

**EFFECTS OF CHEMICAL SUBSTITUTIONS AND
MAGNETIC FIELDS ON MULTIFERROIC AND
MAGNETOELECTRIC MATERIALS**

A Dissertation

Presented to

the Faculty of the Department of Physics

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

By

Kao-Chen Liang

August 2013

**EFFECTS OF CHEMICAL SUBSTITUTIONS AND
MAGNETIC FIELDS ON MULTIFERROIC AND
MAGNETOELECTRIC MATERIALS**

Kao-Chen Liang

APPROVED:

Dr. Ching-Wu Chu, Chairman
Department of Physics, University of Houston

Dr. Shuheng Pan, Co-Chairman
Department of Physics, University of Houston

Dr. Chin-Sen Ting, Co-Chairman
Department of Physics, University of Houston

Dr. Allan J. Jacobson, Co-Chairman
Department of Chemistry, University of Houston

Dean, College of Natural Sciences and Mathematics

ACKNOWLEDGEMENTS

This dissertation is done with many people's help so that it could be finished.

Three years ago, I almost left the U.S. for Taiwan to start a new career path without a Ph.D. I knew that I had to speak to Dr. Chu before I made final decision or I would regret it. My academic advisor, Prof. Paul C.W. Chu, offered me a chance to study the solid state physics in our HPLT lab so I stayed. After I joined, the atmosphere in our group pushed me to do well and make progress to reach a certain standard. I also had some chances to do oral presentation in conferences, which is an important training. Some said that to succeed one need to work with good people, work in a good environment, and work very hard. For all these, I want to thank Prof. Chu. The second person who I want to thank for is Prof. Bernd Lorenz, my research advisor. It is Prof. Lorenz's patient guidance that I am able to finish my dissertation. I hope that I can be as patient as he is when I have a chance to train young people.

I would like to give special thanks to my dissertation committee, Dr. Kevin Bassler, Dr. Shunhang Pan, Dr. Allan J. Jacobson, and Dr. Chin-Sin Ting, for taking time to give me support, encouragement, and criticism.

Our collaborator, Dr. Feng Ye, finished all the neutron scattering measurements and helped us to get a deeper understanding on our multiferroic work.

Other HPLT group members are also important to me. Dr. Yu-Yi Xue always smiled at me and answered my questions. Dr. Bing Lv helped me with my chemistry-related questions. Dr. Rajit Chaudhury taught me all the experiment techniques when I had just joined our group. Dr. Melissa Gooch answered my most naive questions and was my good lunch partner. Dr. Fengyan Wei shared her experience with me. Mr. Wang synthesized huge single crystals and Mrs. Sun orientated the crystals so that I can collect all the nice data. Sarcastic jokes from Chris always help me to release my stress, and he is also my good lunch partner. Duc used his special way

to encourage me. The companionship from Quantum is also there for me. Troy and Helen helped with all my paperwork.

Last but not least, I would like to thank my close family and friends outside of my physics life. Without my mom, dad, brothers, sisters, Michelle, uncles, aunts, and grandparents, I could not of made it this far.

All these people have given me strength at different times through the previous five years.

**EFFECTS OF CHEMICAL SUBSTITUTIONS AND
MAGNETIC FIELDS ON MULTIFERROIC AND
MAGNETOELECTRIC MATERIALS**

An Abstract of a Dissertation
Presented to
the Faculty of the Department of Physics
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

By
Kao-Chen Liang
August 2013

ABSTRACT

We studied the interaction of the magnetic order or magnetic field with polarization or dielectric properties of solids, the so-called magnetoelectric (ME) effect. In this work, we particularly consider three different classes of compounds.

The first class of compound is multiferroic $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. The frustrated spin helix in the multiferroic phase breaks spatial inversion symmetry and induces ferroelectric polarization. Combining neutron scattering results, we found that the strong Co anisotropy affects the orientation and shape of the spin helix, resulting in two flops of ferroelectric polarization at $x_{c1} = 0.075$ and $x_{c2} = 0.15$. At $x_{c1} = 0.075$, $\vec{P}$ rotates from the b -axis into the $a - c$ -plane and, at $x_{c2} = 0.15$, it flips back to the b -axis. The applied external fields force the normal vector k of spin helix rotating to be parallel to the direction of the magnetic fields. This reorientation of the spin helix causes additional field-induced polarization flops.

The second class of materials is ME borates. $R\text{Al}_3(\text{BO}_3)_4$ (R = rare earth) crystallizes in a noncentrosymmetric but also nonpolar lattice structure, not allowing for polarization. Magnetic data show weak coupling of the f -moments in the compounds. However, $R\text{Al}_3(\text{BO}_3)_4$ shows a large ME effect and $\text{HoAl}_3(\text{BO}_3)_4$ sets the record for the highest ME effect in high fields when it was first measured. Upon strong coupling of f -moments to the lattice, the field-induced ionic displacements in a unit cell resulting in a polar distortion and a change in symmetry on the microscopic scale could be the origin of the ME effect.

The third class of compound is polar LiFeP_2O_7 . Macroscopic electric polarization originates from its polar structure. Interestingly, it also has magnetic Fe-moments to form a canted antiferromagnetic ordering at $T_N \simeq 27$ K with a weak ferromagnetic component along the b -axis. The strong internal ME effect is proved by a sharp peak of pyroelectric current at T_N , resulting in a sizable polarization decrease at the onset of the antiferromagnetic phase transition. The ME effect in external fields shows a

superposition of a linear and quadratic ME effect below T_N . Importantly, it proves the existence of strong coupling between magnetic order and lattice polarization, which is well-described by mean field theory.

Contents

1	Purpose and Motivation	1
2	Background	4
2.1	Magnetic orders in matter	4
2.1.1	The Curie-Weiss Law	4
2.1.2	Noncollinear magnetic orders	7
2.1.3	Magnetic anisotropy	10
2.2	Ferroelectricity	11
2.2.1	Polarization	11
2.2.2	General properties of ferroelectric materials	12
2.3	Landau theory of phase transition	12
2.4	Magnetoelectric effect	16
2.5	Multiferroics	17
2.5.1	Ferroelectricity induced by spiral magnets	18
3	Methodology	23
3.1	Sample preparation	23
3.1.1	Monoclinic $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ and $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$: Floating zone technique	23
3.1.2	Trigonal $R\text{Al}_3(\text{BO}_3)_4$: Flux method	24
3.1.3	Monoclinic LiFeP_2O_7 : Flux method	24
3.2	Sample characterization	25
3.2.1	Crystal orientation	25
3.2.2	Magnetic measurements	25

3.2.3	Heat capacity measurements	26
3.2.4	Polarization measurements	29
4	Results and Discussion	32
4.1	Effects of ion substitutions and magnetic field on the multiferroic properties of MnWO_4	33
4.1.1	Multiferroic properties of MnWO_4	33
4.1.2	Multiferroic properties of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ in the absence of magnetic field	37
4.1.3	Magnetic field effects on the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ compounds . . .	64
4.1.4	Multiferroic properties of $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$	94
4.2	Magnetoelectricity in the system $R\text{Al}_3(\text{BO}_3)_4$ ($R = \text{Tb}, \text{Er}, \text{Tm}, \text{Tm}_{0.9}\text{Yb}_{0.1}, \text{Yb}, \text{Ho}_{0.5}\text{Tm}_{0.5}, \text{Ho}, \text{and } \text{Ho}_{0.5}\text{Y}_{0.5}$)	103
4.2.1	Magnetic susceptibility of $R\text{Al}_3(\text{BO}_3)_4$	104
4.2.2	Magnetoelectric (ME) properties of $R\text{Al}_3(\text{BO}_3)_4$	110
4.3	Internal and external magnetoelectricity in LiFeP_2O_7	117
4.3.1	Magnetic susceptibility of LiFeP_2O_7	118
4.3.2	Magnetoelectric effect of LiFeP_2O_7	122
4.3.3	Lattice anomalies at the magnetic transition	125
4.3.4	Landau free energy expansion	127
4.3.5	Critical scaling of magnetization	131
5	Summary	133
A	Publications and Conference Participation	139
A.1	Publications	139
A.2	Conference and Workshop Participation	141
A.2.1	Presentations	141
	Bibliography	143

List of Figures

2.1	Schematic illustration of types of magnetic structure with a long wave length. (a) Collinear up-up-down-down, (b) sinusoidal, (c) screw (d) cycloidal (e, f) conical structures. Geometric configurations of the unit vector connecting the neighbor magnetic moments at i and j sites $\vec{e}_{ij}$ and the vector chirality ($\vec{S}_i \times \vec{S}_j$) are also shown for respective structures. For (a) and (d), frustrated spin chains with nearest-neighbor FM and next nearest-neighbor AFM interactions J and J' for a Heisenberg model as Eq. 2.8 [1, 2, 3].	9
2.2	First-order phase transition: Schematic representation of the temperature profile of (a) polarization. (b) The free energy as a function of polarization.	15
2.3	Schematic illustration of (a) sinusoidal (no polarization) and (b) helical ($\vec{P}$ is perpendicular to both $\vec{e}_3$ and wave vector $\vec{Q}$) magnetic structure.	20
2.4	Schematic illustration of normal vector ($\vec{k} \propto \vec{S}_1 \times \vec{S}_2$) and propagation vector $\vec{c}$ of the helical structure. The polarization $\vec{P}$ is in the direction of ($\vec{c} \times \vec{k}$).	22
3.1	Schematic illustration of the sample platform in PPMS heat capacity option.	26
3.2	(a) Heater power and (b) the responding temperature with time of the heat capacity measurement.	27
3.3	Example of distorted temperature response near a first-order transition.	28
3.4	(a) A pyroelectric crystal with intrinsic dipole moments with (b) two electrodes on the top and bottom, and connected with a Ammeter. The increase of temperature (c) decreases the spontaneous polarization $\vec{P}_S$. At the same time, a current flow compensates the change of the surface charge density, which is proportional to the polarization $\vec{P}_S$	30
4.1	Crystal structure of the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. Nearest neighbor (J_1) and next nearest neighbor (J_1) exchange interactions.	33

4.2	Magnetic structures of (a) collinear, commensurate (CM) AF1 phase, (b) noncollinear, incommensurate (ICM) AF2 multiferroic phase, (c) the collinear, ICM AF3 sinusoidal phase, (d) noncollinear ICM AF5 phase, <i>ac</i> helix from the neutron scattering refinements.	35
4.3	Ferroelectric polarization of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ (a) Low doping range ($x \leq 0.05, P_b$), (b), (c) intermediate doping ($0.075 \leq x \leq 0.135$), P_a and P_c), and (d) high doping range ($x \geq 0.15$), P_b). For $x = 0.12$, warming and cooling data are presented to show thermal hysteresis. The dashed line for $x = 0.075$ shows the maximum polarization achieved in the magnetic field.	39
4.4	(a) Temperature dependent wavevector scans of $x = 0.075$ upon cooling, (b) Temperature dependence of the peak center of the ICM scattering, and the refined spin structure for $x = 0.075$ at (c) 9 K. (d) The pure AF2 helical structure after the low temperature rotation of spiral plane is complete in $x = 0.075$ compound.	41
4.5	Ferroelectric polarization (at 5 K) phase diagram as a function of Co concentration in $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ system, showing three FE phases (I, II, and III). For $x = 0$, the value of P was extrapolated to low temperature based on data in magnetic fields suppressing the AF1 phase.	43
4.6	<i>b</i> -axis magnetic susceptibility of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. Different curves are vertically offset for clarity. Inset of Fig. (b) shows the enlarge scale of $x = 0.135$ data.	45
4.7	Specific heat of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. Different curves are vertically offset for clarity.	47
4.8	Magnetic and multiferroic phase diagram of the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. Phase boundaries are determined from magnetic, specific and polarization measurements. The shaded area indicates the intermediate AF1 phase.	49
4.9	Magnetic structures of (a) collinear, commensurate (CM) AF1 phase, (b) noncollinear, incommensurate (ICM) AF2 multiferroic phase, (c) the collinear, ICM AF3 sinusoidal phase, (d) noncollinear ICM AF5 phase, <i>ac</i> helix, (e) the collinear, CM AF4 phase and (f) the conical AF2/4 phase from the neutron scattering refinements.	50
4.10	Co doping dependence of the angle α between spiral plane normal vector $\vec{k}$ and <i>c</i> -axis of the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$, which is extracted from the neutron scattering experiment results done through a collaboration with Ye <i>et al.</i> The Zn-doped results are also shown for comparison. Inset shows schematics of the spin helix in AF2 phase. The normal vector $\vec{k}$ has an angle of α with <i>c</i> -axis, and the projection of $\vec{k}$ on to the <i>a</i> – <i>b</i> plane has an angle of ϕ to the <i>a</i> -axis. The <i>b</i> -axis polarization as a function of temperature of $x = 0, 0.02, 0.35, 0.42, 0.05$	51

4.11	Temperature-dependent wavevector sans of the magnetic peaks for $x = 0.12$ upon (a) cooling and (b) warming, and 0.135 upon (c) cooling and (d) warming.	53
4.12	Temperature-dependent wavevector sans of the magnetic peaks for $x = 0.15$ along the (a) $[H, 0.5, -2H]$ and (b) $[H, 0, 0]$ directions.	54
4.13	Temperature-dependent wavevector sans along $(H, 0, -H)$ of the magnetic peaks for $x =$ (a) 0.17, (b) 0.20, (c) 0.25, and (d) 0.30.	55
4.14	(a) Temperature-dependent neutron scattering intensity of the ICM AF2 and CM AF4 phases in $x = 0.17, 0.2, 0.25$, and 0.3 of the FE phase III region. (Note: arrows label the transition temperatures where the low-temperature conical AF2/4 phase sets in. (b) The spin configuration of the ICM AF2, CM AF4 and how they add up to form conical AF2/4 phase.	56
4.15	(a) Schematic diagram of normal vector $\vec{k}$ of the helical plane, the angle α between $\vec{k}$ and c -axis, and ϕ is the angle between the projection of $\vec{k}$ onto the $a - b$ plane with the a -axis. (b) Magnetic easy axis of MnWO_4 and CoWO_4 , and the curve arrow indicates the rotation of the magnetic easy axis upon Co doping.	58
4.16	Ferroelectric polarization of (a) $\text{Mn}_{0.98}\text{Co}_{0.02}\text{WO}_4$ and (b) $\text{Mn}_{0.965}\text{Co}_{0.035}\text{WO}_4$ in external magnetic fields oriented along the b -axis	65
4.17	(a) Magnetic susceptibility and (b) specific heat of $\text{Mn}_{0.98}\text{Co}_{0.02}\text{WO}_4$ in external magnetic field oriented along the b -axis.	66
4.18	Ferroelectric polarization of $\text{Mn}_{0.95}\text{Co}_{0.05}\text{WO}_4$ in external magnetic fields oriented along the b -axis. (a) a -axis component and (b) b -axis component.	68
4.19	(a) Magnetic susceptibility and (b) specific heat of $\text{Mn}_{0.95}\text{Co}_{0.05}\text{WO}_4$ in external magnetic fields oriented along the b -axis.	68
4.20	(a) Schematic diagram of the field dependent rotation of the spin spiral plane (red helical plane) about magnetic easy axis at 3 T and (b) magnitude and orientation of the polarization vector of $\text{Mn}_{0.95}\text{Co}_{0.05}\text{WO}_4$ at 3 T. Θ_b is the angle of the polarization vector with the b -axis. The inset shows the polarization magnitude calculated from Eq. 4.9.	71
4.21	Ferroelectric polarization of $\text{Mn}_{0.925}\text{Co}_{0.075}\text{WO}_4$ in external magnetic fields. (a) a -axis component in b -axis magnetic fields $P_a(H_b)$, (b) a -axis component in c -axis magnetic fields $P_a(H_c)$, (c) c -axis component in b -axis magnetic fields $P_c(H_b)$ (d) schematic diagram of the temperature-dependent (Low-T) and field-dependent (H_b or H_c) rotation of the helical plane.	75
4.22	Magnetic susceptibility of $\text{Mn}_{0.925}\text{Co}_{0.075}\text{WO}_4$ in external magnetic fields oriented along the (a) b -axis and (b) c -axis.	77

