dependence of spin wave stiffness coefficient.

### 5.5 Conclusion

The specific heat of the Er$^{3+}$ doped rare earth manganate NdMnO$_3$ has been systematically studied. There are two clear bumps in the temperature dependence of the specific heat: one is associated with the antiferromagnetic transition of the Mn$^{3+}$ sublattice, and the other is due to the Schottky anomaly because of the Nd$^{3+}$/Er$^{3+}$ ground state doublet splitting. The magnetic entropy of the sample with $x = 0.1$ around the antiferromagnetic transition is found to be much higher than for the others, and the spin wave stiffness coefficient is also stronger than for the others, which is likely to be due to the enhanced ferromagnetic component. The magnetic
entropy around the magnetic transition decreases as the doping rate increases, except for the case of $x = 0.1$. The ground state splitting energies show a nonlinear dependence on the doping rate except for the case of $x = 0.1$. Both the molecular exchange field from the Mn$^{3+}$ sublattice and variations in the crystal field are responsible for the ground state doublet splitting, and the effect of their competition decides the nonlinear behaviour of the doping rate dependent Nd$^{3+}$ ground state splitting. The Er$^{3+}$ ground state splitting energy is linearly dependent on the doping rate, which is due to the dominance of the crystal field over the exchange field. The spin wave stiffness coefficient can be well fitted by a linear profile with a negative slope, except for the case of $x = 0.1$. These results provide a quasi-quantitative analysis to determine the relationship between the crystal field and the exchange field, and its effect on magnetic rare earth ions.

5.6 References


6 EXCHANGE BIAS EFFECT IN RARE EARTH AND TRANSITION METAL COMPOUNDS

6.1 Positive and Negative Exchange Bias Effects in the Simple Perovskite Manganite NdMnO₃

6.1.1 Abstract

Exchange bias effects were studied in the simple perovskite NdMnO₃. Nd³⁺ ordering is induced by the Mn³⁺ ferromagnetic component, and they are antiferromagnetically coupled with each other. At 30 K, both negative and positive exchange bias effects are found, which are dependent on the cooling field. The exchange bias fields are around -2400Oe and 1800Oe, respectively. Positive and negative exchange bias effects were also observed at 8 K, but the exchange bias fields are only 130Oe and -120Oe. The coupling intensity between Nd³⁺ ordering and Mn³⁺ ordering, and their initial states determine the polarity of the exchange bias fields.

6.1.2 Introduction

The exchange bias effect usually occurs in ferromagnetic and antiferromagnetic bilayers or multilayers. In such a system, the two coercive fields of the magnetic hysteresis loop are not symmetric, and the centre of the magnetic hysteresis loop shifts to the left or right. A representative system is Co-CoO,¹,² where Co is ferromagnetic and CoO is antiferromagnetic. In this system, exchange bias occurs at the interface between these two different magnetic materials, and the maximum exchange bias field in this system is 9500 Oe.³ In a similar system, Fe-Fe₃O₄,⁴,⁵ the exchange bias field is about 120 Oe, much smaller than that in Co-CoO. Materials with exchange bias effects are widely used in magnetic recording devices.³,⁶ In
recent years, the exchange bias effect has been found in heterostructures and artificial interfaces, in which the exchange bias effect can be adjustable. In the Co$_{0.9}$Fe$_{0.1}$/BiFeO$_3$ system, the intensity of the exchange bias interaction is found to be dependent on the properties of the ferroelectric domain walls in the BiFeO$_3$ layer$^7$, which sheds light on how to control the exchange bias effect by an external electric field$^8$. A similar study was also reported on the Co/BiFeO$_3$ system$^9$ and the BiFeO$_3$/YMnO$_3$ system$^{10}$. Interface interaction may induce unique properties and change the magnetic properties of bulk materials, as in a systematic study of the exchange bias effect that was carried out on LaNiO$_3$-LaMnO$_3$ superlattices.$^{11}$ On the other hand, the exchange bias effect can also exist in compounds or composites which allow the coexistence of both a ferromagnetic component and an antiferromagnetic component. Recently, the exchange bias effect was intensively studied in La$_{1-x}$Pr$_x$CrO$_3$ and Sr$_2$YbRuO$_6$, in which both positive and negative exchange bias effects can be observed and are dependent on the cooling field and temperature.$^{12, 13}$ In these two compounds, the exchange bias effect is different from what appears in bilayer and other interface structures. The coupling between the Pr$^{3+}$ magnetic rare earth ions and the Cr$^{3+}$ transition metal ions at different atomic sites in the ABO$_3$ structure determines the properties of the exchange bias effect in La$_{1-x}$Pr$_x$CrO$_3$.$^{12}$ In Sr$_2$YbRuO$_6$, however, the exchange bias effect originates from the Dzyaloshinsky–Moria interaction induced ferromagnetic component and from the antiferromagnetic coupling between the magnetic rare earth ion Yb$^{3+}$ and the transition metal ion Ru$^{3+}$, which are in the same atomic site in the ABO$_3$ structure. Therefore, it is likely that the exchange bias effect may be observed in some other similar systems. To explore new materials with exchange bias based on this idea, we have chosen to study the simple perovskite manganite NdMnO$_3$, considering that the
Nd$^{3+}$ spins enter into ferromagnetic ordering, while Mn$^{3+}$ is in the antiferromagnetic state at low temperature. Our results show that both a positive and a negative exchange bias effect can be observed for different magnetic states. The cooling field can affect the exchange bias field and change the polarity of the exchange bias effects. A simple scheme is proposed to explain these unique exchange bias effects.

6.1.3 Experimental

Polycrystalline samples of NdMnO$_3$ were made by the traditional solid state reaction method from Nd$_2$O$_3$ (99.9%) and MnCO$_3$ (99.9%) powders bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, followed by pressing into pellets 15 mm in diameter at 20 MPa. Samples were calcined at 950 °C for 10 hours and sintered at 1450 °C for 48 hours. The crystal structures of the samples were examined by X-ray diffraction at room temperature (XRD, model: GBC MMA), using Cu K$_\alpha$ radiation at $\lambda = 1.54056$ Å. The Rietveld refinement calculations were conducted via FULLPROF software. The magnetic measurements were carried out using a 5 T magnetic property measurement system (MPMS) and a 14 T physical property measurement system (PPMS), equipped with a vibrating sample magnetometer (VSM), over a wide temperature range from 5 to 300 K.

6.1.4 Results and discussion

The results of structural characterization of the sample by XRD are given in Figure 6.1-1. We employed Rietveld analysis to refine the diffraction patterns. The quality of the refinement is expressed by the refinement parameter $\chi^2 = 2.4$. All XRD peaks can be assigned to the single phase orthorhombic structure with space group $Pnma$. 
and no detectable impurity phase is present. The lattice parameters are $a = 5.7524$ Å, $b = 7.5623$ Å, and $c = 5.4068$ Å, respectively.

Figure 6.1-1 XRD Rietveld refinement results for NdMnO$_3$, with $\chi^2 = 2.4$ (star symbols, experimental data, and solid red line, fitted pattern from Rietveld structural refinement, respectively). The mismatch between the measured and Rietveld refined spectra is plotted with a slight downshift for clarity. The short vertical solid lines are guides for the eyes to mark the corresponding Bragg positions.
Figure 6.1-2 (a) Zero field cooling and 5000 Oe field cooling temperature dependence of magnetic moment; (b) Curie-Weiss law fitting for spin state calculation.