4.23	Ferroelectric polarization of $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$ in external magnetic fields. (a) a -axis component in b -axis magnetic fields $P_a(H_b)$, (b) a -axis component in c -axis magnetic fields $P_a(H_c)$, (c) c -axis component in c -axis magnetic fields $P_c(H_c)$ (Note: The $P_c(H_c)$ in the field of $H_c \geq 4$ Tesla are very small) and (d) schematic diagram of the field-dependent rotation of the spin helical plane.	78
4.24	Schematic diagram of the field-dependent (H_b or H_c) rotation of the ab and ac spin helix.	81
4.25	Ferroelectric polarization of $\text{Mn}_{0.88}\text{Co}_{0.12}\text{WO}_4$ in external magnetic fields. (a) a -axis component in b -axis magnetic fields $P_a(H_b)$ and (b) a -axis component in c -axis magnetic fields $P_a(H_c)$ (Note: The $P_a(H_c)$ in the field of $H_c \geq 3$ Tesla are very small).	82
4.26	(a) Ferroelectric polarization along the b -axis of $\text{Mn}_{0.88}\text{Co}_{0.12}\text{WO}_4$ in external magnetic fields oriented along the c -axis $P_b(H_c)$ and (b) schematic diagram of the field-dependent (H_c) rotation of the spin helical plane	83
4.27	(a) Magnetic susceptibility and (b) specific heat of $\text{Mn}_{0.88}\text{Co}_{0.12}\text{WO}_4$ in external magnetic fields oriented along the c -axis.	85
4.28	Ferroelectric polarization along the b -axis in the external magnetic oriented along the b -axis of (a) $\text{Mn}_{0.83}\text{Co}_{0.17}\text{WO}_4$, (b) $\text{Mn}_{0.8}\text{Co}_{0.2}\text{WO}_4$ and (c) $\text{Mn}_{0.75}\text{Co}_{0.25}\text{WO}_4$. (d)schematic diagram of the field-dependent (H_b) rotation of the spin conical structure.	87
4.29	(a) Magnetic susceptibility and (b) specific heat of $\text{Mn}_{0.8}\text{Co}_{0.2}\text{WO}_4$ in external magnetic fields oriented along the b -axis.	88
4.30	Ferroelectric polarization of $\text{Mn}_{0.85}\text{Co}_{0.15}\text{WO}_4$ in external magnetic fields oriented along the b -axis. (a) a -axis component and (b) b -axis component.	90
4.31	Ferroelectric polarization along the b -axis of $\text{Mn}_{0.85}\text{Co}_{0.15}\text{WO}_4$ in external magnetic fields oriented along the c -axis $P_b(H_c)$	91
4.32	(a) Magnetic susceptibility and (b) specific heat of $\text{Mn}_{0.85}\text{Co}_{0.15}\text{WO}_4$ in external magnetic fields oriented along the c -axis.	93
4.33	(a) Ferroelectric polarization and (b)specific heat of $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$ ($x = 0, 0.05, 0.1, 0.2$ and 0.3). Specific heat data are vertically offset for better clarity.	95
4.34	Phase diagram of $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$ derived from polarization and specific heat data.	96
4.35	(a) Ferroelectric polarization and (b)specific heat of $\text{Mn}_{0.95}\text{Cu}_{0.05}\text{WO}_4$ in external fields oriented along the b -axis.	97
4.36	Ferroelectric polarization measured along b -axis as a function of function of calculated entropy difference from specific heat data.	98

4.37	(a) Ferroelectric polarization and (b) specific heat of $\text{Mn}_{0.9}\text{Cu}_{0.1}\text{WO}_4$ in external fields oriented along the b -axis.	99
4.38	Ferroelectric polarization of $\text{Mn}_{0.95}\text{Cu}_{0.05}\text{WO}_4$ and $\text{Mn}_{0.9}\text{Cu}_{0.1}\text{WO}_4$ in external magnetic fields oriented along the magnetic <i>easy</i> axis.	100
4.39	(a) Ferroelectric polarization and (b) specific heat of $\text{Mn}_{0.8}\text{Cu}_{0.2}\text{WO}_4$ in external fields oriented along the b -axis.	100
4.40	(a) Ferroelectric polarization and (b) specific heat of $\text{Mn}_{0.7}\text{Cu}_{0.3}\text{WO}_4$ in external fields oriented along the b -axis.	101
4.41	Crystal structure of $R\text{Fe}_3(\text{BO}_3)_4$	104
4.42	In-plane (χ_x) and c -axis (χ_z) magnetic susceptibilities of $R\text{Al}_3(\text{BO}_3)_4$, where $R =$ (a) Tb and (b) Er.	106
4.43	In-plane (χ_x) and c -axis (χ_z) magnetic susceptibilities of $R\text{Al}_3(\text{BO}_3)_4$, where $R =$ (a) Tm, (b) $\text{Tm}_{0.5}\text{Yb}_{0.5}$, and (c) Yb. Inset of (c) shows the intersection of χ_x and χ_z	107
4.44	In-plane (χ_x) and c -axis (χ_z) magnetic susceptibilities of $R\text{Al}_3(\text{BO}_3)_4$, where $R =$ (a) $\text{Ho}_{0.5}\text{Tm}_{0.5}$, (b) Ho, and (c) $\text{Ho}_{0.5}\text{Y}_{0.5}$. The insets reveal the nearly isotropic magnetism of $\text{Ho}_{0.5}\text{Tm}_{0.5}\text{Al}_3(\text{BO}_3)_4$, and $\text{HoAl}_3(\text{BO}_3)_4$	109
4.45	(a) Longitudinal and (b) transverse magnetoelectric polarizations $P_x(H_x)$ and $P_x(H_y)$ of $\text{ErAl}_3(\text{BO}_3)_4$	112
4.46	(a) Longitudinal magnetoelectric polarization $P_x(H_x)$ of $\text{TmAl}_3(\text{BO}_3)_4$. Transverse magnetoelectric polarization $P_x(H_y)$ of $R\text{Al}_3(\text{BO}_3)_4$, where $R =$ (b) Tm, (c) $\text{Tm}_{0.9}\text{Yb}_{0.1}$, and (d) Yb.	114
4.47	(a) Longitudinal magnetoelectric polarization $P_x(H_x)$ of $\text{HoAl}_3(\text{BO}_3)_4$. Transverse magnetoelectric polarizations $P_x(H_y)$ of $R\text{Al}_3(\text{BO}_3)_4$, where $R =$ (b) Ho, (c) $\text{Ho}_{0.5}\text{Tm}_{0.5}$, and (d) $\text{Ho}_{0.5}\text{Y}_{0.5}$. The inset of $\text{HoAl}_3(\text{BO}_3)_4$ shows the $\Delta P_{xy} \propto H^2$ scaling in the magnetic fields below 10 kOe.	115
4.48	The crystal structure of the LiFeP_2O_7	117
4.49	Susceptibility of LiFeP_2O_7 measured at 1000 Oe along a, b and c -axis.	119
4.50	Temperature-depedent (a) b -axis susceptibility (χ_b) at 10Oe and (b) M_b of the LiFeP_2O_7 . Note that the perfect overlap of zero-field-cooled (ZFC) and field-collapsed (FC) data in (a) indicates the single domain property of the magnetic moments. The inset in (a) shows the AC susceptibility near the phase transition.	120
4.51	The magnetic structure of the LiFeP_2O_7 (a) in the a - c -plane and (b) in the a - b -plane. To better see how the spins are tilted, M^Y is shown 50 times larger in (c).	121

4.52	Heat capacity of LiFeP_2O_7 near magnetic transition temperature. . .	122
4.53	Pyroelectric current and polarization change (inset) as a function of temperature of LiFeP_2O_7	123
4.54	(a) Magnetoelectric polarization change ($\Delta P_b(H)$) and (b) magnetoelectric current, I_{me} at 5K, 15K and 35K. The bold circles in (a) show the polarization change in a negative magnetic field. The dash lines in (b) are a linear fit of the magnetoelectric current data.	124
4.55	(a) Relative length change of b , c , and perpendicular ($\perp$) to b and c with reference to 6 K. The inset in (a) shows the c -axis thermal expansivity $\alpha(T)$ (b) schematic plot of the most relevant super-super exchange interactions, J_3 and J_4 , between different iron moments (only FeO_6 octahedra are shown) Ref. [4].	126
4.56	Scaling plot of the magnetization of LiFeP_2O_7 . The critical exponent β is determined by the slope (red dash line).	131

List of Tables

2.1	Notations for the normal vector and propagation vector of the helical structure.	21
4.1	Magnetic anisotropy and effective magnetic moment of $RAl_3(BO_3)_4$ at 5 K, where $R = Tb$ and Er	105
4.2	Magnetic anisotropy and effective magnetic moment of $RAl_3(BO_3)_4$ at 5 K, where $R = Tm$, $Tm_{0.9}Yb_{0.1}$, and Yb	108
4.3	Magnetic anisotropy and effective magnetic moment of $RAl_3(BO_3)_4$ at 5 K, where $R = Ho$, $Ho_{0.5}Tm_{0.5}$, and $Ho_{0.5}Y_{0.5}$	110

Chapter 1

Purpose and Motivation

The first known magnet in human history is lodestone, naturally magnetized iron ore. From the Greek and Chinese antiquities, the ancient people use lodestone to attract iron and determine direction as compasses. On the other hand, the ancient Greeks found that amber attracts small objects after rubbed with fur. Combining with lightning, these are earliest human experience with electricity. In fact, both magnetic and electric phenomena are known for a long time and used in wide application. In recent years, people found the cross-coupling between magnetic and electric phenomena. The coexistence of spontaneous ordering of magnetic moments (magnetism) and electric dipoles (ferroelectricity) and their mutual interaction in solids are of significant both scientific and industrial interest. For physicists, it would be interesting to find new physics and materials with multiple interactions between different kinds of orders. By fine-tuning the multiple interactions, it might also be possible to find a link between ferroelectricity and superconductivity, and higher T_c could be achieved [5]. The recording and sensor industry are also looking into the multiple interaction types of material to explore possible new breakthrough. Therefore, we want to study of the interaction of the magnetic order or magnetic field with polarization or

dielectric properties of solids, the so called magnetoelectric (ME) effect.

The ME interaction can be found in different material systems distinguished by the crystal symmetry. For the first case, it is possible for a central symmetric material, no polarization allowed, becoming noncentrosymmetric and polar structure due to a special magnetic order breaking the inversion symmetry. The second consideration is the noncentrosymmetric but also nonpolar structure and the magnetic interactions transform the nonpolar structure into a polar structure. Last but not least, there are many polar crystals that also show magnetic order. In this type of material, the interaction between magnetic order and lattice polarization is of interest. Then, we consider three characteristic classes of samples for each case of material.

The first class of compound is multiferroics, where the magnetic frustrated system breaks spatial inversion symmetry in a centrosymmetric crystal through spin lattice coupling, allowing for electric polarization. One of ideal multiferroic compounds to study the effects is MnWO_4 since only Mn ion is magnetic. Co replacement for Mn in MnWO_4 controls the multiferroic properties through different spin values, tuning of exchange interactions and strong magnetic anisotropy, resulting in multiple reorientation of the spin spiral, multiple characteristics of magnetic orders and multiple flops of ferroelectric polarization. The applications of magnetic fields allow us to further manipulate the orientation of the spin spiral and electric polarization vector.

The second class of materials is the ME borates. $R\text{Al}_3(\text{BO}_3)_4$ (R = rare earth) compounds crystallize in a noncentrosymmetric but also nonpolar lattice structure, not allowing for polarization. Magnetic field or sometimes magnetic order could break the nonpolar structure through spin lattice coupling, giving rise to polar structure, which is called magnetoelectric (ME) effect. The $R\text{Al}_3(\text{BO}_3)_4$ system shows a paramagnetic feature without magnetic order at low temperature because of the weak coupling between the rare earth moments. However, the single rare earth moment

shows a strong magnetic anisotropy and strong coupling to the lattice, resulting in ME effect. Furthermore, $\text{HoAl}_3(\text{BO}_3)_4$ exhibits a very large ME effect, which is the record of highest ME effect compound in high fields before $\text{CaBaCo}_4\text{O}_7$ was recently reported [6].

The third class of compound is the polar LiFeP_2O_7 . It contains macroscopic electric polarization due to its polar structure, but it also has magnetic Fe-moments to form magnetic order at low temperature. This particular magnetic order is canted antiferromagnetic (AFM). Therefore, we are interested in how the canted AFM order affects the lattice polarization. Importantly, it verifies the existence of strong coupling between magnetic order and lattice polarization, which can be described well by the mean field theory.

The following chapter, Chapter 2, will give a broad but concise review of the fundamental physical phenomena that is important in this work: magnetic order, ferroelectricity, magnetoelectric effect, and multiferroics. In addition, the notations that are frequently used through most of Chapter 4 are also established in Chapter 2. Chapter 3 will cover experimental methods utilized for all measurements, while Chapter 4 will cover the pertinent results from the measurements followed with discussion. Finally, Chapter 5 will summarize the results with highlights on some of the unanswered questions and conclude with ongoing work.

Chapter 2

Background

This chapter will provide a short review of the key concepts that will be used in the latter discussion. The basic definition of magnetoelectric effect is the interaction of the electric (magnetic) orders by magnetic (electric) field due to the coupling of the magnetic and electric subsystems in matter [7]. The discussion will focus on the magnetic order and ferroelectricity in materials. It will then be followed by the magnetoelectric effect and more strict definition of the multiferroic compounds [7, 8].

2.1 Magnetic orders in matter

2.1.1 The Curie-Weiss Law

Since the *Curie – Weiss* Law will be intensively used in Chapter 4, it will be shortly discussed here and explained how it will be used. Assume magnetic moments μ of the ions in materials (from unfilled shell of d – or f –electrons in the ions) have the energy $-\mu \cdot H$ in the magnetic field H . Each atom is independent from the others and satisfies Boltzmann statistics because of the localization of the magnetic moment.

In other words, the important condition for the *Weiss* formula is to assume that there is no interaction between spins. The average moment [9] is

$$\langle \mu \rangle = \int \mu e^{\frac{\mu \cdot H}{kT}} d\Omega / \int e^{\frac{\mu \cdot H}{kT}} d\Omega \quad (2.1)$$

where $d\Omega$ is the element of the solid angle for the rotation of μ . Then, the *Weiss* paramagnetic susceptibility can be derived as [9],

$$\chi = N \frac{\partial \langle \mu \rangle}{\partial H} = \frac{N \langle \mu^2 \rangle}{kT} \quad (2.2)$$

where N refers to the number of atoms per unit volume. The Eq. 2.2 is valid for independent and non-interacting spins, which sometimes is realized if the spins are spatially far-separated to each other, corresponding to the assumption of the independence.

However, most spin systems do interact in a certain way that is difficult to resolve rigorously. Therefore, it is approximately to consider one single spin in a effective field from the surrounding spins. Then, the effective *Weiss field* can be written as $H_I = \lambda N_I \langle \mu \rangle$, where λ is the strength of the interaction. The total field is $H_{total} = H + H_I$, and the magnetic moments become

$$N \langle \mu \rangle = \frac{N \langle \mu^2 \rangle}{kT} (H + \lambda N_I \langle \mu \rangle) \quad (2.3)$$

which gives

$$\chi \equiv N \langle \frac{\partial \mu}{\partial H} \rangle = \frac{N \langle \mu^2 \rangle}{k(T - \Theta)} \quad (2.4)$$

where $\Theta = \frac{\lambda N_I \langle \mu^2 \rangle}{k}$

This is the *Curie – Weiss* Law, where the positive Θ means that the magnetic interaction helps to align the adjacent moments in the same direction, corresponding to the ferromagnetic (FM) response, whereas negative Θ refers to antiferromagnetic (AFM) coupling. At this point, we only consider the single moment μ ; however, for magnetic ions, the total magnetic moment is a superposition of spin and orbital moments. Therefore, it is necessary to consider the total electronic spin and orbital angular momenta, S and L , as well as the total electronic angular momentum $J = L + S$.

For ideal paramagnetic materials, the magnetization of N magnetic ions in a volume V gives [10]

$$\vec{M} = \frac{N}{V} g(J, L, S) \mu_B J B_J \left(\frac{g(J, L, S) \mu_B J H}{kT} \right) \quad (2.5)$$

where g and μ_B are Landé g factor and Bohr magneton, respectively, and the Brillouin function $B_J(x)$ is defined by

$$B_J(x) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J} x - \frac{1}{2J} \coth \frac{1}{2J} x \quad (2.6)$$

For the low temperature ($T \rightarrow 0$) and high field limit, $M \rightarrow (N/V)g(J, L, S)\mu_B J$; i.e., all magnetic ions are aligned in the field direction, which is the saturation moment J . For transition metal ions in an insulating solid, due to the quenching of the orbital momentum by the crystal field splitting, the saturation moment J is equal to the spin moment S so that this value can be directly compared to the spin component in a particular direction from the neutron scattering refinement results.

For the high temperature limit (small x), $\coth x \approx \frac{1}{x} + \frac{1}{3}x$, and therefore, $B_J(x) \approx \frac{J+1}{3J}x$. It will give rise to

$$\chi = \frac{N}{V} \frac{(g\mu_B)^2}{3} \frac{J(J+1)}{kT} \quad (2.7)$$

The inverse relationship of magnetic susceptibility and temperature from *Curie – Weiss* Law could be used to fit the experimental magnetic susceptibility data and to calculate the effective moment $\mu_{eff} = g(J, L, S)\sqrt{J(J+1)}$. It should be noted that the effective moment is the total spin moment for transition metal ions in insulators, and therefore, one should consider all the spin components in different directions while comparing to the neutron scattering refinements.

The *Curie – Weiss* Law provides a fundamental explanation on the FM as well as AFM order and a chance for the bulk measurements to compare with microscopic measurements such as neutron scattering. Besides the FM and AFM orders, there are still other interesting and exotic magnetic orders, which will be discussed in the next subsection.

2.1.2 Noncollinear magnetic orders

The strong competition of different magnetic exchange interactions (FM or AFM) is usually the reason why a magnetic system is highly frustrated and the noncollinear spin spiral is formed. For example, one of the previous work from our group [1] qualitatively describes the conditions for the ground state spin spiral or up-up-down-down E-type magnetic order based on a mean-field model with competing interactions. It considers a simple Heisenberg model as [1],

$$H_H = \sum_n [J \vec{S}_n \cdot \vec{S}_{n+1} + J' \vec{S}_n \cdot \vec{S}_{n+1} - K(S_n^z)^2] \quad (2.8)$$

where competing nearest neighbor interaction (J), next-nearest-neighbor interaction (J') and spin anisotropy (K) are considered. A ground state phase diagram in mean-field approximation is therefore obtained [1]. At $K = 0$, the ground state is FM for $J'/|J| < 1/4$, and the ground state becomes noncollinear spin spiral structure if J' is large enough. The spin spiral can be described as

$$\vec{S}_n = S[\vec{e}_1 \cos \vec{Q} \cdot \vec{x}_n + \vec{e}_2 \sin \vec{Q} \cdot \vec{x}_n] \quad (2.9)$$

where $\vec{e}_1$ and $\vec{e}_2$ are two orthogonal unit vectors and the wavevector $\vec{Q}$ is determined by $\cos(\vec{Q}/2) \cdot \vec{x}_n = -J'/(4J)$. The non-collinear spiral magnetic structure spontaneously breaks spatial inversion symmetry, which sometimes allows for the presence of ferroelectric polarization, as shown in Fig. 2.1(d). In contrast, a sinusoidal structure as Fig. 2.1(b), $\vec{S}_n = S \cos \vec{Q} \cdot \vec{x}_n$, preserves the spatial inversion symmetry. Furthermore, with large enough K value, the ground state becomes collinear again and stabilizes up-up-down-down E-type magnetic order (Fig. 2.1(a)) when $J'/|J| > 1/2$ condition is fulfilled.

There are actually other types of exotic magnetic ordering possibly due to magnetic frustration and anisotropy. Fig. 2.1(c) shows the a screw spiral structure, whose spin rotation axis is parallel to the propagation $\vec{Q}$ vector. A cycloidal spiral structure is realized if the spin rotation axis is perpendicular to the $\vec{Q}$ vector (Fig. 2.1(d)). The most complex cases are conical structures, where a ferromagnetic component coexists with the screw (Fig. 2.1(e)) or cycloidal (Fig. 2.1(f)) component. These conical structures are generally obtained by applying an additional magnetic field to

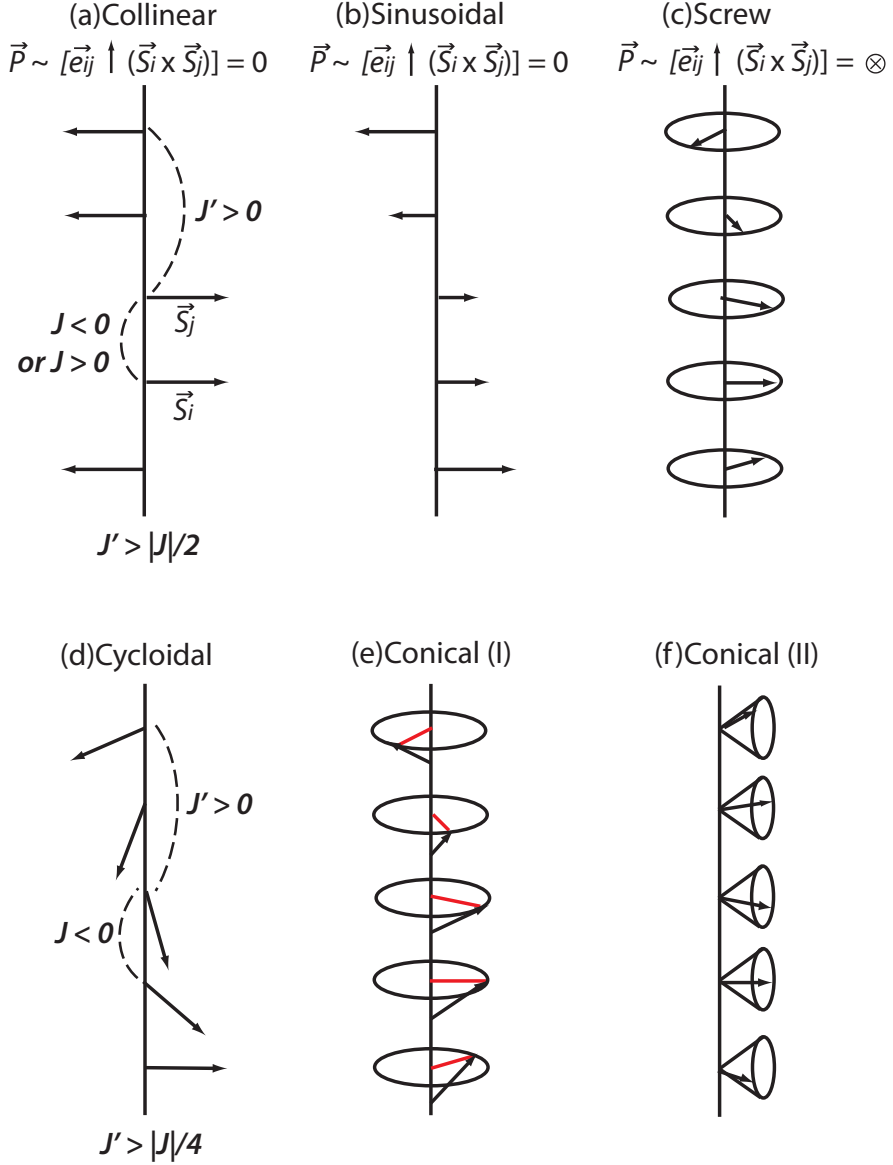


Figure 2.1: Schematic illustration of types of magnetic structure with a long wave length. (a) Collinear up-up-down-down, (b) sinusoidal, (c) screw (d) cycloidal (e, f) conical structures. Geometric configurations of the unit vector connecting the neighbor magnetic moments at i and j sites $\vec{e}_{ij}$ and the vector chirality $(\vec{S}_i \times \vec{S}_j)$ are also shown for respective structures. For (a) and (d), frustrated spin chains with nearest-neighbor FM and next nearest-neighbor AFM interactions J and J' for a Heisenberg model as Eq. 2.8 [1, 2, 3].

the existing screw or cycloidal spiral structure.

2.1.3 Magnetic anisotropy

The magnetic anisotropy generally exists in materials, which might also give rise to noncollinear magnetic ordering due to a preferred orientation of the magnetic moments. There are several kinds of anisotropy as,

- Magnetocrystalline anisotropy is from the interactions of the magnetic moments with the crystal lattice. It mostly arises from spin-orbit coupling and is also strongly dependent on the crystal symmetry .
- Shape anisotropy is due to the unequal demagnetization depending on the shape of the sample.
- Magnetoelastic anisotropy comes from crystal structure change due to stress in the presence of magnetic field.
- Exchange anisotropy occurs when the magnetic exchange interactions are different along different orientations in the structure.

It is the magnetic anisotropy in combination with the conservation of inversion symmetry that the sinusoidal ordering usually appears at higher temperature than the spiral structure, which explains that the temperature of ferroelectric in frustrated magnets is typically lower than the temperature of the first magnetic transition [11, 12, 13].

2.2 Ferroelectricity

2.2.1 Polarization

The polarization $\vec{P}$ is defined as the dipole moment per unit volume, averaged over the volume of unit cell. The electrostatic potential in CGS units of a dipole $\vec{p}$ is $\Phi(r) = \vec{p} \cdot (\nabla \frac{1}{r})$. Then, it can be expressed in terms of $\vec{P} dV = \vec{p}$ as [14]

$$\Phi(r) = \int dV (\vec{P} \cdot (\nabla \frac{1}{r})) \quad (2.10)$$

Integrating by parts, it becomes

$$\Phi(r) = \int dV (-\frac{1}{r} \nabla \cdot \vec{P} + \nabla \cdot (\frac{\vec{P}}{r})) \quad (2.11)$$

Using the divergence theorem,

$$\Phi(r) = \oint_S \frac{1}{r} \vec{P} \cdot d\vec{a} - \int dV \frac{1}{r} (\nabla \cdot \vec{P}) \quad (2.12)$$

The first term in Eq. 2.12 refers to the surface bound charge $\sigma_b \equiv \vec{P} \cdot \vec{n}$, where $\vec{n}$ is the normal vector to the surface. The second term is related to volume charge $\rho_b \equiv -\nabla \cdot \vec{P}$, and however, all our samples for pyroelectric current measurement are insulators so that this term is zero. Therefore, polarization is equivalent to the surface charge density ($|P| = Q/A = \sigma_b$). The change of $\vec{P}$, therefore, results in the change of σ_b . If there are metallic contacts on the sample, it causes measurable pyroelectric current due to the change of the $\vec{P}$.

2.2.2 General properties of ferroelectric materials

Ferroelectricity is a property of certain materials which have spontaneous electric polarizations that can be reversed by the application of external electric field. The polarization is dependent not only on the current electric field but its history, yielding a hysteresis loop. Therefore, there are some features of ferroelectricity that we can use to identify ferroelectricity during the experiments:

- At the ferroelectric (FE) transition temperature T_C , a FE crystal transforms to a phase of higher symmetry, and the higher temperature phase is paraelectric.
- The hysteresis loop with respect to external electric fields disappears above the Curie temperature T_C .
- Ferroelectricity generally gives rise to a large dielectric constant ε right at the transition temperature, indicating that charges are extremely susceptible to external electric field when the transition just happens. After the transition is finished, the polarization tends to be saturated so that the ε decreases, resulting in a rise of a peak of ε at T_C
- Above T_C , the dielectric constant usually obeys the *Curie – Weiss* Law.

2.3 Landau theory of phase transition

In the previous sections, it was discussed about the orders of magnetic moments and electric polarization. All these orders have experienced a phase transition at a critical temperature. If the first derivative of the free energy with respect to temperature (entropy) is non-analytical at the transition temperature, it is a first-order phase transition. Furthermore, if the first derivative is analytical but the second derivative term (specific heat) is not, it is a second-order phase transition. The Landau theory

of phase transition is established in the attempt to investigate the question about second-order phase transition from the general thermodynamic point of view by L. Landau [15].

At the temperature close to the transition temperature, a phenomenological expression for the Landau free energy F can be written down as a series expansion of the order parameter, and here, polarization P is used [16]. All the involved terms should be invariant to all the necessary symmetry operations at the high temperature phase. For example, the odd powers of P are not invariant with respect to spatial inversion symmetry, and are not allowed. In the mean-field consideration without any spatial fluctuation of the order parameter P , the free energy has the form of

$$F(P, T, t) = -EP + \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \dots \quad (2.13)$$

where a, b and c are in general temperature dependent coefficients. In thermal equilibrium, P is determined from the minimum of the free energy F as

$$\frac{\partial F}{\partial P} = 0 = -E + aP + bP^3 + cP^5 + \dots \quad (2.14)$$

To approach the ferroelectric state, the aP^2 term in Eq. 2.13 is assumed to pass through zero at a temperature T_0 ,

$$a = a_0(T - T_0) \quad (2.15)$$

where a_0 is a positive constant and $T_0 \leq$ transition temperature.

For the modeling of a second-order transition, b is assumed to be positive and

c can be neglected, and therefore, the polarization for zero external electric field is obtained from Eq. 2.14 as,

$$0 = a_0(T - T_0)P + bP^3 = (a_0(T - T_0) + bP^2)P \quad (2.16)$$

Except for the $P = 0$ solution, the $P \neq 0$ for $T < T_0$ is the second solution for Eq. 2.16, and therefore, T_0 is referred to Curie temperature T_C so the spontaneous polarization P_S has the following expression,

$$P_s = \left[\frac{a_0}{b} (T - T_0) \right]^{1/2} \quad (2.17)$$

P_S is therefore continuously increasing with decreasing temperature below T_C , which corresponds to the nature of the second-order phase transition.

To extend the Landau theory to the description of the first-order phase transition, the coefficient b is assumed to be negative and c to be positive in Eq. 2.13. It is important to take c a positive value to reach a converging finite value of P . From Eq. 2.14, the equilibrium condition for $E = 0$ is,

$$a_0(T - T_0)P - |b|P^3 + cP^5 = 0 \quad (2.18)$$

So the solution is either $P_s = 0$ or

$$a_0(T - T_0) - |b|P^2 + cP^4 = 0 \quad (2.19)$$

For the first-order phase transition, the T_0 is less than T_C because there are unpolarized phases exist as a local minimum of the free energy. At the same time, a more

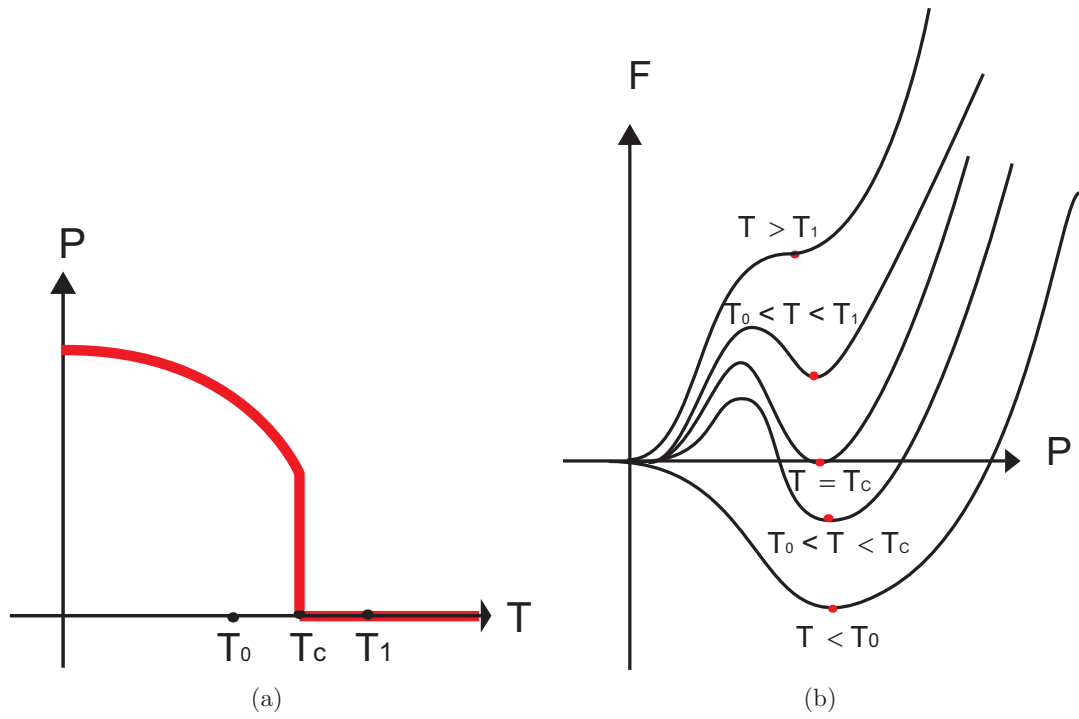


Figure 2.2: First-order phase transition: Schematic representation of the temperature profile of (a)polarization. (b) The free energy as a function of polarization.

important feature for the first-order phase transition is that the P shows a sudden drop and decreases discontinuously to zero at T_C as shown in Fig. 2.2(a). For the free energy density, following the conditions for the first-order transition in Eq. 2.19, the resulting free energy as a function of polarization P in different temperature range is shown in Fig. 2.2(b). At $T = T_0$, the only minimum of the free energy refers to the high value of the P at the temperature range below $T = T_0$. As shown in Fig. 2.2(b) with $T_0 < T < T_1$ condition, there are three solutions shown by the extremum of the free energy, and the corresponding maximum value is an unstable stable. Thermal equilibrium state is at T_c with two minima referring to $P = 0$ and the maximum polarization at $F = 0$. For $T = T_1$, it is the highest temperature for a metastable ferroelectric state.

Therefore, the identification of the first-order phase transition in temperature-dependent experiment is guided by the above discussion. The characteristic is the sudden jump of the polarization value P (Fig. 2.2(a)) at T_c with a possible temperature hysteresis of $\Delta T = T_1 - T_0$.

2.4 Magnetoelectric effect

The coexistence of magnetic and polarization orders in a material allows for the cross-control of these two order parameters by electric (magnetic) field to be realized, so called magnetoelectric (ME) effect [7]. Curie [17] first conjectured the existence of materials that can be electrically polarized by an external magnetic field. Debye [18] coined the term "magnetoelectric". After few decades, Dzyaloshinskii [19] showed the possibility of the linear ME effect in the antiferromagnetic Cr_2O_3 , which was soon experimentally confirmed by Astrov [20].

The ME effect can also be described by Landau free energy expansion in terms of

electric field E_i and magnetic field H_i as,

$$F(\vec{E}, \vec{H}) = F_0 - P_i^S E_i - M_i^S H_i - \frac{1}{2} \epsilon_0 \epsilon_{ij} E_i E_j - \frac{1}{2} \mu_0 \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j - \frac{\beta_{ijk}}{2} E_i H_j H_k - \frac{\gamma_{ijk}}{2} H_i E_j E_k - \dots \quad (2.20)$$

where P_i^S and M_i^S are the spontaneous polarization and magnetization, respectively. Permittivity (permeability) in free space is ϵ_0 (μ_0), and the relative permittivity (permeability) tensor is $\epsilon_{ij}(T)$ ($\mu_{ij}(T)$). Then, the field dependent polarization and magnetization can be derived as,

Polarization

$$P_i(\vec{E}, \vec{H}) = - \frac{\partial F}{\partial E_i} = P_i^S + \epsilon_0 \epsilon_{ij} E_j + \alpha_{ij} H_j + \frac{\beta_{ijk}}{2} H_j H_k + \frac{\gamma_{ijk}}{2} H_i E_k + \dots \quad (2.21)$$

and Magnetization

$$M_i(\vec{E}, \vec{H}) = - \frac{\partial F}{\partial H_i} = M_i^S + \mu_0 \mu_{ij} H_j + \alpha_{ij} E_j + \frac{\beta_{ijk}}{2} E_j H_k + \frac{\gamma_{ijk}}{2} E_j E_k + \dots \quad (2.22)$$

The linear magnetoelectric effect (finite value in α tensor) refers to induction of electric polarization (magnetization) by a magnetic (electric) field in a linear relationship. In some materials, higher order terms become more significant.

2.5 Multiferroics

In 1994, Schmid [8] started the use of the term "multiferroics", defined as that two or more of the ferroic properties (ferromagnetic, ferroelectric, ferroelastic, or ferrotoroidic) coexist in the same phase. Why is the multiferroics so interesting to people?