The temperature dependence of the magnetic moment was measured under both zero field cooling (ZFC) and 5000 Oe field cooling (FC) conditions in warming up mode, and the results are given in Figure 6.1-2(a). A clear peak can be identified in the ZFC
curve around 13 K, which is assigned to the occurrence of the Nd$^{3+}$ long-range ordering. This result is consistent with the neutron diffraction results. When the temperature increases, there is a sudden decrease in the ZFC moment, due to the dropping out of the Nd$^{3+}$ long-range ordering. The bump starting at around 79 K (shown by the black arrow) is ascribed to the Mn$^{3+}$ magnetic ordering. The Curie-Weiss law fitting over the interval from 150 K to 300 K, as shown in Figure 6.1-2(b), gives a positive Curie temperature of about 50 K, indicating that there is relatively strong ferromagnetic interaction in the Mn$^{3+}$ sublattice. It is also true that we observe an increasing moment below 79 K, which suggests ferromagnetic behaviour. Meanwhile, the Curie-Weiss law fitting also gives a total effective moment of about 6.0 µB. If we calculate the theoretical moment, the high spin state will produce an effective moment of about 6.09 µB, while the low spin state will produce an effective moment of about 4.59 µB (Mn$^{3+}$: 2.828 µB/atom in the low spin state and 4.9 µB/atom in the high spin state; Nd$^{3+}$: 3.62 µB/atom). The close agreement between the experimental effective moment and the theoretical moment in the high spin state indicates that the Mn$^{3+}$ is in the high spin state. This high spin state determines the relatively strong trend towards antiferromagnetic interaction among the Mn$^{3+}$ ions, because the Mn$^{3+}$ 3$d$ orbital has four electrons. Neutron studies also confirm the antiferromagnetic property of Mn$^{3+}$ ordering. Similar to the case of LaMnO$_3$, it was reported that the Mn$^{3+}$ ordering in NdMnO$_3$ is also A-type antiferromagnetic ordering. In this case, the ferromagnetic component should originate from the canted A-type antiferromagnetic spin arrangement. The FC moment is negative at low temperature and reaches its maximum value at 13 K. This abnormal phenomenon indicates that the Nd$^{3+}$ ordering is antiferromagnetically coupled with the Mn$^{3+}$ ferromagnetic component. A higher measuring field, such as 5 T, can force
the Nd$^{3+}$ spins to flip below 13 K and give a positive total moment (not shown), which follows the trend of a common ZFC and FC temperature dependence of the magnetic moment. Our previous work has claimed that short-range Nd$^{3+}$ ordering still exists above 13 K.$^{15}$ This means that the Nd$^{3+}$ ordering is induced by the strong Mn$^{3+}$ ferromagnetic component, which is similar to the case of SmMnO$_3$.$^{16}$ This phenomenon can also be confirmed by the magnetic hysteresis loops in Figure 6.1-3, which will be discussed later. Therefore, in NdMnO$_3$, ferromagnetic ordering and antiferromagnetic ordering coexist, and they are coupled with each other. Exchange bias may occur in such a system.

To study the possible exchange bias effect, we measured the magnetic hysteresis loops when the Nd$^{3+}$ was in the short-range ordering state at 30 K and in the long-range ordering state at 8 K. The magnetic hysteresis loops at 30 K and 8 K are presented in Figure 6.1-3 and Figure 6.1-4, respectively. Figure 6.1-3 shows the cooling field dependence of the magnetic hysteresis loop at 30 K, after the sample was cooled down from 150 K (which is much higher than the Mn$^{3+}$ ordering temperature) to 30 K in various positive cooling fields. The measuring fields range from -3 T to 3 T, in which Nd$^{3+}$ spins will remain relatively still, while the Mn$^{3+}$ spins will easily follow the external field (as will be discussed later). When the sample is cooled down to 30 K without magnetic field, a nearly symmetric hysteresis loop is obtained, and no obvious exchange bias effect is presented, because of the disordered nature of the ferromagnetic-like initial domain state, as shown in Figure 6.1-3(a).
Figure 6.1-3 (a-d) Magnetic hysteresis loop measured at 30 K while the Nd$^{3+}$ is in the short range ordering state after cooling down from 150 K in various positive cooling fields: 0 T, 2 T, 5 T, and 10 T, respectively.

However, a significant negative exchange bias effect is observed when the cooling field is 2 T, with the exchange bias field reaching about -2400 Oe, as shown in Figure 6.1-3 (b). The negative exchange bias effect will become weaker when the cooling field increases to 5 T, at which there is only a shift of about -340 Oe, as shown in Figure 6.1-3 (c). On the contrary, a significant positive exchange bias effect occurs when the cooling field is 10 T, at which the exchange bias field is about 1800 Oe, as shown Figure 6.1-3 (d). The cooling field dependence of the exchange bias field at 30 K is presented in Figure 6.1-5(a).
Figure 6.1-4 (a-d) Magnetic hysteresis loop measured at 8 K, at which temperature the Nd$^{3+}$ is in the long-range ordering state after cooling down from 150 K in various positive cooling fields: 0 T, 2 T, 5 T, and 10 T, respectively.

On the other hand, Figure 6.4 presents the cooling field dependence of the magnetic hysteresis loop at 8 K. When the sample is cooled down from 150 K to 8 K in the zero field, below the Nd$^{3+}$ ordering temperature, no obvious shift can be observed, as shown in Figure 6.1-4 (a). However, a positive exchange bias effect can be observed in a 2 T cooling field, and the exchange bias field is about 130 Oe, as shown in Figure 6.1-4 (b). Because of the strong Nd$^{3+}$ ferromagnetic contribution at 8 K, the coercive fields are very strong, and the shift is not as significant as that measured above the Nd$^{3+}$ ordering temperature. When the cooling field increases to 5 T, a negative exchange bias effect occurs with an exchange bias field of about -70 Oe, as shown in Figure 6.1-4 (c). When the cooling field further increases to 10 T, the exchange bias field reaches -120 Oe, as shown in Figure 6.1-4 (d). The cooling field dependence of the exchange bias field at 8 K is presented in Figure 6.1-5 (b).
We also measured the exchange bias effect in the vicinity of the Nd$^{3+}$ ferromagnetic ordering temperature at 13 K and found that only a very weak exchange bias effect occurs, which can be neglected (not shown). In this case, the exchange bias effect is strongly dependent on the coupling intensity between the Nd$^{3+}$ ordering and the Mn$^{3+}$ ordering, and on the initial states as well.

Figure 6.1-5 (a) Cooling field dependence of the exchange bias field at 30 K (red solid circles); (b) cooling field dependence at 8 K (pink triangles).
Figure 6.1-6 (a) Scheme of the spin arrangement when Nd\(^{3+}\) is in the short-range ordering state at 30 K; (b) scheme of the spin arrangement when Nd\(^{3+}\) is in the long-range ordering state at 8 K.

The positive and negative exchange bias effects take place in different magnetic states, which indicates that their mechanisms may be different. First of all, we discuss the case of the negative exchange bias observed at 30 K. When the Nd\(^{3+}\) is in the short-range ordering state, local ferromagnetic spin arrangements could form, as shown in Figure 6.1-6, which are not strictly antiferromagnetically coupled with the ferromagnetic component of Mn\(^{3+}\). When the sample is cooled down in a relatively low cooling field, which doesn’t exceed the exchange field (~6 T, which can be obtained from Figure 6.1-5(a)) between Mn\(^{3+}\) and Nd\(^{3+}\), the spin arrangement between Mn\(^{3+}\) and Nd\(^{3+}\) spins doesn’t change too much, so that the Mn\(^{3+}\) spins will be aligned along the cooling field, and the Mn\(^{3+}\) and Nd\(^{3+}\) ions still tend to couple with each other antiferromagnetically. A positive measuring field will favour this Nd\(^{3+}\)/Mn\(^{3+}\) antiferromagnetically coupled state if the maximum field is much smaller than the exchange field. When an opposite measuring field (compared with that of
the Mn$^{3+}$ ferromagnetic component is applied, the Mn$^{3+}$ ferromagnetic component becomes unstable and begins to break free, which weakens the exchange interaction between Mn$^{3+}$ and Nd$^{3+}$. In this case, the antiferromagnetic exchange field is not ~6 T any longer, but begins to decrease, which further favours the switching of Mn$^{3+}$ spins. During this process, the Nd$^{3+}$ spins remain relatively still and offer a strong pinning force, while the Mn$^{3+}$ spins follow the measuring field. Once Mn$^{3+}$ spins are aligned along the negative measuring field, the Mn$^{3+}$ and Nd$^{3+}$ spins are ferromagnetically coupled, which is a metastable state with a ferromagnetic exchange field and could be favoured by the negative measuring field. The Nd$^{3+}$/Mn$^{3+}$ antiferromagnetically coupled state, however, is more stable in terms of energy than the ferromagnetically coupled state. Therefore, it is much easier for the measuring field to achieve the antiferromagnetically coupled state than to achieve the ferromagnetically coupled state. Consequently, the negative exchange bias effect can be observed. When the cooling field is higher than the exchange field, both Nd$^{3+}$ and Mn$^{3+}$ ions will be aligned along the external field, and run in the same direction. The positive measuring field favours this metastable Nd$^{3+}$/Mn$^{3+}$ ferromagnetically coupled state, but it is easy to go back to the more stable antiferromagnetically coupled state once the measuring field changes from positive to negative. A positive exchange bias can then be observed. As illustrated in Figure 6.1-6(a), a low positive cooling field could give a negative exchange bias effect because the Nd$^{3+}$ spins are always opposite to the direction of the cooling field; when the positive cooling field is very high, high enough to align both the Nd$^{3+}$ spins and the Mn$^{3+}$ spins, then a positive exchange bias effect occurs, because the Nd$^{3+}$ spins are always along the direction of the cooling field. When the cooling field is moderate, the Nd$^{3+}$ spin arrangement will be disturbed, and the ions are unable to order along the same
direction any more, but enter into a disorder-like state. In that case, the total pinning force will decrease, and the previous significant negative exchange bias effect will be suppressed.

On the other hand, when Nd$^{3+}$ is in the long-range ordering state at 8 K, as shown in Figure 6.1-6(b), a strong ferromagnetic spin arrangement is present, which could always antiferromagnetically couple with the ferromagnetic component of the Mn$^{3+}$ ordering, considering that the exchange field is about 10 T.$^{17}$ Then, the Nd$^{3+}$ and Mn$^{3+}$ spin system can be simply regarded as a ferromagnetic or ferrimagnetic state at 8 K, and we could also only consider the contribution from Nd$^{3+}$ spins because their moments are much larger than those of the Mn$^{3+}$ spins. Therefore, when the sample is cooled down from high temperature in an external magnetic field, the ferromagnetic component of the Mn$^{3+}$ ordering will be in the direction of the external field above the Nd$^{3+}$ ordering temperature. Below the Nd$^{3+}$ ordering temperature, the Mn$^{3+}$ ions are still aligned along the external cooling field, if it is not high enough to flip all the Nd$^{3+}$ spins. Normally, the cooling field should be no more than ~1 T, which is the coercive field of Nd$^{3+}$ spins, as illustrated in Figure 6.1-4. In this case, negative Nd$^{3+}$ domains have formed before we measure the hysteresis loop. If the cooling field is higher than ~1 T, but lower than the field which could switch all the negative domains, then there are still minority negative domains which could offer a pinning force to prevent the switching of majority domains, as illustrated in Figure 6.1-6 (b). Consequently, the negative domain state is easier to achieve than the positive domain state, and a positive exchange bias effect occurs. If the cooling field is high enough to flip the Nd$^{3+}$ below 13 K or above 13 K, positive domains will form before we measure the hysteresis loop, and then the positive domain state is easier to achieve, and a negative exchange bias effect occurs. Therefore, the
exchange bias effects at 8 K stem from domain-domain interaction, which could be suppressed by a very high measuring field.\textsuperscript{18, 19}

6.1.5 Conclusion

In summary, positive and negative exchange bias effects in the simple perovskite manganite NdMnO\textsubscript{3} were studied. The temperature dependence of the magnetic moment reveals that Mn\textsuperscript{3+} has canted A-type antiferromagnetic ordering below 79 K. On the other hand, Nd\textsuperscript{3+} shows long-range ferromagnetic ordering below 13 K and short-range ordering below the Mn\textsuperscript{3+} ordering temperature. The ferromagnetic component of the Mn\textsuperscript{3+} sublattice is antiferromagnetically coupled with the ferromagnetic ordering of the Nd\textsuperscript{3+} sublattice, which provides the possibility for the exchange bias effect to occur. Systematic magnetic hysteresis loop measurements have confirmed the exchange bias effect. At 30 K, Nd\textsuperscript{3+} is in the short-range ordering state, so a significant negative exchange bias effect occurs when the cooling field is relatively small, reaching -2500 Oe when the cooling field is 1 T. Meanwhile, a positive exchange bias can also be achieved by using a big cooling field such as 10 T, in which the exchange bias field reaches 1800 Oe. In addition, a negative cooling field can also switch the negative exchange bias effect to the positive exchange effect, with almost same absolute values of the exchange bias fields. On the other hand, both positive and negative exchange bias effects can also be observed at 8 K. They can reach 130 Oe in 2 T cooling field and -120 Oe in 10 T cooling field, respectively. The polarity of the exchange bias field depends on the coupling intensity between the Nd\textsuperscript{3+} ordering and the Mn\textsuperscript{3+} ferromagnetic component, and on the initial states as well.
6.1.6 References


6.2 Significant Exchange Bias Effect in the Single Phase Bulk Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ Alloy

6.2.1 Abstract

Exchange bias effect has been observed in the single phase bulk Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ alloy. At 30K, the exchange bias field reaches ~230 Oe when the sample is cooled down from high temperature in external magnetic fields. When the temperature is further lower, the exchange bias fields increase to ~400 Oe at 20K and ~650 Oe at 10K. The strong interaction between magnetic rare earth Pr and transitional metal Mn is responsible for this effect. This work extends the family of materials with exchange bias effect, based on which more similar materials could be found in the future.