That is because the linear ME effect has been shown to be limited by the relation $\alpha_{ij}^2 < \chi_{ij}^e \chi_{ij}^m$ [21, 22, 23], where χ_{ij} refer to electric (e) and magnetic (m) susceptibility. With the coexistence of ferroelectric and ferromagnetic orders in a phase, multiferroics has the potential to maximize both electric and magnetic susceptibility to enlarge the ME effect, particularly near phase transitions. Some typical examples of multiferroic compounds are TbMnO_3 [24], $\text{Ni}_3\text{V}_2\text{O}_8$ [11] and MnWO_4 [25, 26]. People found antiferromagnetic (AFM) multiferroic compounds so that the definition of ferroic was extended to include the AFM order. MnWO_4 is known to exhibit ferroelectricity induced by helical magnetic order, where helical order breaks the inversion symmetry to allow the polarization, which will be discussed in the next subsection.

2.5.1 Ferroelectricity induced by spiral magnets

The free energy expansion that couples the electric polarization $\vec{P}$ and magnetization $\vec{M}$ can be derived by Ginzburg-Landau type of the continuum field based on the general symmetry arguments [13]. Time reversal operation, $t \rightarrow -t$, transforms $\vec{P} \rightarrow \vec{P}$ and $\vec{M} \rightarrow -\vec{M}$ so that $\vec{M}$ is limited to be quadratic. Upon the spatial inversion, $\vec{x} \rightarrow -\vec{x}$, the $\vec{P} \rightarrow -\vec{P}$ and $\vec{M} \rightarrow \vec{M}$ is excepted. Therefore, the lowest order coupling of uniform polarization to an inhomogeneous magnetization is linear in $\vec{P}$ and contains a gradient of $\vec{M}$, where the gradient of an order parameter is the Lifshitz invariant (LI). The LI is allowed by symmetry when the specific magnetic structure breaks the inversion symmetry.

With consideration of simple cubic symmetry, the coupling is

$$\Phi_{em}(\vec{P}, \vec{M}) = \gamma \vec{P} \cdot [\vec{M}(\nabla \cdot \vec{M}) - (\vec{M} \cdot \nabla)\vec{M} + \dots] \quad (2.23)$$

where Φ_{em} is the ME energy.

Assuming that in the absence of magnetism the system is paraelectric. We only keep the quadratic term in the electric part of the thermodynamic potential, $\Phi_e(P) = \frac{P^2}{2\chi_e}$, where χ_e is the dielectric susceptibility. Minimizing $\Phi_{em} + \Phi_e$ with respect to P , we get

$$\vec{P} = \gamma\chi_e[\vec{M}(\nabla \cdot \vec{M}) - (\vec{M} \cdot \nabla)\vec{M}] \quad (2.24)$$

Consider a spin spiral with propagation vector $\vec{Q}$,

$$\vec{M} = M_1 \vec{e}_1 \cos \vec{Q} \cdot \vec{x} + M_2 \vec{e}_2 \sin \vec{Q} \cdot \vec{x} + M_3 \vec{e}_3 \quad (2.25)$$

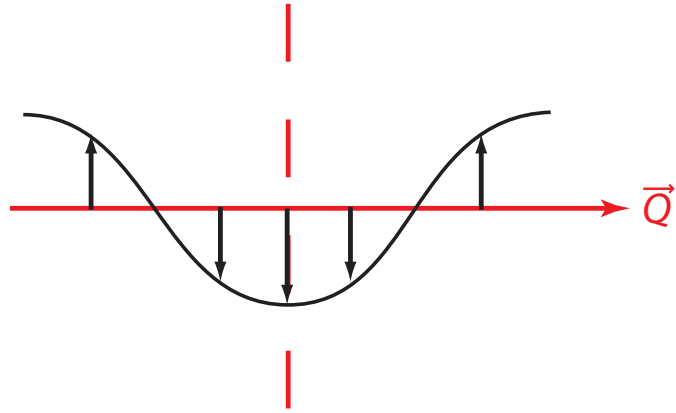
where the $\vec{e}_i$, $i = 1, 2, 3$, are unit vectors forming a orthogonal coordinate. If either M_1 or M_2 is zero (and $M_3 = 0$), Eq. 2.25 becomes a sinusoidal wave [Fig. 2.3(a)]. While both M_1 and M_2 have finite value, it represents an elliptical helix [Fig. 2.3(b)] with spin rotation axis along $\vec{e}_3$ (if $M_3 \neq 0$, it is a conical structure). By Eq. 2.24 and 2.25, the direction of polarization is transverse to both $\vec{e}_3$ and $\vec{Q}$ and independent of M_3 ,

$$\vec{P} = \gamma\chi_e M_1 M_2 [\vec{e}_3 \times \vec{Q}] \quad (2.26)$$

No polarization can be induced by a sinusoidal phase because either zero M_1 or M_2 gives rise to zero value in Eq. 2.26.

The result is consistent with the spin-current model in microscopic picture for the local polarization as [27]

(a) Sinusoidal $P = 0$



(b) Helix

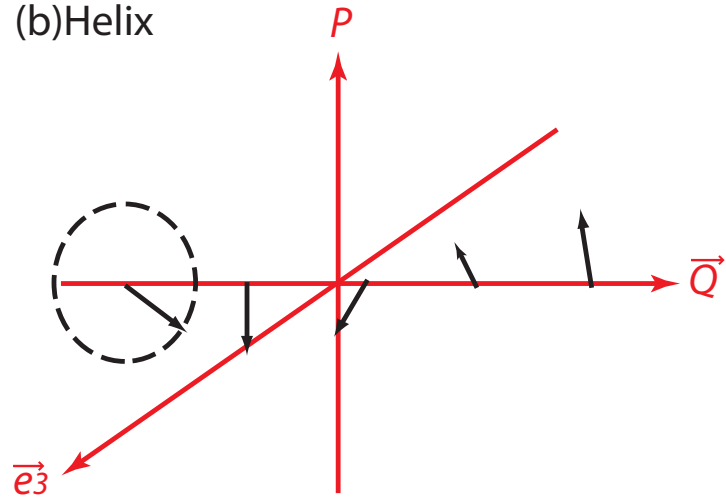


Figure 2.3: Schematic illustration of (a) sinusoidal (no polarization) and (b) helical ($\vec{P}$ is perpendicular to both $\vec{e}_3$ and wave vector $\vec{Q}$) magnetic structure.

$$\vec{P}_e \sim \vec{e}_{12} \times [\vec{S}_1 \times \vec{S}_2] \quad (2.27)$$

where $\vec{S}_1$ and $\vec{S}_2$ are noncollinear spins. The $\vec{e}_{12}$ connects these two spins (Fig. 2.4).

From the Eq. 2.26 and 2.27, as long as the vector product of normal vector of the spin helix and its propagation vector is not zero, the spin helix gives rise to finite polarization along the direction perpendicular to both vectors. Therefore, the notations for the above-mentioned two vectors from Eq. 2.26, 2.27 and chapter 4 are summarized in table 2.1. In the Co or Cu doped MnWO_4 system (chapter 4), the direction of spin helix and polarization becomes very complex when the temperature or applied field is changed so that the bottom line is to first find $\vec{k}$ and $\vec{c}$ vectors and calculate the vector product to evaluate the direction of the polarization, as shown in Fig. 2.4.

Table 2.1: Notations for the normal vector and propagation vector of the helical structure.

	Eq. 2.26	Eq. 2.27	Chapter 4
Normal vector of helical plane	$\vec{e}_3$	$\vec{S}_1 \times \vec{S}_2$	$\vec{k}$
Propagation vector direction	$\vec{Q}$	$\vec{e}_{12}$	$\vec{c}$

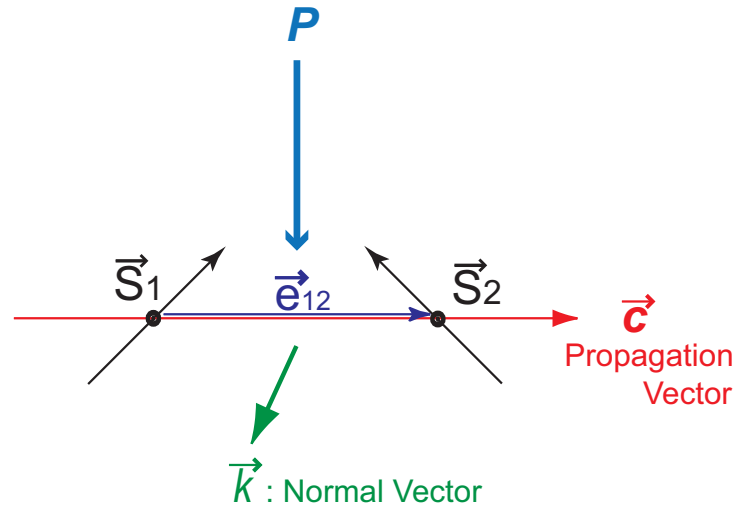


Figure 2.4: Schematic illustration of normal vector ($\vec{k} \propto \vec{S}_1 \times \vec{S}_2$) and propagation vector $\vec{c}$ of the helical structure. The polarization $\vec{P}$ is in the direction of $(\vec{c} \times \vec{k})$.

Chapter 3

Methodology

3.1 Sample preparation

3.1.1 Monoclinic $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ and $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$: Floating zone technique

Polycrystalline $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ ($x = 0, 0.02, 0.035, 0.042, 0.05, 0.075, 0.1, 0.12, 0.135, 0.15, 0.17, 0.2, 0.25$, and 0.3) was synthesized by solid state reaction of proper stoichiometric amounts of MnO_2 (99.9%), WO_3 (99.9%), and Co_3O_4 (99.9%), and further annealed at 850°C for 24 hours. X-ray diffraction study was then done to check the formation of single phase. The compressed polycrystalline feed rod was annealed at 1010°C for 24 hours to prepare the single crystal in an optical floating zone halogen furnace. The vertical movement speed of the feed rod is usually $0.8 - 1.5$ mm/hour.

The precursor of $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$ ($x = 0.05, 0.1, 0.2$, and 0.3) was made also by a solid state reaction of appropriate mixture of MnO_2 (99.9%), WO_3 (99.9%), and

CuO (99.9%) at 850°C for 24 hours. The single crystals are also grown in an optical floating zone furnace. The single crystals of $Mn_{1-x}Co_xWO_4$ and $Mn_{1-x}Cu_xWO_4$ were made by Y. Q. Wang in HPLT laboratory, TcSUH.

3.1.2 Trigonal $RAl_3(BO_3)_4$: Flux method

$RAl_3(BO_3)_4$ ($R = Tm, Tm_{0.9}Yb_{0.1}$, and Yb) were made by fluxes based on bismuth trimolybdate $Bi_2Mo_3O_{12}$ and lithium molybdate $LiMoO_4$. The flux was prepared by alloying proper stoichiometric amounts of $(Bi_2O_3 + MoO_3)$, B_2O_3 , $(Tm_2O_3 + Yb_2O_3 + Al_2O_3)$, and $(L_2CO_3 + MoO_3)$ oxides at $T = 1050-1100^\circ C$. Once the flux is well-prepared, it was placed in a crystallization furnace with a vertical temperature gradient of 1–2°C from highest temperature of 1000°C (details in Ref. [28]). $RAl_3(BO_3)_4$ ($R = Tb, Er, Tm, Tm_{0.9}Yb_{0.1}$, Yb, $Ho_{0.5}Tm_{0.5}$, Ho, and $Ho_{0.5}Y_{0.5}$) samples are provided by L. N. Bezmaternykh *et al.* from Institute of Physics, Siberian Division, Russian Academy of Sciences, Russia.

3.1.3 Monoclinic $LiFeP_2O_7$: Flux method

Polycrystalline $LiFeP_2O_7$ was synthesized by solid state reaction of proper stoichiometric amounts of LiH_2PO_4 (97%), Fe_2O_3 (certified) and $NH_4H_2PO_4$ (98.0%), and further annealed in three different process (details in Ref. [29]). Powder XRD measurements were done to confirm the purity of the polycrystalline samples. Single-crystalline $LiFeP_2O_7$ was made by top seeded growth method (details in Ref. [29]). Single crystals were provided by W. Zhang *et al.* from Department of Chemistry, University of Houston.

3.2 Sample characterization

3.2.1 Crystal orientation

The analysis of the structural quality of the crystals was done using a GADDS X-ray diffractometer (Bruker) by Y. Y. Sun in the HPLT Laboratory, TcSUH, and the crystals were aligned along the principal crystallographic directions by the same method.

3.2.2 Magnetic measurements

Magnetic properties of the samples were characterized with SQUID magnetometer in commercial Magnetic Property Measurement System (MPMS, Quantum Design). Either DC or AC magnetization measurements can be done in the temperature range from 2 K to 400 K and the maximum magnetic field can be applied along different crystallographic orientations up to 5 Tesla. In this work, DC $M(T)$ was measured mostly at magnetic field of ~ 100 to 1000 Oe due to small signal of antiferromagnetic or paramagnetic orders to identify magnetic phases (Sec. 4.1.2.2). To determine the *Weiss* temperature and effective moment (Sec. 4.2.1 and 4.3.1), we measure $M(T)$ of samples up to 300 K, and fit the inverse susceptibility from the $M(T)$ data to the *Curie – Weiss* formula (Eq. 2.7), as mentioned in Sec. 2.1.1. Because of the interest in the magnetoelectric effect, it is particularly important to measure $M(T)$ in different magnitude and orientations of magnetic fields to investigate the magnetic responses. In Sec. 4.3.1, the AC susceptibility was measured in frequency 117 HZ with field amplitude of 1 Oe to identify the second-order phase transition and the transition temperature.

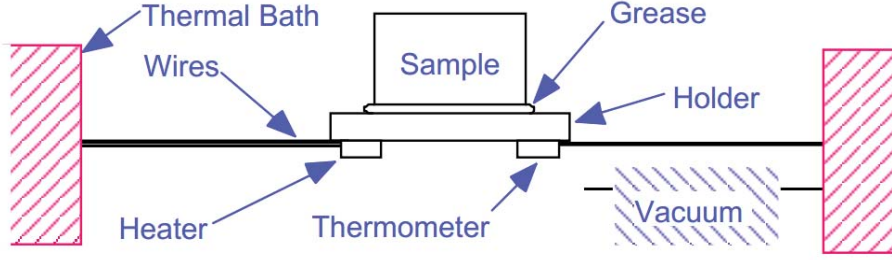


Figure 3.1: Schematic illustration of the sample platform in PPMS heat capacity option.

3.2.3 Heat capacity measurements

Specific heat measurements were done with heat capacity option of the Physical Property Measurement System (PPMS, Quantum Design) [30]. It measures the heat capacity at a constant pressure as

$$C_p = \left(\frac{dQ}{dT} \right)_p \quad (3.1)$$

where Q is heat in energy units (Joules). The specific heat is defined as heat capacity per amount of material. The Quantum Design heat capacity option utilizes a relaxation technique. Each measurement cycle contains a heating period followed by a cooling period, and fits the entire temperature response of the sample platform to a thermal relaxation model.

The sample is mounted on a sample platform, and a thin layer of grease is put in between sample and platform to ensure a good thermal contact, as shown in Fig. 3.1. Both platform heater and platform thermometer are attached to the bottom side of the sample platform. Eight small wires are used for the electrical connections to the heater and thermometer, and provide structural support for the sample platform. At the desired temperature, the system waits until thermal equilibrium of the sample

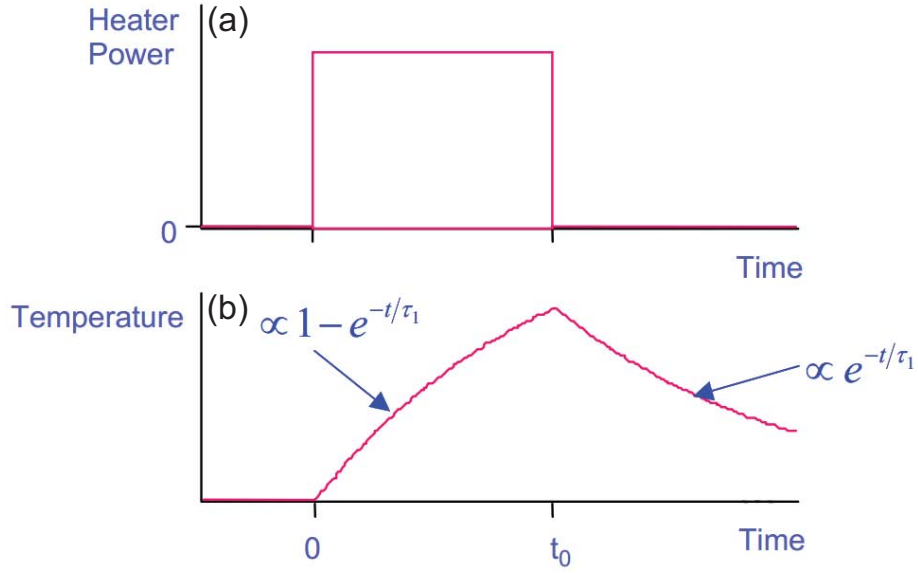


Figure 3.2: (a) Heater power and (b) the responding temperature with time of the heat capacity measurement.

platform and thermal bath (puck) is established. The sample platform is also in high vacuum so that the heat link between sample platform and the heat bath is established by pure thermal conductance through the wires. Once it is in thermal equilibrium, a known amount of heat is first applied to the sample at a fixed period of time with a constant power [from $Time = 0$ to t_0 in Fig. 3.1(a)], and then, the sample is cooled down in the same duration of time.

Fig. 3.2(b) shows the temperature response during the measurement. Then, if the sample and sample platform are in good thermal contact, the software of the heat capacity option will try to fit the temperature response with a thermal relaxation model. The software always first uses two- τ model to fit the temperature response. The two- τ model simulates the effect of heat flowing between the sample and platform, and the heat flow between the platform and thermal bath [30] because the temperature difference due to poor thermal contact is produced between sample and platform.