6.2.2 Introduction

The materials with exchange bias (EB) effect show great interest for their potential application on memory storage unit. In such materials, the centre of the magnetic hysteresis loop shifts to the left or right, giving two asymmetric coercive fields. A typical system is Co-CoO bilayer, where Co is ferromagnetic (FM) and CoO is antiferromagnetic (AFM). The EB effect is also observed in other similar materials such as Fe-Fe$_3$O$_4$, Ni-NiO. Interface interaction may induce unique properties and change the magnetic properties of bulk materials, as in a systematic study of the EB effect that was carried out on LaNiO$_3$-LaMnO$_3$ superlattices. On the other hand, the EB effect can also exist in oxide compounds which allow the coexistence of both a FM component and an AFM component. Recently, the EB effect was intensively studied in La$_{1-x}$Pr$_x$CrO$_3$ and Sr$_2$YbRuO$_6$, in which both positive and negative EB effects can be observed and are dependent on the cooling field and temperature.
Beyond the EB effect found in bilayers and oxide compounds, this effect has also been reported to exist in some single phase alloys, such as Ni-Mn-Sn and Ni-Mn-Sb Heusler alloys.\textsuperscript{12-15} In these Ni-Mn-based magnetic shape memory alloys, the coexistence of the FM and AFM orderings in martensitic phase allows the occurrence of the EB effect.\textsuperscript{16} Considering the magnetic property of some rare earth and transitional metal elements, we expect to find the coexistence of two different magnetic sublattices when the magnetic rare earth element and transitional metal element form an alloy. In this sort of system, the exchange anisotropy of two magnetic sublattices may allow the occurrence of the EB effect. Therefore, we have chosen to study the single phase bulk Pr\textsubscript{0.5}Y\textsubscript{0.5}Mn\textsubscript{2}Ge\textsubscript{2} alloy at low temperature, considering the Pr and Mn are magnetic. In fact, Pr\textsubscript{0.5}Y\textsubscript{0.5}Mn\textsubscript{2}Ge\textsubscript{2} belongs to the big family of 122-type magnetocaloric alloy compounds, in which the general magnetic properties have been well studied.\textsuperscript{17-19} Our results show that a significant negative EB effect is observed, and the EB field reaches \textasciitilde650 Oe at 10K. This work extends the family of materials with EB effect and proposes a way to design EB materials, based on which more similar materials could be found in the future.

6.2.3 Experimental

The Pr\textsubscript{0.5}Y\textsubscript{0.5}Mn\textsubscript{2}Ge\textsubscript{2} alloy was prepared by conventional argon arc melting from the starting elements: the Pr and Y, 99.9%; Mn, 99.99%; Ge, 99.999%. The starting materials contained \textasciitilde3% excess Mn to compensate for the Mn loss due to evaporation during melting and the ingot was melted five times for improved homogeneity. The crystal structures of the sample was examined by X-ray diffraction at room temperature (XRD, model: GBC MMA), using Cu Ka radiation at $\lambda = 1.54056$ Å. The magnetic measurements were carried out using a 14 T physical...
property measurement system (PPMS), equipped with a vibrating sample magnetometer (VSM), over a wide temperature range from 5 to 300 K.

6.2.4 Results and Discussion

At the first, we measure the field cooling temperature dependence of magnetic moment in cool-down mode to check the magnetic transitions in this alloy system. The result is presented in Figure 6.2-1. The measuring field is 100 Oe, which is relatively small and will not disturb the intrinsic magnetic property. There are three obvious transitions from high temperature to low temperature. To better display the transition temperatures, we have done the derivation processing and the result is presented in the inset in Figure 6.2-1. The first transition locates at ~184K, the second locates at ~136K and the third transition locates at ~60K. According to previous similar report\textsuperscript{20}, the transition at 184K should correspond to the transition from interlayer ferromagnetic ordering to interlayer antiferromagnetic ordering, due to the unit cell contract during the cooling process. The sharp $dM/dT$ change at 136K is due to the strongly enhanced interlayer AFM interaction. The bump at ~100K may be the temperature at which the short-range ordering of Pr starts to form. The transition at 60K is ascribed to the FM ordering of rare earth Pr and the FM ordering of Mn induced by the FM Pr sublattice. The difference in the transition temperatures from those in Ref.\textsuperscript{19} may be due to the slight difference in the actual element ratio or inhomogeneity.
Figure 6.2-1 The cooling field temperature dependence of magnetic moment in cool-down mode; inset: Temperature dependence of $dM/dT$, which helps to display the two transitions clearly.
Figure 6.2-2 The magnetic hysteresis loops measured in zero cooling field at 295K (a), 130K (b) and 100K (c) from -2000 Oe to 2000 Oe
To better understand the magnetic state in different temperature range, we measured the magnetic hysteresis (MH) loops at 295K, 130K and 100K, as demonstrated in Figure 6.2-2 (a-c), respectively. The MH loops below 60K will be presented and discussed later. The MH loops in Figure 6.2-2 suggest that there is obvious ferromagnetic ordering at 295K, 130K and 100K as well. Therefore, the AFM transition starting from 184K is not a sharp transition but a gradual process. In addition, the AFM ordering could be enhanced and the FM ordering still exists when the temperature goes lower when the temperature is cooled from 295K to 60K.

In order to achieve the EB effect, there should be two magnetic components: one of them is FM ordering while the other one is AFM ordering (here, we don’t discuss the EB effect in the spin glass state). These two magnetic orderings can origin from the magnetic phase separated states, in which allow their coexistence.21, 22 Otherwise, they can also origin from two different magnetic sublattices. Therefore, it is impossible to observe the EB effect above 136K, because there is only ferromagnetic ordering of Mn sublattice (to be exactly, Mn sublattice is in canted antiferromagnetic ordering)19, 20. Between 136K and 60K, although both the AFM and FM orderings could exist, considering that they come from the same Mn atomic sites, the EB effect is also hard to achieve, confirmed by the symmetric magnetic hysteresis loops at 130K and 100K shown in Figure 6.2-3. Below 60K, however, Pr atoms start to order ferromagnetically and polarize Mn atoms at the same time. Consequently, Mn atoms have a ferromagnetic component with the same vector as that of Pr FM ordering. In this case, the anisotropic exchange interaction between Pr and Mn may allow the EB effect. The Figure 6.2-4 presents the magnetic hysteresis loop measured at 10K, 20K and 30K, respectively, after the sample was cooled down from 200K in zero magnetic field and a 3T field.
Figure 6.2-3 The magnetic hysteresis loops measured at 130K (a) and 100K (b) after the sample was cooled down from 200K in the 3T external field, respectively.

When the cooling field is zero, the EB effect cannot be identified clearly at low temperature, as displayed in Figure 6.2-4 (a-c). This phenomenon should be ascribed to the disorder-like initial state at low temperature when the cooling field is zero. On the contrary, significant EB effect can be observed when the sample was cooled down from 200K in a 3T magnetic field, as presented in Figure 6.2-4 (d-f).
Figure 6.2-4 The magnetic hysteresis loops measured at 30K (a), 20K (b) and 10K (c), after the sample was cooled down from 200K in the 0T external field, respectively; The magnetic hysteresis loops measured at 30K (d), 20K (e) and 10K (f), after the sample was cooled down from 200K in the 3T external field, respectively.
Figure 6.2-5 The cooling field dependence of the exchange bias fields at 30K, 20K and 10K.