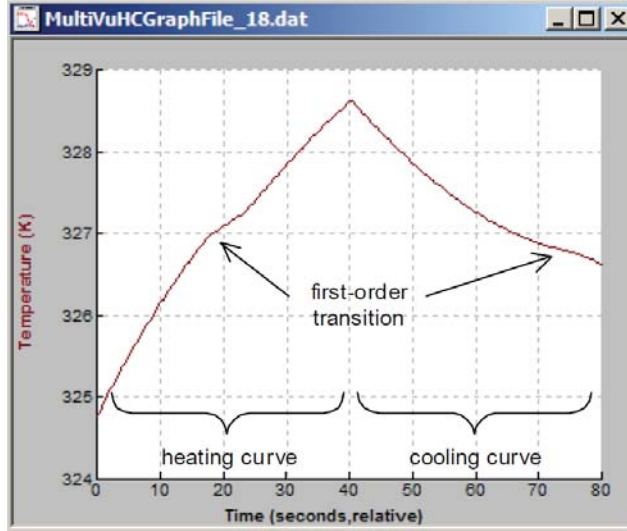


Figure 3.3: Example of distorted temperature response near a first-order transition.

When the analysis of the sample heat capacity measurement fails to find a fit to a two- τ solution, the simple fit of one- τ model is used. In the simple model, the temperature T of the platform as a function of time t obeys the equation,

$$C_{total} \frac{dT}{dt} = -K(T - T_b) + P(t) \quad (3.2)$$

where C_{total} is the total heat capacity of the sample and the sample platform; K is the thermal conductance of the supporting wires. T_b is the temperature of the thermal bath (puck), and $P(t)$ is the heat power from the heater, which is a constant during the heating period as shown in Fig. 3.2(a). The solution of this equation is an exponential function with a time constant $\tau = C_{total}/K$.

However, if the sample experiences a first-order phase transition, the latent heat causes a distorted temperature response during the relaxation measurement as shown Fig. 3.3. The first-order transition associated with the latent heat appears as a very sharp and narrow peak in the heat capacity. If the width of this peak is smaller than

the temperature rise in the heating period, there is a certain level of missing entropy change depending on the overlap of the peak width and temperature rise. Therefore, a special procedure regarding performing slope analysis with modified simple relaxation model is necessary to reveal the best of the measurement [30].

3.2.4 Polarization measurements

The polarization generates a surface charge density as $\sigma_b \equiv \vec{P} \cdot \vec{n}$, from Eq. 2.12. Fig. 3.4(a) shows a polar crystal with intrinsic dipole moments, and spontaneous polarization $\vec{P}_S$ corresponds to the surface charge density. In order to measure the change of spontaneous polarization $\vec{P}_S$ with temperature, the sample was polished to around 1mm thick followed with the preparation of two electrodes (silver paste) on the top/bottom of the sample and the electronic connection to the ammeter (Keithley electrometer K6517A), as shown in Fig. 3.4(b). The coax cables (99% shielded) were used for the electronic connection to reduce the noise current from the order of 10^3 pA for standard cable down to 0.1 pA [31]; the use of coax cables significantly increases the resolution of our pyroelectric current measurements. Then, the increase of temperature may decrease the spontaneous polarization $\vec{P}_S$, for example through the rotation of the dipole moments or the decrease of the magnitude of dipole moments, resulting in the decrease of bound surface charges. Because the surface charges bind with free charges in the metal electrodes, the free charges produce a current flow from the ammeter to compensate the change of the surface charge density, which is the same to the polarization $\vec{P}_S$ as shown in in Fig. 3.4(c).

Our setup is sensitive enough to measure current of the order of 0.1 pA, and it allows us to measure small polarization changes of $\sim 1 \mu C/m^2$ by integration of the pyroelectric current. However, special precautions are necessary to ensure that the

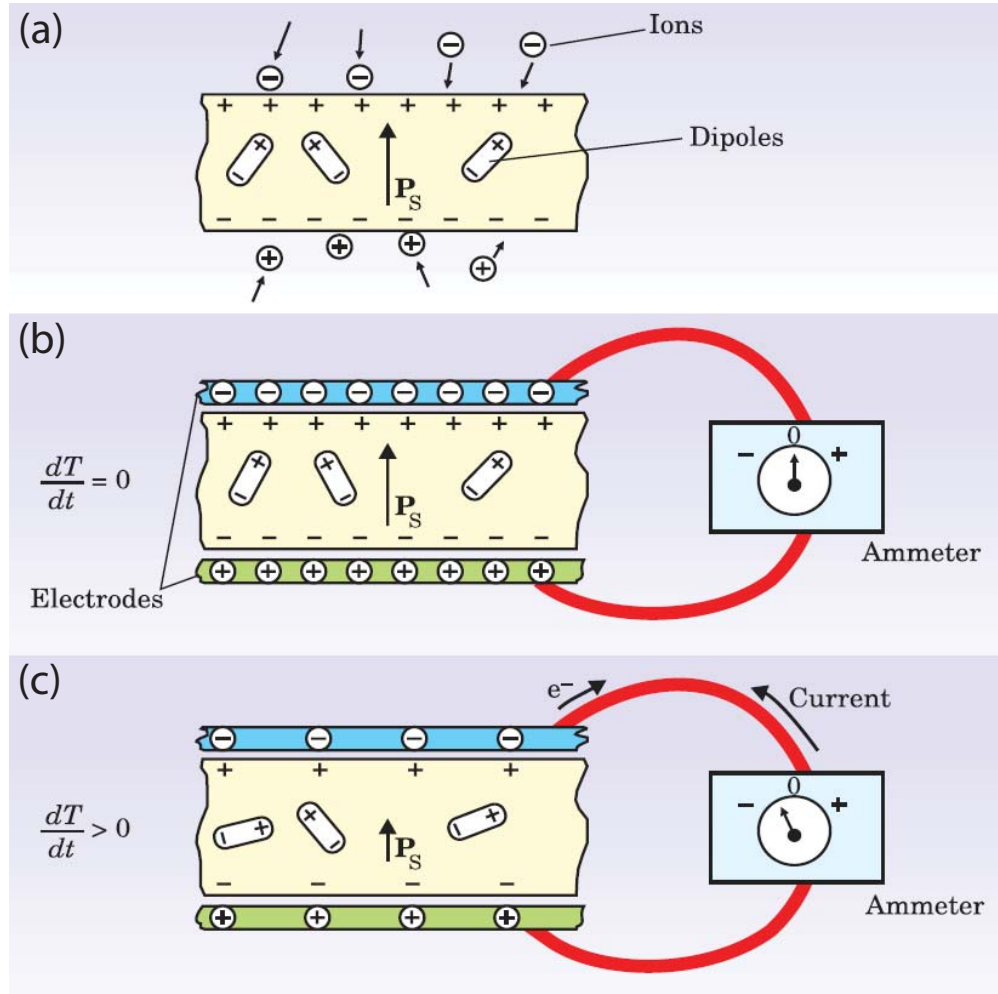


Figure 3.4: (a) A pyroelectric crystal with intrinsic dipole moments with (b) two electrodes on the top and bottom, and connected with a Ammeter. The increase of temperature (c) decreases the spontaneous polarization $\vec{P}_S$. At the same time, a current flow compensates the change of the surface charge density, which is proportional to the polarization $\vec{P}_S$.

measured current reflects the pure polarization change and is free from artifacts such as charge transport or capacitive effects from the dielectric properties of the sample [32]. The measured current has the following general expression

$$i = \frac{V}{R} + C \frac{dV}{dt} + \frac{dC}{dt} V + A \frac{dP}{dt} \quad (3.3)$$

where V , R and C are applied bias voltage, resistance and capacitance of the sample, respectively. P and A are electric polarization and sample contact area, respectively. The $\frac{V}{R}$ term is the resistive current that is avoidable if the sample is well-insulating. Furthermore, in insulators, the current due to the release of possibly trapped charges is insignificant. The second $C \frac{dV}{dt}$ term is the charging current of the capacitor, which is zero while the applied voltage is a constant. The $\frac{dC}{dt} V$ term may cause a current if the capacitance of the sample changes significantly with temperature when a bias voltage is applied. It is avoidable by applying no voltage bias. This $A \frac{dP}{dt}$ term corresponds to the electric polarization. All the samples in this work are good insulators. The multiferroic Co or Cu doped MnWO_4 compounds were cooled with applied poling voltage to align the ferroelectric domains, and measured in heating without voltage applied. The rare earth aluminum borates and lithium iron diphosphate are measured without any bias voltage. To measure magnetoelectric polarization, we use a similar way to measure magnetoelectric currents with sweeping the magnetic fields up to 7 Tesla at a constant temperature.

Chapter 4

Results and Discussion

This chapter will present our results in the field of magnetoelectric research. Experimental results will be followed by qualitative/quantitative explanation, discussion and future research possibility. In the search of new magnetoelectric material, there are three possible methods: (1) In multiferroic materials, the magnetic structure might be affected by application of magnetic field, and therefore, modify the polarization. (2) Magnetic fields transform the noncentrosymmetric nonpolar crystal structure into a polar structure so the magnetoelectric polarization increases with applied magnetic fields. (3) When magnetic moments ordered in a polar crystal, the magnetic order is possible to couple with the lattice and cause polarization change, which might be affected by external magnetic field. Therefore, our results will be discussed in three main sections: (1) effects of ionic substitution and magnetic field on multiferroic compounds, (2) magnetoelectric effect in rare-earth borate systems, (3) magnetoelectric effects in the lithium iron diphosphate.

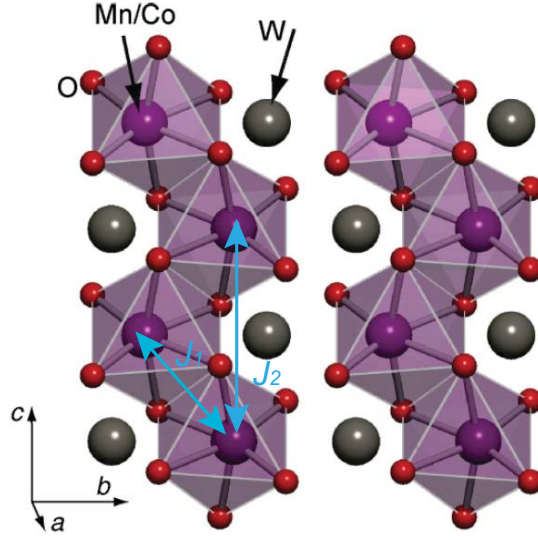


Figure 4.1: Crystal structure of the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. Nearest neighbor (J_1) and next nearest neighbor (J_2) exchange interactions.

4.1 Effects of ion substitutions and magnetic field on the multiferroic properties of MnWO_4

4.1.1 Multiferroic properties of MnWO_4

The mineral Hübnerit MnWO_4 crystallizes in a monoclinic b -axis unique structure (space group $\text{P}2_1/\text{c}$). From previous reports [25, 26], there are several interesting magnetic phase transitions and multiferroic properties to get peoples' attention. The magnetic ions $[\text{Mn}^{2+}, (S=5/2)]$ form a zigzag chain along the c -axis (Fig. 4.1) and strong magnetic interactions, resulting in competition between neighbor spin and next nearest neighbor spin. This causes different frustrated magnetic orders upon decreasing temperature. Below the T_N , a sinusoidal magnetic order with an incommensurate modulation is realized with the vector $\vec{q}_3 = (0.214, 0.5, -0.457)$ at $T_N = 13.5\text{K}$ (as shown in Fig. 4.2(c)). The collinear Mn-spins of AF3 phase are confined to

the $a - c$ -plane at an angle of 34° with the a -axis, where the magnetic easy axis is also defined. At the multiferroic phase below $T_C = 12.6$ K, the spins form a noncollinear order by tilting partially out of the $a - c$ -plane toward the b -axis (Fig. 4.2(b)). The magnetic order in this AF2 phase is described by a spin helix with the same propagation vector, $\vec{q}_2 = \vec{q}_3$. Because the spin helical order breaks the spatial inversion symmetry and allows the ferroelectric polarization order parameter, the AF2 phase is therefore ferroelectric (FE) with a polarization vector pointing along the b -axis, which can be explained by the spin-current model [27] and the Ginzburg-Landau theory [13]. At even lower temperature, at $T_L = 7.5$ K, the magnetic order locks into a commensurate structure (Fig. 4.2(a)) with the modulation vector of $\vec{q}_1 = (0.25, 0.5, -0.5)$. The magnetic order of the AF1 phase shows the highly frustrated $\uparrow\uparrow\downarrow\downarrow$ spin sequence, which obeys the spatial inversion symmetry so that the AF1 phase is paraelectric.

The high degree of magnetic frustration causes the complex phase sequence (AF3 $\rightarrow$ AF2 $\rightarrow$ AF1). The frustration comes from competition of magnetic exchange interactions (J_1 and J_2 in Fig. 4.1 as example), and results in several magnetic states with almost the same energy to compete with the AF1 phase for the ground state [33]. The inelastic neutron-scattering experiments have revealed the long-range character of the magnetic interactions involving with up to 11 different exchange coupling constants and magnetic anisotropy to explain the low-energy magnetic excitations [34], for example, $J_1 < 0$ and $J_2 > 0$. The replacement of the magnetic Mn ion by other transition metal ions with different spin, exchange coupling and magnetic anisotropy can be used to tune those parameters including the magnetocrystalline anisotropy. MnWO_4 is therefore a good candidate since it forms stable compounds when Mn is completely replaced by Fe [35], Co, Ni, Cu [36], or Zn [37]. A uniform solid solution

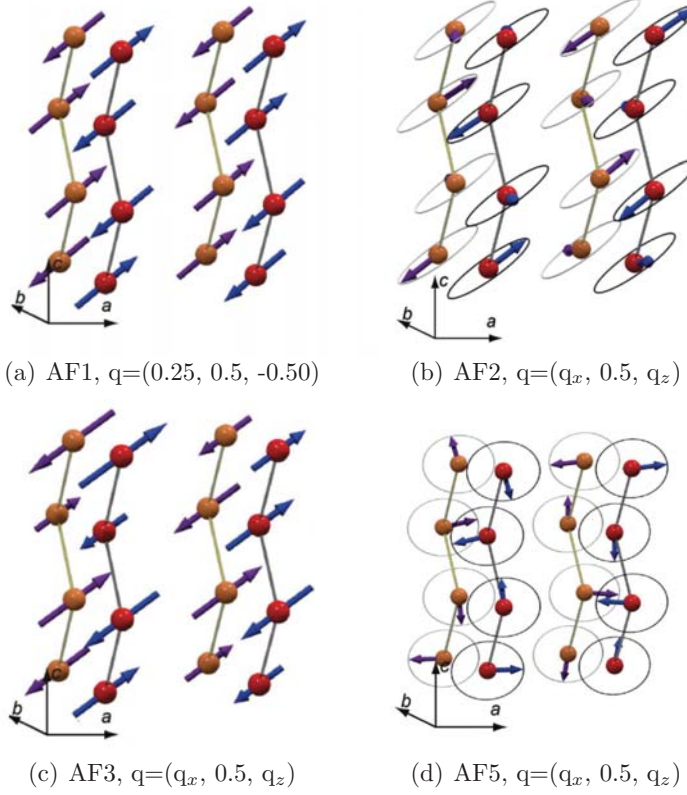


Figure 4.2: Magnetic structures of (a) collinear, commensurate (CM) AF1 phase, (b) noncollinear, incommensurate (ICM) AF2 multiferroic phase, (c) the collinear, ICM AF3 sinusoidal phase, (d) noncollinear ICM AF5 phase, ac helix from the neutron scattering refinements.

of MnWO_4 with $(\text{Fe}, \text{Co}, \text{Ni}, \text{Zn})\text{WO}_4$ is expected to form over the whole concentration range to two extreme ends because all ternary compounds are isostructural with relatively small variations of the lattice constants except the CuWO_4 .

The replacement of Mn^{2+} (spin = 5/2) with Fe^{2+} (spin = 2) has shown an interesting magnetic phase diagram [38] with coexisting phases at some critical Fe concentrations [39]. The multiferroic properties of $\text{Mn}_{1-x}\text{Fe}_x\text{WO}_4$ have been investigated earlier [1] and it shows that the substitution of more than 4% Fe suppresses the multiferroic AF2 phase. The doping of Fe-moments increases the average magnetic anisotropy in the system so that the AF2 helical phase is suppressed and the AF1 phase is stabilized. On the contrary, the substitution of nonmagnetic Zn^{2+} in $\text{Mn}_{1-x}\text{Zn}_x\text{WO}_4$ did stabilize the AF2 phase to become the ground state, and therefore, the commensurate ($\uparrow\uparrow\downarrow\downarrow$) AF1 phase was completely suppressed [40, 41]. A similar effect was also observed in the Co-substituted compound, $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$, based on the magnetic and neutron scattering experiments of polycrystalline samples [42]. The neutron scattering data further suggested the rotation of the spiral plane to the $a - c$ -plane plane, and therefore, the cross product of the normal vector $\vec{k}$ to the $a - c$ spiral plane and the propagation vector $\vec{c}$ gives rise to a -axis polarization, as shown in Fig. 4.2(d). A sizable a -axis component of the polarization was indeed recently observed in the single-crystalline $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$ [43, 44]. At slightly higher doping (15% Co), however, the only component of the FE polarization was found aligned with the b -axis [45]. These conflicting results indicate an extreme complex multiferroic phase diagram of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ and warrant further exploration of single crystals of various Co concentrations.

In this section, the multiferroic and magnetic states and the polarization rotations between b - and a -axes of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ will be discussed in more detail, where $x = 0, 0.02, 0.035, 0.042, 0.05, 0.075, 0.1, 0.12, 0.135, 0.15, 0.17, 0.2, 0.25$, and 0.3 through

magnetic, pyroelectric current (polarization), specific heat and neutron scattering (through collaboration) measurements. We also studied the $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$ ($x=0.05, 0.1, 0.2$, and 0.3) through magnetic, pyroelectric current (polarization), and specific heat measurements.