The EB field increases as the temperature reduces from 30K to 10K. At 30K, the EB field can reach ~-230 Oe at 30K while the EB field is about -400 Oe at 20K and -650 Oe at 10K. In our work, the EB field at 10K is more than 3 times as large as that in Ref.12 and Ref.13. This change in the EB fields at various temperatures suggests the enhanced pinning force and the increased content of FM component when the temperature becomes lower. To study the cooling field dependence of the EB fields, we measured a series of magnetic hysteresis loops in different cooling fields at 30K, 20K and 10K. The results are given in Figure 6.2-5. The EB fields show relatively strong dependence on the cooling field when the cooling field is small. When the cooling field is as high as 2T or above 2T, the EB fields don’t change too much. This trend is much clear in the case of 10K, indicating the strong thermal disturbance on one of the two FM sublattices at 20K and 30K.
After we know the results, let us figure out the mechanism and reveal what happened behind this unique phenomenon. Below 60K, the Pr atoms are in FM ordering and polarize the Mn atoms, which allows a weak FM component from Mn sublattice and it is along the same direction with the FM vector of Pr sublattice. Hence, the spontaneous exchange interaction between Pr and Mn is ferromagnetic and could be favoured by a magnetic field applied along the FM vector direction. When the sample is cooled down in a positive cooling field, the Pr and Mn spins will be aligned in the same direction and the Pr/Mn ferromagnetically coupled state can be stabilized by the external magnetic field, which is a stable state in terms of energy. When a negative measuring field is applied, the Pr spins become unstable and begins to break free, which weakens the exchange interaction between Pr and Mn spins. During this process, the Mn spins remain relatively still and offer a strong pinning force, while the Pr spins follow the measuring field, considering that the moment of Pr spins is much larger than that of Mn spins and then Pr spins could be forced to switch relatively easier than the Mn spins (if the Pr spins are still and Mn spins are switched during the hysteresis loop measurement, there should be a positive moment when the scanning field is -10000 Oe, which conflicts the experimental result). Once Pr spins are aligned along the negative measuring field, the Pr and Mn spins are antiferromagnetically coupled, which is a metastable state with an antiferromagnetic exchange field. Therefore, it is much easier for the measuring field to achieve the ferromagnetically coupled state than to achieve the antiferromagnetically coupled state. Consequently, the negative exchange bias effect can be observed. The Mn-Mn spin interaction should be stronger compared with the Pr-Pr interaction and the 10000 Oe measuring field will not switch all the Mn spins but can switch all Pr spins. Then the EB could occur. The temperature dependent EB fields are due to the change
of the exchange interaction between Pr and Mn at different temperatures. The coupling between Pr and Mn is relatively stronger at low temperature, such as 10K, than that at 30K.

6.2.5 Conclusion

In summary, systematically magnetic measurement was carried out in the single phase bulk Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ alloy and significant exchange bias effect is observed at low temperature, which can reach about -650 Oe at 10K. The temperature dependence of magnetic moment shows that there are three main transitions, and two of them are assigned to the enhancement of AFM ordering staring from 184K and becoming extremely strong at 136K, while the other is due to the FM ordering of Pr and Mn spins below 60K. Despite that the AFM and FM orderings can coexist from 184K to 60K, no exchange bias effect can be observed because the AFM and FM orderings both come from the same Mn sublattice and there is no strong coupling between AFM and FM orderings. The exchange bias can only occur when both Pr and Mn spins are in ferromagnetic state. The coupling between Pr and Mn sublattices is responsible for the exchange bias effect. This work extends the family of materials with the exchange bias effect and also provides a way to design new materials with the exchange bias effect.

6.2.6 References


7 ROOM TEMPERATURE FERROELECTRICITY IN EPITAXIAL PSEUDOCUBIC SMFEO$_3$ FILM

7.1 Abstract

The epitaxial pseudocubic SmFeO$_3$ on (100) Nb-SrTiO$_3$ was studied based on ferroelectric (FE) characterization and magnetic measurement. High resolution TEM images clarify the nature of the epitaxial growth, the stress induced structural distortion at the film/substrate interface, and the existence of two different orientation lattices. Clear grain boundaries can be seen, which could introduce an extra local distortion. Rectangle FE loop can be observed at room temperature even just applying a small voltage ranging from -1V to 1V indicative of the presence of ferroelectric polarization. The piezoelectric force microscope image confirms the existence of ferroelectric domains and the switchable property. A strong ferromagnetic-like transition occurs around 185K, which is much lower than the transition observed in bulk sample. It is regarded the pseudocubic structure enhances ferroelectric polarization and decrease the magnetic ordering temperature. Meanwhile, the ferroelectricity in this thin film may origin from distortion and modification in the structure module rather than the exchange striction interaction in the bulk SmFeO$_3$.

7.2 Introduction

The wide application of traditional data storage is attributed to giant magnetoresistant effect $^{1,2}$. Due to increasing demand of computing and storage room, new type cell unit with higher data density and lower power consumption is required. Ferroelectric random access memory seems to be a good choice in which vertical polarization can be easily achieved, meaning that high density could be obtained. Meanwhile, the
stability of ferroelectric domain assures that information can be well saved for a long
time. On the other hand, in one special type of materials in which magnetic ordering
and ferroelectric ordering can coexist, so-called multiferroic materials, also shows
great potential for the next generation of the data storage application and other kinds
of spintronic devices because spin freedom can be operated beyond the charge
freedom. Therefore, exploring new functional materials having multiferroic property
is a hot research field in these years. \(^3\,^4\) \(\text{BiFeO}_3\) has shown its priority due to room
temperature multiferroic property. \(^5\) However, \(\text{Bi}^{3+}\) is not environmental and healthy
friendly, and to obtain single phase in scale is still a problem, which could increase
the cost of production. Furthermore the weak magnetization at room temperature,
weak magnetoelectric coupling and large electrical conceive field strongly limits its
practical application. Rare earth manganites, such as \(\text{DyMnO}_3\)\(^6\,^8\) and \(\text{TbMnO}_3\)\(^7\)
(space group: \(Pnma\)), are of great interest in which electric polarization is induced by
spiral magnetic ordering because of the simultaneous broken spatial inversion and
time-reversal symmetries. \(^9\) In addition, FE property can also be found in
antiferromagnetic hexagonal \(\text{HoMnO}_3\) and \(\text{YMnO}_3\) (space group: \(P6_3cm\)). The FE
property of these two materials origins from the buckling of layered \(\text{MnO}_5\)
polyhedral units, driving by the size effect and electrostatic interaction as well. In
these manganites, the spiral magnetic ordering temperatures are very low and far
away from room temperature, which restricts their application at common ambient
temperature. In most traditional ferroelectric materials, such as \(\text{PZT}\) and \(\text{BaTiO}_3\),
aren’t magnetic. Therefore, to find new multiferroic materials with high ferroelectric
and magnetic transition temperature seems to be an inevitable way to achieve real
application. Up to now, there are few reports on ferroelectric study in orthoferrites
except \(\text{DyFeO}_3\) and \(\text{SmFeO}_3\).\(^{10,12}\) Viewing from the point of symmetry, it is nearly
impossible to achieve ferroelectric phase in orthorhombic ferrite. In case of DyFeO$_3$, the ferroelectric transition happens below the transition temperature of Dy$^{3+}$ lattice around 3.5K, which can be explained by exchange-striction interaction. As for SmFeO$_3$, a small polarization is supposed to occur due to symmetric exchange striction interaction among the canted antiferromagnetic spins$^{13, 14}$, sharing the similar ferroelectric origin of DyFeO$_3$$^{10}$ and CaMn$_7$O$_{12}$$^{15-17}$. Strain engineering has been employed to produce low dimensional materials such as functional thin films, and this method has introduced many unique properties which do not belong to their bulk forms. Recently, the ferroelectric property has been reported in the artificially hexagonal YbFeO$_3$ thin film on a hexagonal substrate.$^{18}$ However, in this work, we study the epitaxial pseudocubic orthoferrite SmFeO$_3$ on (001) Nb-STO substrate prepared by pulse laser deposition. Supposed that the mismatch between two sets of lattices could introduce strain and lead to the local structure distortion at the film/substrate interface, the structure and the physical properties of the thin film may consequently be modified. Our characterization shows that good ferroelectric loop is observed, and piezoresponse force microscopy images confirm the switchable ferroelectric domain structure. Meanwhile, magnetic measurement results show that the SmFeO$_3$ experiences a ferromagnetic-like (canted antiferromagnetic) transition around 185K, quite different from bulk SmFeO$_3$, which is indicative of multiferroic property in this material, which may also be due to the strain effect induced by local structural distortion and consequent symmetry change at the interface.