4.1.2 Multiferroic properties of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ in the absence of magnetic field

The phase diagram of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ is more complex than $\text{Mn}_{1-x}\text{Fe}_x\text{WO}_4$ and $\text{Mn}_{1-x}\text{Zn}_x\text{WO}_4$ ones. Ferroelectric phases of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ systems are studied through pyroelectric measurements (Sec. 4.1.2.1), and then, expanded to the whole phase diagram through magnetic (Sec. 4.1.2.2) and specific heat (Sec. 4.1.2.3) measurements for those paraelectric phases so that the phase diagram (Sec. 4.1.2.4) can be constructed. Furthermore, for better understanding of the details of magnetic order, single-crystalline neutron scattering measurements were done through a collaboration with Ye *et al.* from Oak Ridge National Lab, and therefore, some important results will also be shown in section 4.1.2.4. The possible origin the the complex phase diagram is discussed in the section 4.1.2.5.

4.1.2.1 Ferroelectricity of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

The FE polarization $\vec{P}(T)$ in the AF2 phase of MnWO_4 is directed along the monoclinic b -axis [25]. This is consistent with the symmetry consideration and prediction of the spin current model, with the following assumptions: (1) normal vector of spin helix in the $a-c$ -plane (2) the possibility of J along the a -axis (3) no sizable J along the b -axis. At $x = 0.1$, the corresponding magnetic structure was changed, and the polarization was found rotated by 90° into the $a-c$ -plane [43]. At the same time,

a smaller c -axis component found in the $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$ was due to the magnetic interaction along the a -axis between different chains of spins [43, 44]. In order to account for all possible orientations of $\vec{P}(T)$ for $0 \leq x \leq 0.3$, we have measured for each composition the polarization components along a , b and c .

In FE phase I ($0.02 \leq x \leq 0.05$), with Co doping levels up to 0.05, $\vec{P}(T)$ was found to be aligned with the b -axis in Fig. 4.3(a). The undoped MnWO_4 shows the sharp drop of $\vec{P}(T)$ to zero at T_L into the AF1 phase, in agreement with earlier reports [25, 26]. At $x = 0.02$, however, the paraelectric AF1 phase is completely quenched, and therefore, the FE AF2 phase becomes the ground state. The low-temperature polarization at 5 K decreases with x and drops below 50% of the value of MnWO_4 ($P_b \approx 60 \mu\text{C}/\text{m}^2$) at $x = 0.05$. Because the ground state of AF1 phase is paraelectric, the reference value for MnWO_4 at 5 K ($\approx 60 \mu\text{C}/\text{m}^2$) was determined from data measured at a magnetic field of 3 T which suppresses the paramagnetic AF1 phase [25]. The FE transition temperature T_C decreased slightly from 12.8 K ($x = 0$) to 12.3 K ($x = 0.05$). At the upper limit of the FE phase I, for $x = 0.042$ and 0.05, a small a -axis component of the polarization was observed. The magnitude of P_a was more than one order of magnitude smaller than P_b . This small P_a could be due to a minute misalignment of the crystal or the onset of the polarization flop from b - to the a -axis.

At slightly higher Co concentration interval in FE phase II (from $x = 0.075$ to $x = 0.135$), the FE polarization does not show any significant b -axis component within the resolution of the measurement. Although small values of P_b are observed in some measurements, this could be due to a minute misalignment (typically less than 3°) from the crystallographic axis. However, a large polarization was found aligned along the a -axis followed with a smaller component along c , as shown in Fig. 4.3(b) and 4.3(c), respectively. The magnitude of P_c is too large to be explained

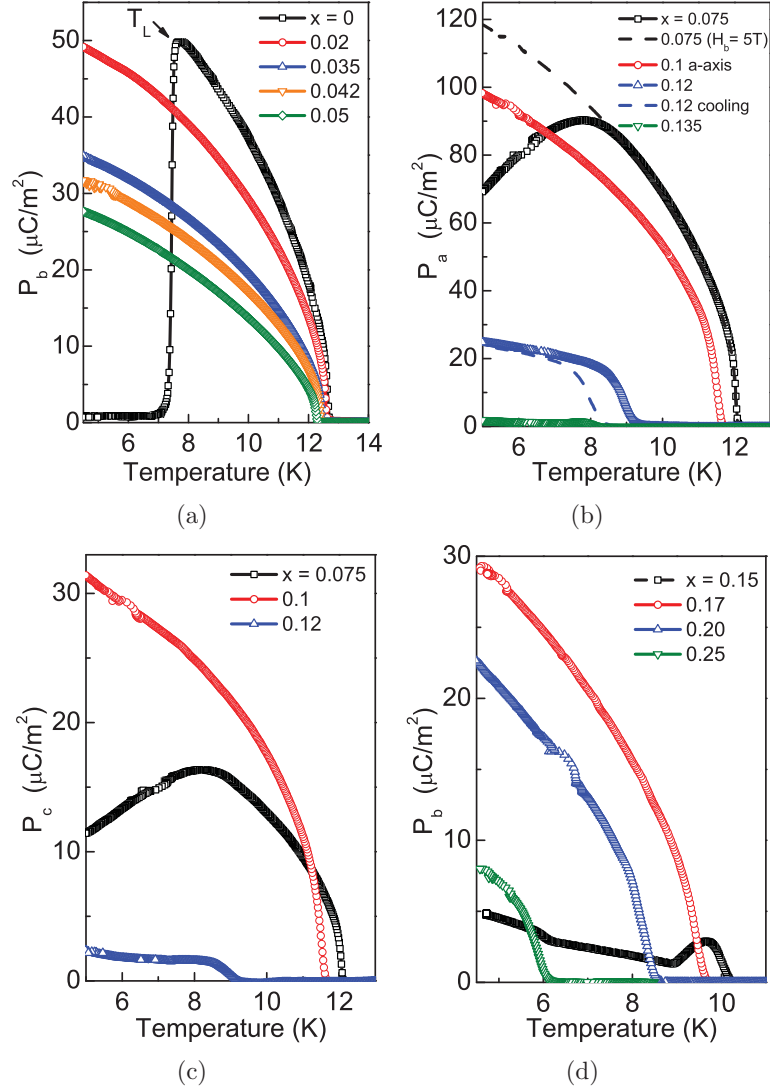


Figure 4.3: Ferroelectric polarization of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ (a) Low doping range ($x \leq 0.05, P_b$), (b), (c) intermediate doping ($0.075 \leq x \leq 0.135, P_a$ and P_c), and (d) high doping range ($x \geq 0.15, P_b$). For $x = 0.12$, warming and cooling data are presented to show thermal hysteresis. The dashed line for $x = 0.075$ shows the maximum polarization achieved in the magnetic field.

by a misalignment of the crystal, and it has to be considered as an intrinsic effect. Since the nearest neighbor intrachain magnetic couplings are oriented along the zigzag chain c -axis, they cannot cause c -axis polarization, and therefore, it is necessary to consider the interchain magnetic interactions along a -axis. This will be discussed in more detail in Sec. 4.1.2.5.

In FE phase II, the magnitudes of P_a and P_c at 5K decrease quickly with higher x and almost drop to zero at $x = 0.135$. At $x = 0.075$, both P_a and P_c pass through a maximum at 9K and decrease at low temperature. The underlying physics can be understood by the neutron scattering measurements. The measurements on the wavevector scans of magnetic orders show a peak center shifts upon cooling from $\vec{q}_a \approx (0.234, 0.5, -0.668)$ [sinusoidal AF3 phase] to intermediate $\vec{q}_b \approx (0.232, 0.5, -0.664)$ [AF5 phase] in temperature range of $7 \text{ K} < T < 10 \text{ K}$ and further down to $\vec{q}_c \approx (0.229, 0.5, -0.458)$ at low temperature (in Fig. 4.4(a) and Fig. 4.4(b)). From the scattering refinements, the magnetic structure of $x = 0.075$ compound experiences a reorientation of the helical plane from the optimal position in the $a - c$ -plane at 9 K (Fig. 4.4(c)) to a spin ellipse with one axis along b -axis and the other axis aligned in the $a - c$ plane (Fig. 4.4(d)). From our polarization data (Fig. 4.3(b)), the finite value of the P_a at low temperature suggests that the rotation of the spiral plane at low temperature is incomplete. It is the reorientation of ac helical plane that causes the reduction of P_a and P_c at low temperature. Furthermore, the canted angle α (in Fig. 4.4(d)) between spiral normal vector and c -axis is small ($\sim 5^\circ$) so that there is no P_b measured within the experiment resolution. Another reorientation of ac helical plane is observed in the presence of magnetic fields (discussed more in Sec. 4.1.3.2). The P_a of $x = 0.075$ sample in a field $H_b = 5$ Tesla rises continuously through low temperature and reaches the maximum value of more than $120 \mu\text{C}/\text{m}^2$ at 5 K, labeled as dashed line in Fig. 4.3(b). This value is the highest observed in any doped

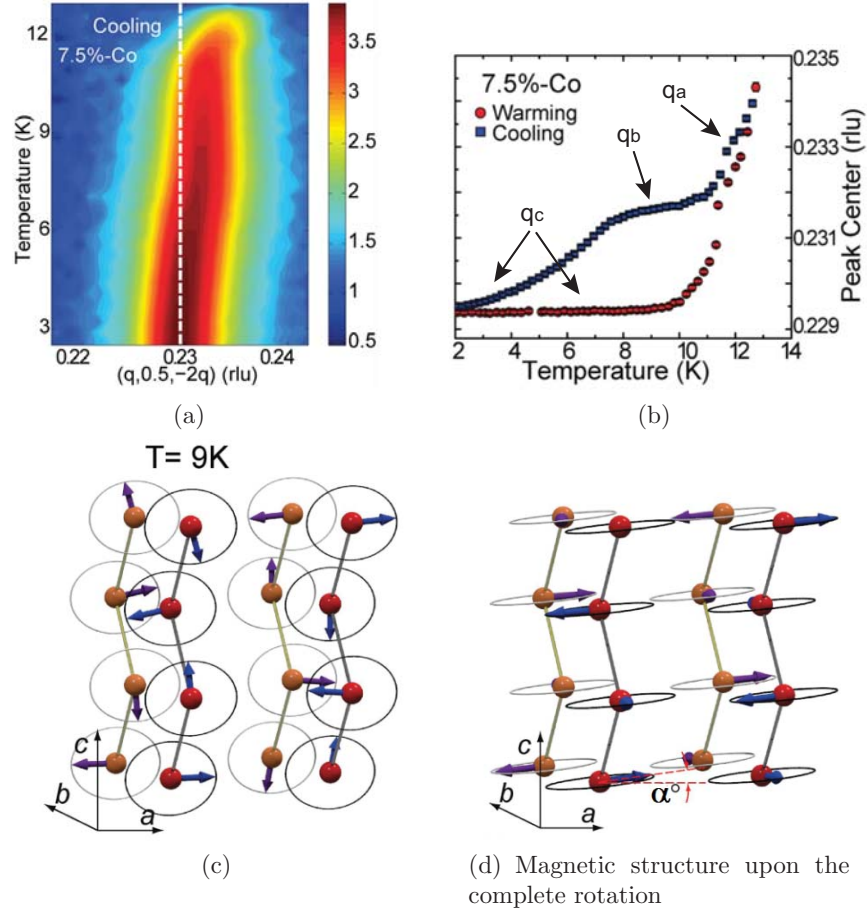


Figure 4.4: (a) Temperature dependent wavevector scans of $x = 0.075$ upon cooling, (b) Temperature dependence of the peak center of the ICM scattering, and the refined spin structure for $x = 0.075$ at (c) 9 K. (d) The pure AF2 helical structure after the low temperature rotation of spiral plane is complete in $x = 0.075$ compound.

or undoped MnWO_4 system. Therefore, $x = 0.075$ is the critical Co concentration where the rotation of the polarization from the b -axis into the $a - c$ -plane happens and the FE polarization is maximized.

The data for $x = 0.1$ are consistent with previous reports [43, 44]. With further increasing x , $\vec{P}(T)$ decreases quickly within a short range of Co concentration, and the critical temperature T_C of the FE phase shows a sharp decrease from 11.3K ($x = 0.1$) to 7.6K ($x = 0.135$). A significant thermal hysteresis with more than 1K develops above $x = 0.1$, as the warming and cooling data of $x = 0.12$. Fig. 4.3(b) shows the values of T_C of the FE phase match perfectly with the temperatures of the small peak of the specific heat data (Fig. 4.7(b)). At the upper limit of FE phase II ($x = 0.135$), the a -axis polarization at 5K dropped already to below $2 \mu\text{C}/\text{m}^2$. The fast decrease of $\vec{P}$ with increasing x and the fact that no sizable component of $\vec{P}$ was observed along $\vec{b}$ indicate a major change of the spin helix in a narrow doping range.

In FE phase III ($x \geq 0.175$), the further increase of the Co doping level x above 0.135 results in another flop of the FE polarization from the a -axis back to the b -axis with a sudden increase of its magnitude. Data for $x > 0.15$ are shown in Fig. 4.3(d). The b -axis polarization of $x = 0.15$ is shown as the dashed line. The recovery of the b -axis polarization up to $30 \mu\text{C}/\text{m}^2$ at 5K suggests another sudden rotation of the spin helix in $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ at a critical doping of $x = 0.15$. No sizable a - or c -axis components of $\vec{P}$ could be detected in FE phase III.

The magnitude of FE polarization at 5 K as a function of Co concentration x is summarized in Fig. 4.5. The critical concentrations that separate FE phase I, II and III near $x_{c1} = 0.075$ and $x_{c2} = 0.135$ are clearly shown, and it is obvious that the rotation of $\vec{P}$ happens when its magnitude drops below a critical value. Above $x = 0.3$, $\vec{P}$ decreases quickly to zero, and the helical magnetic phase is suppressed

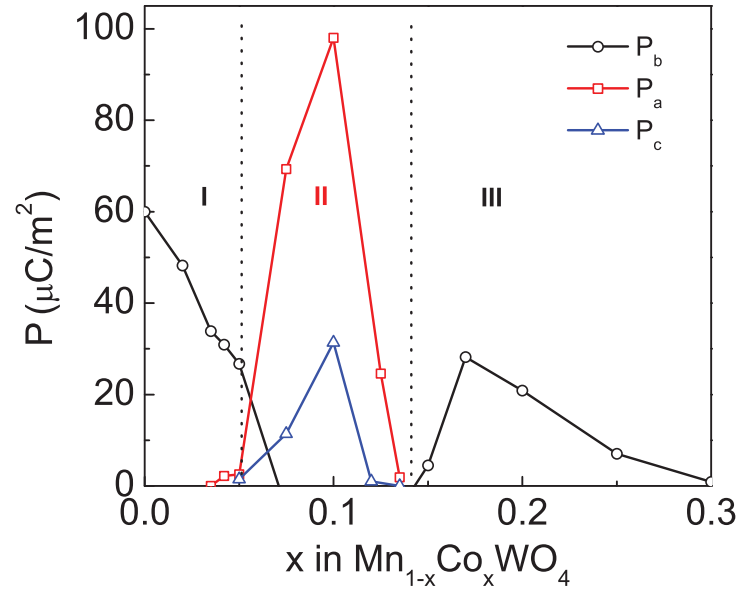


Figure 4.5: Ferroelectric polarization (at 5 K) phase diagram as a function of Co concentration in $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ system, showing three FE phases (I, II, and III). For $x = 0$, the value of P was extrapolated to low temperature based on data in magnetic fields suppressing the AF1 phase.

completely. The collinear AF4 phase (Fig. 4.9(e)) with the characteristic spin modulation defined by $\vec{q}_4 = (0.5, 0, 0)$ becomes the ground state. This is consistent with the AF4 magnetic structure that is realized for CoWO_4 [46]. In order to investigate all other magnetic phases and to resolve the whole phase diagram, the magnetization and specific measurements are done and discussed in more detail in the following two sections.

4.1.2.2 Magnetic susceptibility of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

As mentioned in the polarization data, the small amount of Co doping of 0.02 suppresses the low-temperature paraelectric AF1 phase. This is exactly what the magnetization data show in Fig. 4.6(a). The transitions into the sinusoidal (T_N) and the helical magnetic phase (T_C) are observed as the changes of slope in the b -axis magnetic susceptibility (Fig. 4.6(a)). The phase transition from the helical AF2 to the commensurate AF1 phase (T_L) is only detected in MnWO_4 as a sharp step-like increase of $\chi_b(T)$ at T_L , but, in $\text{Mn}_{0.98}\text{Co}_{0.02}\text{WO}_4$, this transition is, however, missing. The suppression of the collinear AF1 phase extends the FE AF2 phase to the lowest temperature. This result is in agreement with results from the study of polycrystalline $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ [42]. A similar doping effect on the stability of the AF2 helical phase was observed recently in single-crystalline $\text{Mn}_{1-x}\text{Zn}_x\text{WO}_4$ [31]. With the further Co doping levels $0.02 \leq x \leq 0.05$, $\chi_b(T)$ changes very little (different curves in Fig. 4.6(a) are offset vertically for clarity) but T_N and T_C show a slight decrease.