7.3 Experimental

SmFeO$_3$ thin films were deposited at 830°C on (001) Nb-STO in a dynamic flowing oxygen atmosphere of 200 mTorr, using a pulsed laser deposition (PLD) system. The SmFeO$_3$ target was prepared by solid state reaction method and X-ray diffraction
(XRD, model: GBC MMA, Cu Kα radiation) shows it is single phase with orthorhombic structure. The Nd:YAG laser source was used with 355nm wavelength. During the deposition process, the laser is stabilized at 6-7 J/cm² and repeats 10 cycles per second. The crystal structures of the films were examined by x-ray XRD at room temperature. The thickness of the films was checked by scanning electron microscope (SEM, model: JEOL JSM-6460A) and is around 450 nm. The high resolution transmission electron microscope (HRTEM, model: JEOL JEM-4000EX) clarified the epitaxial growth of the thin film at the interface and the existence of boundaries which separate the majority [010]o and the minority [101]o lattices. Magnetic property were measured by superconducting quantum interference device (SQUID) magnetometer. Pt electrodes were deposited on the film for ferroelectric measurement by magnetron sputtering with a standard shadow mask. Ferroelectric Analysers (TF2000, aixACCT) were employed to characterize the ferroelectric property (ferroelectric hysteresis loops and fatigue). Meanwhile, PUND mode measurements were performed to reveal the real switch process. Nano-scale ferroelectric measurements of as-grown SmFeO₃ film were carried out via piezoresponse force microscopy (PFM, model: MFP-3D Asylum Research). Typical scan size and rate were 500nm and 0.1Hz. Positive and negative dc bias of 5V was applied to the tip to produce switched domain structure and subsequent scan was done at 370 kHz by DART PFM mode.
Figure 7.4-1 X-ray diffraction of the SmFeO$_3$ film deposited on (001) Nb-STO single crystal substrate, lattice parameter: STO $c_c$=3.905 and SFO $c_c$=3.720.

The SmFeO$_3$ thin film was prepared by pulsed laser deposition on (001) Nb-STO single crystal substrate. The basic structure was checked by the X-ray diffraction, as shown in Figure 7.4-1. It reveals that the SmFeO$_3$ is epitaxially grown and three satellite peaks are found near the (001), (002) and (003) Nb-STO peaks. This is similar to the LuFeO$_3$ and BiFeO$_3$ film on (001) STO substrate, which are both “cube-on-cube” grown epitaxially with pseudocubic structure. According to these three diffraction peaks, we can estimate the out-of-plane pseudocubic lattice parameter $a$=3.72Å, which is quite close to the (010) growth of bulk SmFeO$_3$. Considering the similarity between epitaxial BiFeO$_3$\cite{19, 20} and SmFeO$_3$, it is reasonable to tentatively assign the SmFeO$_3$ film to rhombohedral structure or hexagonal structure. The structural study based on diffraction peak calculation shows
that the three peaks of pseudocubic structure can successfully be assigned to (012),
(024), (217) peaks of rhombohedral structure\((R3c, a_r = 5.638Å, \alpha_r = 52.64°)\), or
(102), (204), (217) of hexagonal structure\((P6_3cm, a_h = b_h = 5.00Å, c_h = 14.53Å, \alpha = \beta = 90°, \gamma = 120°)\).

Compared with the sharp diffraction peaks from substrate, the three peaks from the
thin film are relatively broad, which may origin from two sets of reflection with close
lattice parameters. To check the real case how the thin film grows, high resolution
transmission electron microscope (HRTEM) is employed to determine the interface
structure, as shown in Figure 7.4-2. The cross-section of the thin film was imagined
in bright-field mode presented in Figure 7.4-2 (a), in which clear interface between
the thin film and substrate can be seen. In addition to the epitaxial growth along
\(\text{SmFeO}_3\text{ [010]}_o\) direction, growth along \([101]_o\) is also found in some area of the film
(these two orientation index are simply assigned to those of the orthorhombic bulk
\(\text{SmFeO}_3\)). In Figure 7.4-2(a), a specifically selected film/substrate interface with
\((010)_o\) and \((101)_o\) grain boundary is shown.

Figure 7.4-2 (a) The interface between the \(\text{SmFeO}_3\) thin film and the STO substrate,
on which the grain boundary of \([010]_o\) and \([101]_o\) is also shown. (b) the HRTEM
image of the film/substrate interface, magnified the selected \([010]\) growth area in (a).
showing the epitaxial growth. (d) Selected area electron diffraction pattern, the high
level diffraction spot shows the splitting, indicating of the different structures existing in the film.

Considering the lattice mismatch between the orthorhombic SmFeO$_3$ and cubic STO, the stress induced distortion should exist around the interface. In addition, the boundary between the [010] and [101] lattices should also introduce extra stress and local distortion in these system. Significant structural distortion can be identified around the interfaces in Figure 7.4-2 (b) which presents a small interface area selected from the rectangle frame in Figure 7.4-2 (a). The atoms of SmFeO$_3$ are forced to stack according to the structure of STO at the initial several layers, which is around 10nm in scale. However, this distortion will become weaker and weaker when the depositing process goes further. On the contrary, the boundaries between two different orientation lattices always exist, which is beyond the stress scale on the interface.

![Graph](image-url)
Figure 7.4-3 (a) Electric hysteresis loop of SmFeO$_3$ films on Nb-STO at room temperature, (b) time dependence of applied voltage and corresponding current.

Figure 7.4-4 Fatigue test result after $10^6$ cycles (10 data points every decade)
Electric hysteresis loop of SmFeO$_3$ films on Nb-STO was carried out at room temperature. When the applied voltage exceeds 1.2V (electric field ~22 kV / cm), a rectangle-like shape loop can be observed as shown in Figure 7.4-3(a), indicating of good FE property. A higher applied voltage will increase the leakage current and a relative round FE loop will present (not shown). The time dependence of applied voltage and consequent current is given in Figure 7.4-3(b), in which obvious switching current can be seen and it is quite different from typical resistor or capacitor’s behaviour. The small current behaviour difference between opposite voltages is probably due to the electrode effect (Au and Nb-STO). To check the fatigue property, the P-E loops were measured for $10^6$ times and the remanent polarizations were presented in Figure 7.4-4. The remanent polarization is about 0.08$\mu$C/cm$^2$. There is no significant change of remanent polarization after the fatigue test, indicating the good stability of this FE material.

Considering the leakage effect which can also contribute to P-E loop, we used PUND method to confirm the real polarization. The PUND method uses an up-up-down-down wave to exclude the leakage effect. The standard PUND wave form is presented in Figure 7.4-5. At the beginning, the system uses a negative write pulse to polarize the film. After that, a positive pulse V1 is applied to the film and a current will produce due to leakage and domain flop. Then another positive pulse V2 is applied and a current will produce only due to leakage. Therefore, the integrity of current difference produced between up-up or down-down processes is accordant with two time remain polarization $2Pr$. This also applies to the down-down process. V3 pulse will switch the FE domain to opposite direction and V4 just measures the leakage current contribution. In the Figure 7.4-5, clear current difference between I1 and I2 or I3 and I4 can be observed (the pure leakage current peak is lower and
narrower than that with switching current), indicating that polarization in the P-E loop is real. However, the real current contribution from FE switching is reduced to half, meaning that the remanent polarization is about $0.04\mu\text{C/cm}^2$. This value is very close to that found in the orthorhombic HoMnO$_3$\textsuperscript{21,22}, in which Mn$^{3+}$ spins are in E-type antiferromagnetic ordering. To some extent, considering the different magnetic states between the orthorhombic HoMnO$_3$ and the orthorhombic SmFeO$_3$, this similarity suggests that the mechanism in the orthorhombic bulk SmFeO$_3$ may not apply to the SmFeO$_3$ thin film.