By increasing x between 0.075 and 0.15, $\chi_b(T)$ is changed significantly below T_C . The b -axis magnetic susceptibility data in this range of Co substitutions is shown in Fig. 4.6(b). The relatively sharp decrease of χ_b below T_C observed in Fig. 4.6(a) also appears in $x = 0.075$, and it corresponds to the rotation of the ac helix at low temperature, resulting in the reduction of the P_a below 8 K (Fig. 4.3(b)). At $x =$

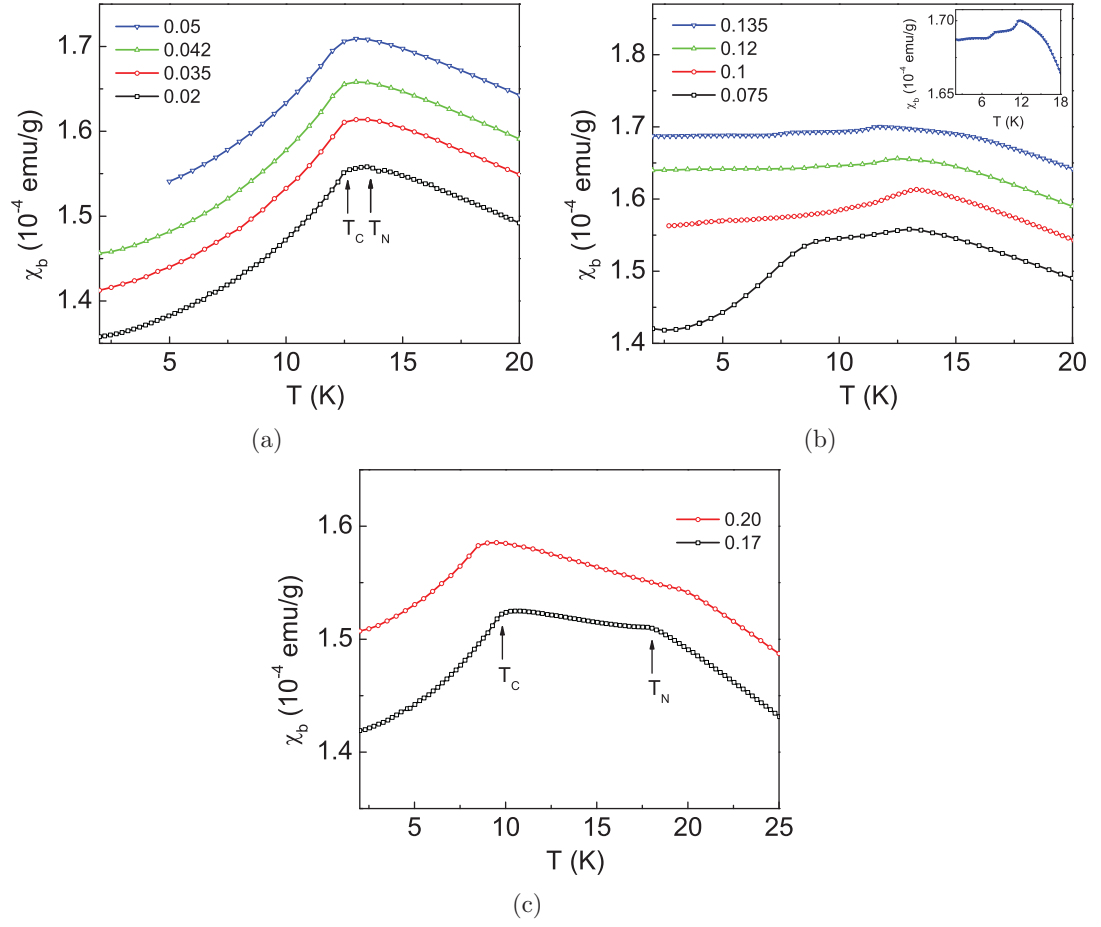


Figure 4.6: b -axis magnetic susceptibility of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. Different curves are vertically offset for clarity. Inset of Fig. (b) shows the enlarge scale of $x = 0.135$ data.

0.1, the low-temperature magnetic susceptibility becomes a plateau-like feature. The plateau exhibits additional anomalies in the form of small step-like changes of $\chi_b(T)$ for $x > 0.12$ (inset of Fig. 4.6(b)), indicating changes of the magnetic orders and a more complex magnetic phase in the upper limit interval of FE phase II.

With further increasing $x > 0.17$, the T -dependent χ_b changes its features again shown in Fig. 4.6(c). While the Neél temperature is determined by the first sharp slope change of $\chi_b(T)$, the magnetic susceptibility keeps increasing to lower temperature until it decreases sharply below the second transition temperature, T_C . The T -dependent χ_b below T_C is similar to the χ_b data in Fig. 4.6(a) in the low-doping range. Combining the observed b -axis polarization in Fig. 4.3(d), these results suggest that the helical structure in the FE phase III is similar to the low-doping AF2 helix. These two anomalies of T_N and T_C separate two main magnetic phases.

4.1.2.3 Specific Heat of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

Different kinds of phase transitions between magnetic phases could be better resolved by distinct peaks or anomalies in the specific heat measurements, $C_p(T)$. For example, the specific heat of the undoped MnWO_4 exhibits pronounced peaks at all three magnetic transitions from the paramagnetic phase to AF3, from AF3 to AF2, and from AF2 to AF1 [25]. For $0.02 \leq x \leq 0.1$, the specific heat data (shown in Fig. 4.7(a)) display mainly two peaks between 11 and 14 K, representing the phase transitions from the paramagnetic to the sinusoidal AF3 and subsequently to the AF2 helical phases, respectively.

Upon increasing x above 0.12, the onset of magnetic order at T_N becomes a step-like increase feature of C_p instead of a peak and a large peak of C_p with a shoulder develops near 11K together with a small third peak at lower temperature between x

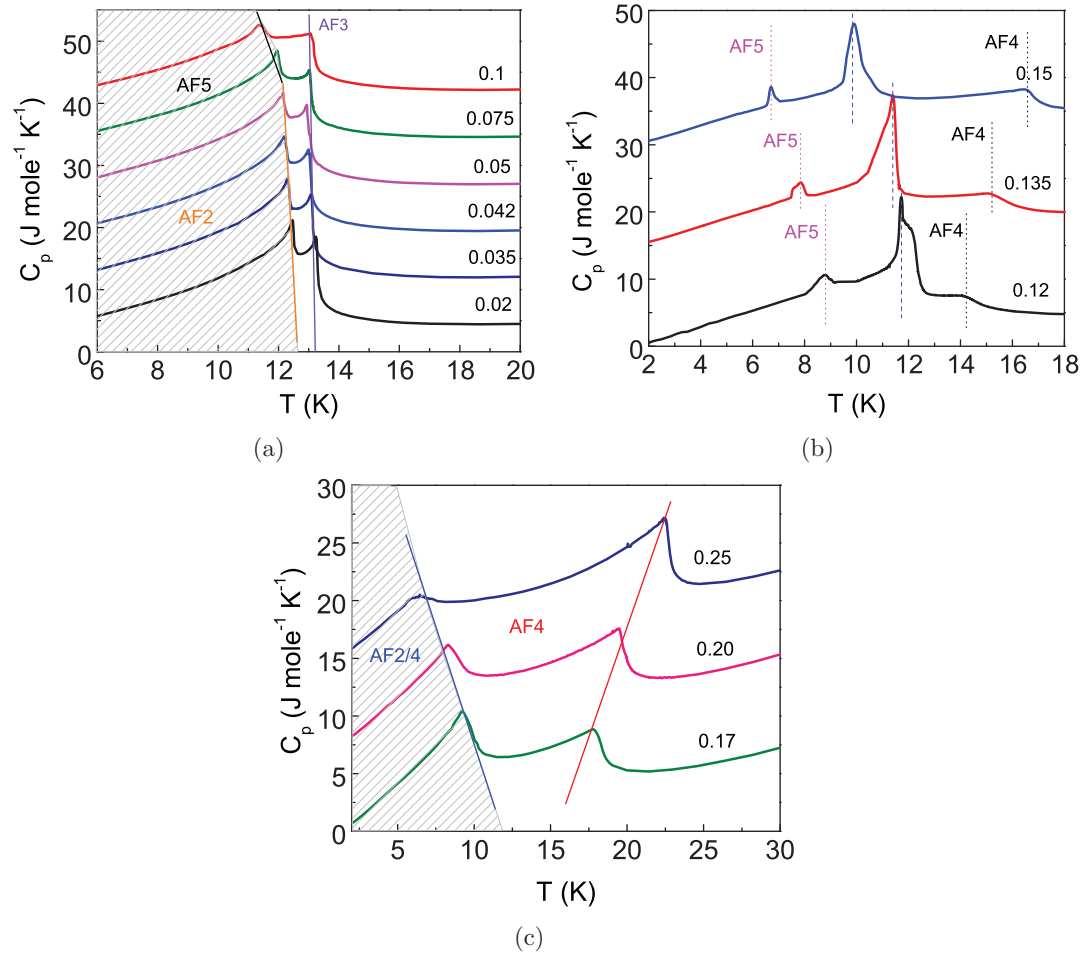


Figure 4.7: Specific heat of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. Different curves are vertically offset for clarity.

$= 0.12$ and $x = 0.15$ (Fig. 4.7(b)). For $x > 0.17$, the low-temperature small peak of $C_p(T)$ seen in the FE phase II disappears and only two anomalies remain, indicating that two magnetic phases dominate this part of phase diagram (Fig. 4.7(c)). The two transition temperatures change significantly with Co concentration x . The first transition temperature (T_N) quickly increases, and the second transition temperature (T_C) shifts in a opposite way to lower temperatures.

The three doping ranges (denoted as FE I, II and III) defined by the orientation of $\vec{P}$ in the phase diagram of Co-doped MnWO_4 system between $x = 0$ and $x = 0.3$ are also distinguished by their magnetic and thermodynamic properties. In the ranges of FE phase I ($0.02 \leq x \leq 0.05$) and FE phase III ($0.17 \leq x \leq 0.3$) only two transitions are observed, separating two different magnetic phases. In range II, the phase sequence upon decreasing temperature is way more complex involving more than two magnetic orders. Since we already know all involved magnetic phases including those FE (or multiferroic) phases, the phase diagram of the transition temperature as a function of Co content x can therefore be constructed. Furthermore, for better understanding of the microscopic pictures, single-crystalline neutron scattering measurements were performed through a collaboration with Ye *et al.* from Oak Ridge National Lab, and therefore, will be discussed in the next section.

4.1.2.4 Magnetic and multiferroic phase diagram of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

The above-mentioned polarization measurements (Sec. 4.1.2.1) define the FE (or multiferroic) AF2 (Fig. 4.9(b)) and AF5 (Fig. 4.9(d)) phases of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. Furthermore, other magnetic phases, e.g., the paraelectric AF1 (Fig. 4.9(a)), AF3 (Fig. 4.9(c)), or AF4 (Fig. 4.9(e)) phases, are also defined through the magnetic and thermodynamic anomalies at the phase boundaries (Sec. 4.1.2.2 and 4.1.2.3). Combining all these experimental data, we can completely resolve the magnetic and

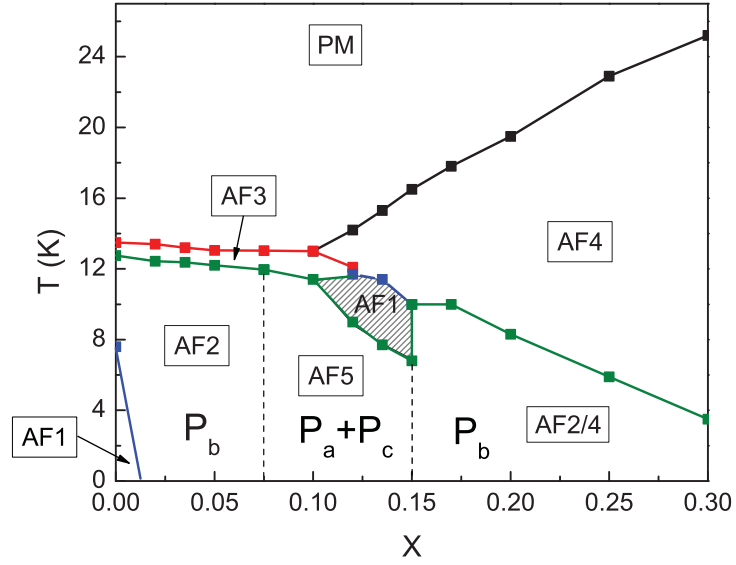
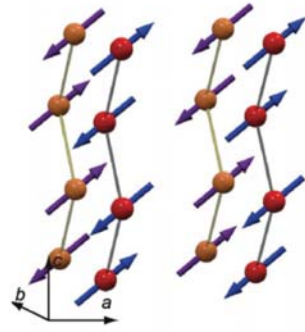


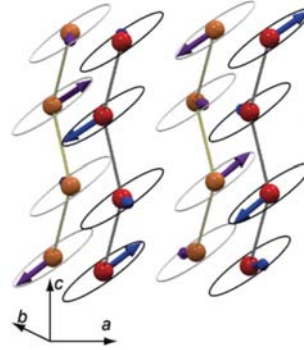
Figure 4.8: Magnetic and multiferroic phase diagram of the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$. Phase boundaries are determined from magnetic, specific and polarization measurements. The shaded area indicates the intermediate AF1 phase.

multiferroic phase diagram as shown in Fig. 4.8. The phase assignment of different magnetic structures used in Fig. 4.8 is based on previous powder [42] and most recent single-crystalline [47] neutron scattering results.

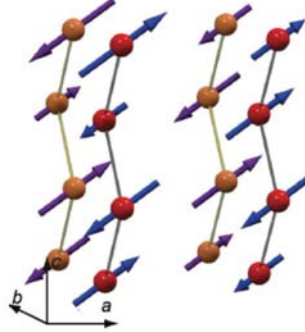
Most features of the phase diagram, such as the quick suppression of the AF1 phase and the overall onset of magnetic order at T_N , are consistent with the powder neutron scattering results [42]. The sinusoidal AF3, the first magnetic structure in the FE phase I region, phase transition temperature T_N decreases slightly with x for $x \leq 0.1$. In contrast, T_N increases significantly above $x > 0.1$ of Co doping levels, and this is when the commensurate collinear AF4 phase replaces the incommensurate collinear AF3 phase. The transition from the sinusoidal AF3 phase to the helical AF2 phase with the P_b polarization extends to $x \simeq 0.075$, which is also shown in Fig. 4.5 and 4.8. In order to understand the microscopic details of the different magnetic orders, we have initiated single-crystalline neutron scattering experiments through a



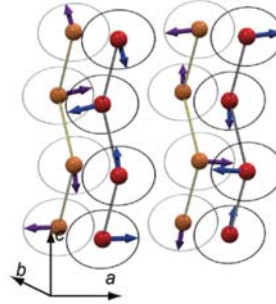
(a) AF1, $q=(0.25, 0.5, -0.50)$



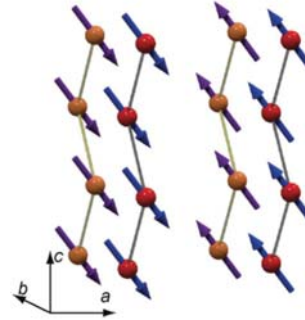
(b) AF2, $q=(q_x, 0.5, q_z)$



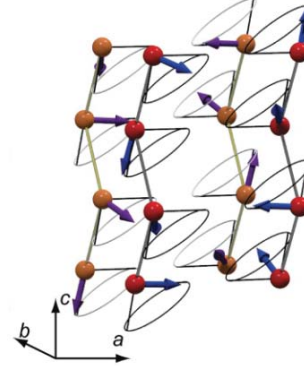
(c) AF3, $q=(q_x, 0.5, q_z)$



(d) AF5, $q=(q_x, 0.5, q_z)$



(e) AF4, $q=(0.5, 0, 0)$



(f) AF2/4, $q_1=(q_x, 0.5, q_z) + q_2=(0.5, 0, 0)$

Figure 4.9: Magnetic structures of (a) collinear, commensurate (CM) AF1 phase, (b) noncollinear, incommensurate (ICM) AF2 multiferroic phase, (c) the collinear, ICM AF3 sinusoidal phase, (d) noncollinear ICM AF5 phase, *ac* helix, (e) the collinear, CM AF4 phase and (f) the conical AF2/4 phase from the neutron scattering refinements.

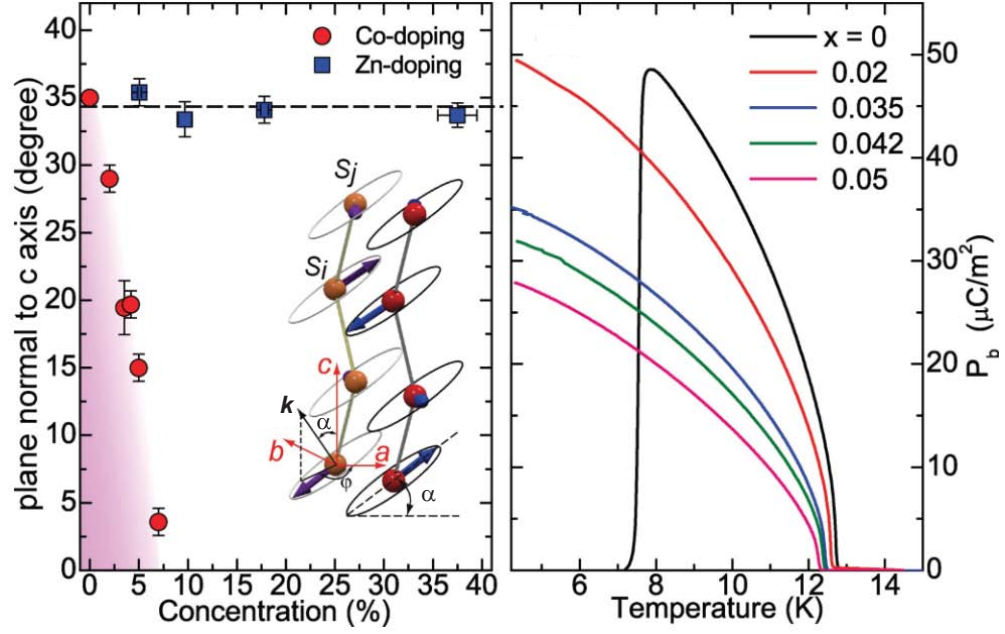


Figure 4.10: Co doping dependence of the angle α between spiral plane normal vector $\vec{k}$ and c -axis of the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$, which is extracted from the neutron scattering experiment results done through a collaboration with Ye *et al.* The Zn-doped results are also shown for comparison. Inset shows schematics of the spin helix in AF2 phase. The normal vector $\vec{k}$ has an angle of α with c -axis, and the projection of $\vec{k}$ on to the $a-b$ plane has an angle of ϕ to the a -axis. The b -axis polarization as a function of temperature of $x = 0, 0.02, 0.35, 0.42, 0.05$.

collaboration with Ye *et al.* The results show a continuous rotation of the AF2 spin spiral plane in the Co doping range $0 \leq x \leq 0.075$ in Fig. 4.10. Because the P_b polarization is proportional to $\sin\alpha$ (as Eq. 4.4 in the next section), the decrease of the α angle with increasing Co concentration x causes the reduction of P_b . Especially, the $\sin\alpha$ angle in $x = 0.075$ is so small that P_b polarization is barely detectable, and therefore, the P_b polarization extends only to $x \simeq 0.075$. The decrease of the P_b polarization causes an instability due to the decrease of the magnetoelectric energy so the system flops the spiral plane to the $a - c$ plane to regain the free energy to stabilize the multiferroic state (more details will be discussed in the next section). At higher Co doping levels, between $x_{c1} = 0.075$ and $x_{c2} = 0.135$, the spin spiral of FE polarization is then constrained to the $a - c$ plane in the AF5 phase.