![Figure 7.4-5](image_url)

**Figure 7.4-5** The time dependence of (a) applied voltage (ranging from -2V to 2V) and (b) consequent current measured by PUND mode.
PFM image presented in Figure 7.4-6 shows the existence of FE domains, which are mainly dominated by two types of domains with opposite vectors. This means that the domain walls in this film are mostly 180° domain walls. Meanwhile, the information surface morphology is also obtained and results show an average roughness about 1.8nm indicative of good quality of film. Compared the morphology with phase pattern, it is not difficult to find that there are more than one domain in some single grain. The average domain size is around 0.1 µm, much smaller than domain size in BiFeO₃ film. One important character of the ferroelectric property is that the ferroelectric domains can be controlled and reversed by external electric field, so-called “write”. To do it, we carried out FPM lithography on the SmFeO₃ film. A cubic in cubic pattern is obtained as shown in Figure 7.4-6(c), in which inset is the pre-set pattern. The amplitude distribution along the red line across the pattern is presented in Figure 7.4-6(d). It is clear that these two cubic boxes show opposite amplitude values, suggesting that they are truly two types of domains with opposite polarization directions.
Figure 7.4-6 Nano-scale ferroelectric domain structure characterized by PFM: (a) amplitude image and (b) phase image; (c) PFM lithography, inset: the pre-set pattern and (d) amplitude distribution along the red line across the lithography pattern in (c).

To investigate the magnetic property of this pseudocubic SmFeO$_3$ film, we carried out the measurement by using the MPMS. Field cooling temperature dependence of magnetic moment was measured from 10K to 300K, as shown in Figure 7.4-7. A sharp FM-like transition can be found around 185K. The FM behaviour can be confirmed by magnetic hysteresis loop at 100K. Curie-Weiss law fitting result gives a positive intercept which corresponds to a negative Curie-Weiss temperature, indicating the AFM interaction starting below 240K. Hence, the FM-like behaviour should origin from a canted AFM ordering. This is quite different from what happens in bulk SmFeO$_3$, in which a spin reorientation happens around 433K from a canted antiferromagnetic (WFM) ordering to simple antiferromagnetic ordering. Such big change may be attributed to Fe$^{3+}$ spin frustration in rhombohedra/hexagonal lattice, which weakens the interaction between Fe$^{3+}$ ions compared with that in orthorhombic lattice. The stress induced distortion on the interface and boundaries should be responsible for the significant change in the magnetic properties. This result indicates that the ferroelectricity in the SmFeO$_3$ at room temperature may be not from the magnetic exchange striction interaction but from the structure distortion.
Figure 7.4-7 (a) Temperature dependence of magnetic moment from 10K to 300K, and Magnetic hysteresis loop measured at 100K; (b) Antiferromagnetic interaction of Fe$^{3+}$ sublattice confirmed by Curie-Weiss law fitting with temperature range from 100-300K.
7.5 Conclusion

In summary, the structure, ferroelectric and magnetic properties were studied in the epitaxial pseudocubic SmFeO$_3$ on Nb-STO substrate. Clear structure distortion can be identified on the [010]$_o$ grown film/substrate interface and boundaries of [010]$_o$ and a small fraction of [101]$_o$ grains. A strong ferromagnetic-like transition is observed around 185K, which should be due to a canted antiferromagnetic ordering. The PFM images clarify the existence of ferroelectricity, and the switchable domain structure. Ferroelectric measurement also presents a saturating hysteresis loop and the loops are very stable even after $10^6$ cycles’ measurement. PUND method was used to determine the intrinsic ferroelectric polarization and the remanent polarization is about 0.04 $\mu$C/cm$^2$, which is comparable to that in orthorhombic HoMnO$_3$. The structure distortion in this system should responsible for the significant change in magnetic property and the small polarization as well.

7.6 References


This thesis reviews three important physical phenomena in magnetic material systems: the magnetoresistance effect, exchange bias, and the multiferroic/magnetoelectric coupling effect. Memory or storage devices have been designed or will be designed based on these three significant physical effects.

Manganese oxides have aroused great interest in these phenomena. A spiral magnetic ordering exists in DyMnO$_3$ and produces ferroelectric ordering at low temperature. Therefore, DyMnO$_3$ is a multiferroic material. To better understand the magnetic interaction and the stability of spiral magnetic ordering in such materials, we choose to study the perovskite DyMn$_{1-x}$Fe$_x$O$_3$ system, based on X-ray diffraction pattern refinement, Raman spectroscopy at room temperature, magnetic measurements, and dielectric analysis. The lattice parameters show that static orbital ordering exists in the samples with $x \leq 0.2$, while phonon modes of Raman spectra show clear hardening or softening and are strongly dependent on Fe content. Abnormal changes in these phonon modes are observed at $x \approx 0.3$, corresponding to the appearance of dynamic orbital ordering instead of static orbital ordering. At the composition $x > 0.5$, as Jahn-Teller orbital ordering starts to disappear, spin reorientation starts to appear, which is confirmed by the temperature dependence of the magnetic moment. For the samples with $x < 0.5$, the antiferromagnetic transition temperature increases as $x$ increases, as identified by the temperature dependence of modified $d\chi/dT$. For samples with $x > 0.5$, the spin reorientation temperature ($T_r$) and the antiferromagnetic Néel temperature ($T_N$) gradually separate and widen the temperature range of the magnetic metastable state between $T_r$ and $T_N$, reaching $T_r = 65$ K and $T_N = 680$ K for $x = 1$. The change in the antiferromagnetic transition
temperature is due to the stronger antiferromagnetic interaction induced by Fe$^{3+}$ ion substitution, with its e$_g$ orbital half-occupied, with respect to the Mn$^{3+}$ ion, with its e$_g$ orbital quarter-occupied. The spin reorientation is modified by the competition between the Fe$^{3+}$-Fe$^{3+}$ interaction and the Dy$^{3+}$-Fe$^{3+}$ interaction.

The dielectric constant and loss of perovskite DyMn$_{1-x}$Fe$_x$O$_3$ samples show strong dispersion in various frequencies, which is indicative of relaxation. The activation energies were obtained through Arrhenius law fitting and range from 0.213 eV to 0.385 eV. The Fe content dependence of the characteristic frequency $f_0$ and the activation energy $E_\alpha$ shows two transitions which are well consistent with the change in orbital ordering. Meanwhile, different magnetic orderings could affect the relaxation and induce the change in $E_\alpha$. Magnetodielectric properties were studied around the spin reorientation transition temperature of 290 K (which is close to room temperature) in DyMn$_{0.33}$Fe$_{0.67}$O$_3$. Both giant positive and giant negative magnetodielectric coupling (MDC) were observed near room temperature. The MDC shows strong temperature and frequency dependence, and the sign changes from positive to negative when the magnetic state makes a transition from a canted antiferromagnetic state to a collinear antiferromagnetic state. Possible mechanisms are proposed based on the Maxwell-Wagner model, the phase transition, the magnetoresistance effect, and spin-phonon coupling.

The interaction between rare earth ions and transition metal ions plays a critical role in determining the magnetic configuration. At the same time, the interaction between magnetic rare earth ions has not been studied in detail. Therefore, the structural properties, magnetic properties, and heat capacity have been systematically studied in perovskite Nd$_{1-x}$Er$_x$MnO$_3$ (0 $\leq$ x $\leq$ 0.5). Er$^{3+}$ doping enhances the Jahn-Teller distortion, strongly affects the Nd$^{3+}$-Mn$^{3+}$ interaction, destroys the intermediate state
below the antiferromagnetic transition temperature in NdMnO$_3$, and breaks the antiparallel arrangement between Nd$^{3+}$ and Mn$^{3+}$ spin ordering. In spite of the high compression of the lattice along the $c$ axis, the spin states of Mn$^{3+}$ are stable and are always high spin states. For $x < 0.5$, both the Mn$^{3+}$ antiferromagnetic transition temperatures and the Nd$^{3+}$ ferromagnetic transition temperatures decrease after Er$^{3+}$ doping. For $x = 0.5$, Mn$^{3+}$ probably enters a pure A-type antiferromagnetic (AFM) state at lower temperature, which is different from the canted A-type AFM state found in other samples, and there is no Nd$^{3+}$ ordering observed above 5 K. The decreasing ferromagnetic component in magnetic hysteresis loops at 30 K indicates that the canted angles vary with $x$. Otherwise, the coincidence between the magnetic entropy abnormality and the structural change suggests that the magnetic transition may accompany structural change. These results offer strong evidence for the interaction between rare earth ions and transition metal ions, and for competition among rare earth ions as well. The specific heat study on Nd$_{1-x}$Er$_x$MnO$_3$ shows that anomalies in the magnetic entropy, contributed by the antiferromagnetic transition, and the spin wave stiffness coefficient are found in the sample with $x = 0.1$ due to a stronger ferromagnetic component, which is consistent with previous magnetic measurements and analysis. Careful investigation of the specific heat in the low temperature range below 25 K shows that the ground state splitting of Nd$^{3+}$ has been modified by the Er$^{3+}$ doping, showing a nonlinear dependence on the Er$^{3+}$ doping rate, due to the competition between the crystal field and the exchange field. On the other hand, the ground state splitting of Er$^{3+}$ has a linear dependence on the doping rate, which is attributed to the dominance of the crystal field over the exchange field. Hence, the competition between the crystal field and the exchange field must be considered for the low temperature study of rare earth ions when they are comparable.
in other similar systems. The spin wave coefficients decline linearly with increasing 
Er$^{3+}$ doping content, except in the case of $x = 0.1$, in line with the weaker 
antiferromagnetic interaction.

Considering the strong coupling between the magnetic rare earth ion Nd$^{3+}$ and the 
transition metal ion Mn$^{3+}$ in NdMnO$_3$, it is possible to find the exchange bias effect 
in this kind of magnetic system. In this thesis, we report the exchange bias effects in 
this simple perovskite manganese oxide. Nd$^{3+}$ ordering is induced by the Mn$^{3+}$ 
ferromagnetic component, and they are antiferromagnetically coupled with each 
other. At 30 K, both negative and positive exchange bias effects are found, which are 
dependent on the cooling field. The exchange bias fields are around -2400 Oe and 
1800 Oe, respectively. Positive and negative exchange bias effects were also 
observed at 8 K, but the exchange bias fields are only 130 Oe and -120 Oe. The 
coupling intensity between Nd$^{3+}$ ordering and Mn$^{3+}$ ordering, and their initial states 
determine the polarity of the exchange bias fields. In fact, this idea may also apply to 
other systems containing magnetic rare earth ions and transition metal ions. Based on 
this assumption, we found that the exchange bias effect can be achieved in the single 
phase bulk Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ alloy. At 30 K, the exchange bias field reaches $\sim$230 Oe 
when the sample is cooled down from high temperature in external magnetic fields. 
When the temperature is further reduced, the exchange bias fields increase to $\sim$400 
Oe at 20 K and $\sim$650 Oe at 10 K. The strong interaction between the magnetic rare 
earth Pr and the transition metal Mn is responsible for this effect. This work extends 
the family of materials with an exchange bias effect, based on which, more similar 
materials could be found in the future.

The last work reported is the strain engineering induced ferroelectric property in 
epitaxial pseudocubic SmFeO$_3$ on (100) Nb-SrTiO$_3$. High resolution TEM images
clarify the nature of the epitaxial growth, the stress induced structural distortion at the film/substrate interface, and the existence of two different orientation lattices. Clear grain boundaries can be seen, which could introduce an extra local distortion. A rectangular FE loop can be observed at room temperature, even when just applying a small voltage, ranging from -1 V to 1 V, which is indicative of the presence of ferroelectric polarization. The piezoelectric force microscope image confirms the existence of ferroelectric domains and the switchable property.

The magnetic and electric properties in such magnetic systems promise the potential application in spintronics. The exchange bias research in single phase bulk materials will attraction more attention for their simple structures and the exchange bias effect may still exist in their thin film form, which deserves further study and preludes the production of the memory storage devices with the single phase materials. The low thermodynamic investigation helps to understand the magnetic behaviour, which sheds the light of the effective control of the magnetic ordering and the crystal structure by the element doping. The possible high performance ferroelectric memory device is worthy to be designed based on the room temperature ferroelectric thin films.
9 PUBLICATIONS

1. Competition between the crystal field and the exchange field in Er$^{3+}$ doped NdMnO$_3$

2. Positive and negative exchange bias effects in the simple perovskite manganite NdMnO$_3$

3. Strong 4f electron interaction and magnetic ordering modification in Nd$_{1-x}$Er$_x$MnO$_3$ ($0 \leq x \leq 0.5$)

4. Continuously tunable magnetic phase transitions in the DyMn$_{1-x}$Fe$_x$O$_3$ system

5. Temperature and frequency dependent giant magnetodielectric coupling in DyMn$_{0.33}$Fe$_{0.67}$O$_3$

6. Dielectric relaxation in the DyMn$_{1-x}$Fe$_x$O$_3$ system

7. Magnetocaloric effect and critical behavior in the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy
Anisotropy of crystal growth mechanisms, dielectricity, and magnetism properties of multiferroic Bi$_2$FeMnO$_6$ thin films


Band structure, magnetic and transport properties of two dimensional compounds Sr$_{2-x}$Gd$_x$CoO$_4$


The flux pinning mechanism, and electrical and magnetic anisotropy in Fe$_{1.04}$Te$_{0.6}$Se$_{0.4}$ superconducting single crystal


On the crystal structure and magnetic properties of the Mn$_{0.94}$Ti$_{0.06}$CoGe Alloy


Spin switching and magnetization reversal in single-crystal NdFeO$_3$


Magnetic field induced discontinuous spin reorientation in ErFeO$_3$ single crystal


A comparative study of magnetic behaviors in TbNi$_2$, TbMn$_2$ and TbNi$_2$Mn compounds

Unpublished work

1. Neutron diffraction study in the strongly frustrated TbMn$_{1-x}$Fe$_x$O$_3$

2. Significant exchange bias effect in single phase magnetocaloric alloy

3. Artificial stress induced ferroelectricity in orthoferrite at room temperature