For $0.12 \leq x \leq 0.15$, it should also be noted that more than two magnetic transitions are observed in magnetic (Fig. 4.6) and specific heat (Fig. 4.7) data. The second phase (shaded area in Fig. 4.8) is sandwiched between the AF4 and AF5 phases. This phase is a paraelectric phase known from the polarization measurements. In specific heat measurements, it shows as a large peak at the temperature of transition into this paraelectric phase (Fig. 4.7(b)). From the detailed neutron scattering experiments (Fig. 4.11 and 4.12), magnetic structure of this phase is a commensurate collinear magnetic structure with the wavevector of $\vec{q}_1 = (0.25, 0.5, -0.5)$, the same as the low temperature AF1 phase (Fig. 4.9(a)) of MnWO_4 . The presence of this sandwiched phase explains the sudden decrease of the FE transition temperature in this range.

With further increasing $x(>0.15)$, there are only two phase transitions observed. A commensurate magnetic order (AF4 phase) first develops at T_N , as reflected in the kink of χ_b (Fig. 4.6(c)) and the high-temperature peak of C_p (Fig. 4.7(c)). The second phase transition at T_C recovers the b -axis polarization, indicating that the specific magnetic structure is noncollinear to allow for P_b polarization. Both the

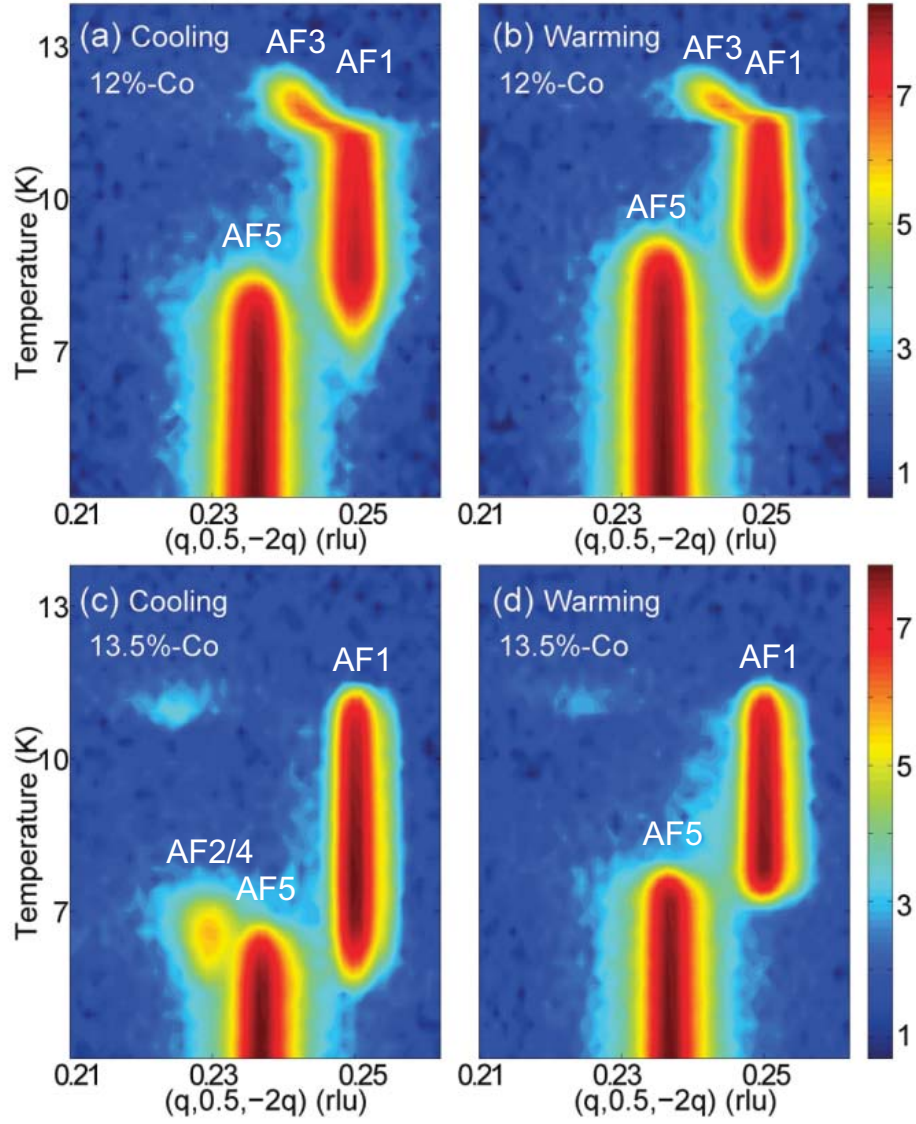


Figure 4.11: Temperature-dependent wavevector scans of the magnetic peaks for $x = 0.12$ upon (a) cooling and (b) warming, and 0.135 upon (c) cooling and (d) warming.

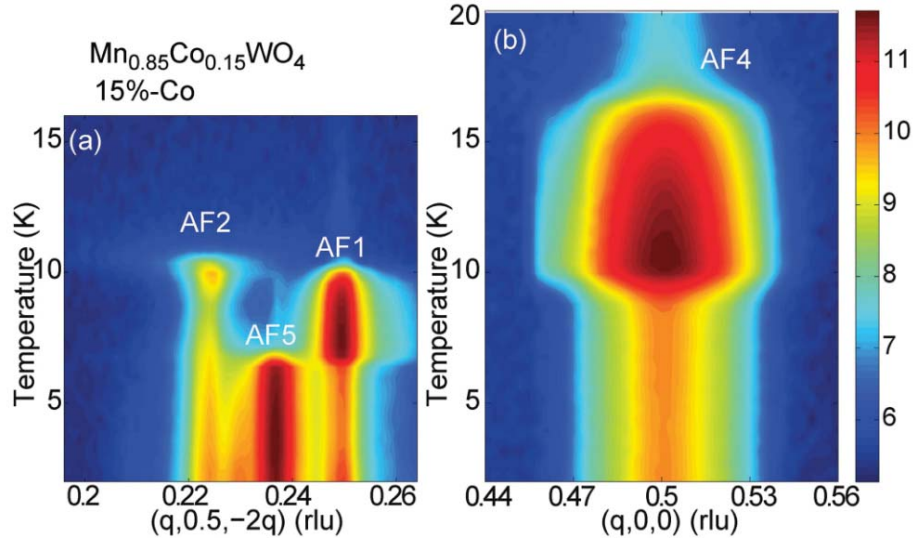


Figure 4.12: Temperature-dependent wavevector scans of the magnetic peaks for $x = 0.15$ along the (a) $[H, 0.5, -2H]$ and (b) $[H, 0, 0]$ directions.

magnitude of P_b and critical temperature T_C decrease quickly with x to $P_b(2K) = 0.6 \mu\text{C}/\text{m}^2$ and $T_C = 3.6 \text{ K}$, respectively, at $x = 0.3$. The presence of the AF2 spiral phase at high Co doping range (also called AF2/4 phase) is confirmed by the neutron scattering measurements, shown in Fig. 4.13 and 4.14. The wavevector scans experiments along $(H, 0, -H)$ identify the incommensurate $\vec{q}_{2/4} = (0.225, 0.5, -0.45)$ phase. The scattering intensity of the incommensurate AF2 phase as a function of temperature also shows the decrease of critical temperatures T_C with higher x . At the same time, the significant decrease of intensity with increasing x corresponds to the decrease of the polarization magnitude with x . The weakening intensity of AF2 phase with x in Fig. 4.14(a) explains that the reduction of P_b is due to the decrease of the magnetic moments contributing to the spin helix and increasing influence of the AF4 magnetic structure (as seen in the AF4 intensity data). The coexistence of the AF4 modulation with the AF2 modulation makes this AF2/4 phase in the $x(>0.15)$ region different from the $x \leq 0.05$ one. The AF4 scattering intensity reveals the onset of

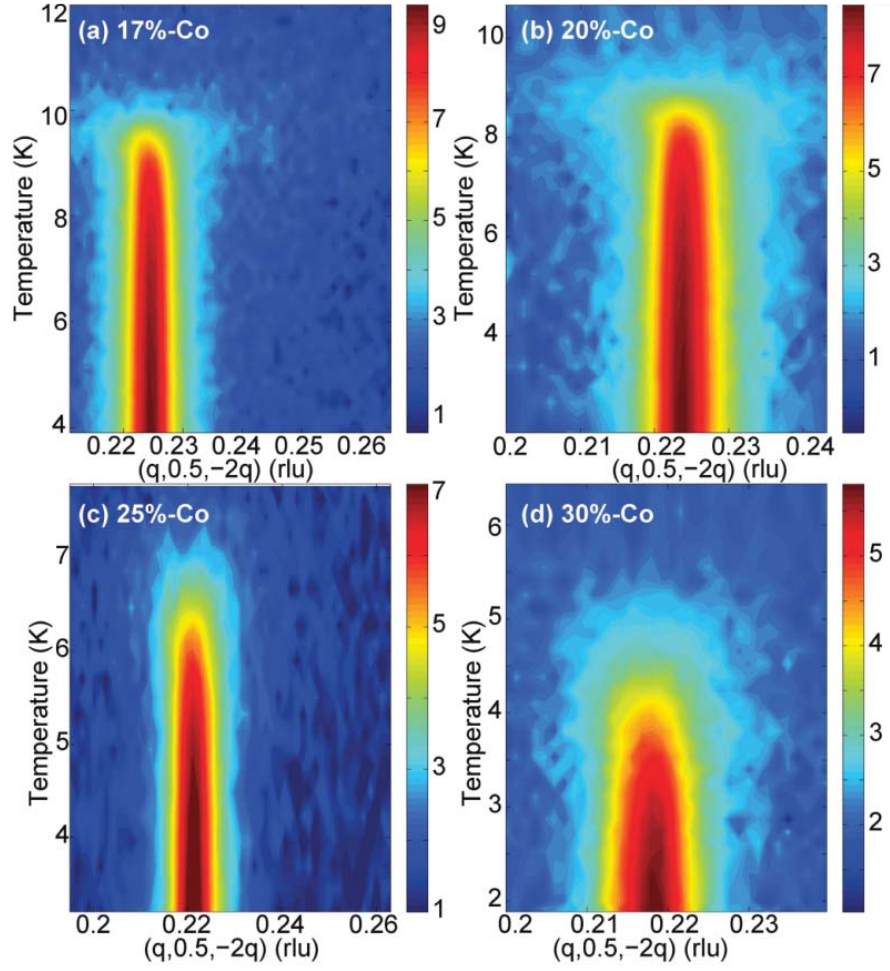
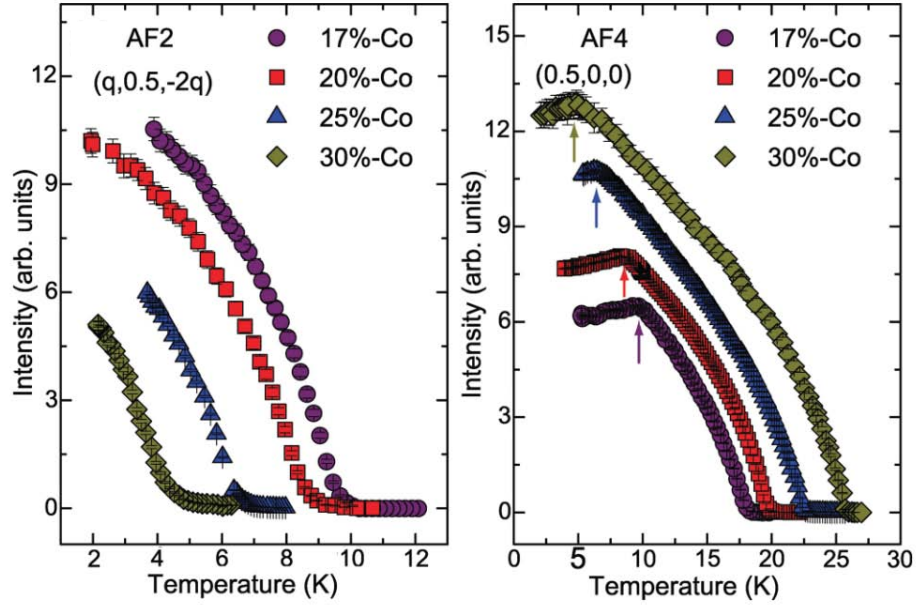
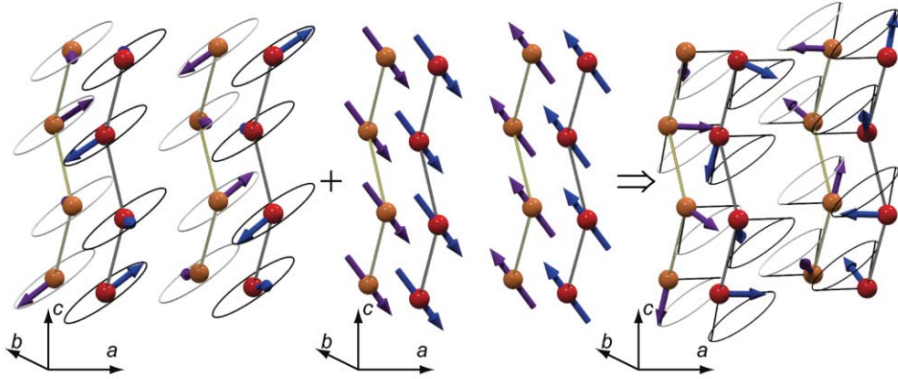


Figure 4.13: Temperature-dependent wavevector scans along $(H, 0, -H)$ of the magnetic peaks for $x =$ (a) 0.17, (b) 0.20, (c) 0.25, and (d) 0.30.



(a)



(b)

Figure 4.14: (a) Temperature-dependent neutron scattering intensity of the ICM AF2 and CM AF4 phases in $x = 0.17, 0.2, 0.25$, and 0.3 of the FE phase III region. (Note: arrows label the transition temperatures where the low-temperature conical AF2/4 phase sets in. (b) The spin configuration of the ICM AF2, CM AF4 and how they add up to form conical AF2/4 phase.

AF2/4 modulation as a kink at T_C , labeled as arrows in Fig. 4.14(a). The increasing influence of the AF4 phase is also observed as an increase of the AF4 phase neutron scattering intensity. It is because of the interplay between AF2 and AF4 modulation that the magnetic structure in the FE phase III develops a two- k structure from a single phase and forms a conical spin configuration, so called AF2/4 conical phase, as shown in Fig. 4.14(b).

4.1.2.5 Discussion and possible origin of the multiple polarization flops in $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$

The spin helical orders of the multiferroic state in MnWO_4 is a classical example of a polar structure allowed by breaking inversion symmetry [25, 13, 48]. The strong coupling between the lattice and the spin helix (as investigated, e.g., through significant anomalies of the thermal expansion [49]) causes the polar distortion of the lattice and the FE state. Both the microscopic theory and symmetry arguments relate the magnitude and the direction of the electrical polarization to the vector cross product of the term $(\vec{m}_i \times \vec{m}_j)$ with the position vector $\vec{R}_{ij}$ (connecting both magnetic moments at sites i and j along the propagation direction of the spin helix). Considering the specific structure of MnWO_4 with two spins per unit cell, the magnetic moment in the helical state can be expressed as [33],

$$\vec{m}(\vec{R}_{il}) = \vec{m}_{\parallel} \cos(\vec{q} \cdot \vec{R}_i + \Phi_l) + \vec{m}_{\perp} \sin(\vec{q} \cdot \vec{R}_i + \Phi_l), \quad (4.1)$$

where $\vec{R}_{il}$ is the position vector to the Mn site l ($= 1, 2$) in the unit cell i , $\vec{q}_i$ is the propagation vector of the spin helix defined as $\vec{q}_i = 2\pi/\lambda_i$ (λ_i is the wavelength of the spin modulation along the i th direction), and $\Phi_2 = \Phi_1 + q_z c/2 + \pi$. The two perpendicular vectors $\vec{m}_{\parallel}$ and $\vec{m}_{\perp}$ define the helical plane with $\vec{m}_{\parallel}$ and $\vec{m}_{\perp}$,

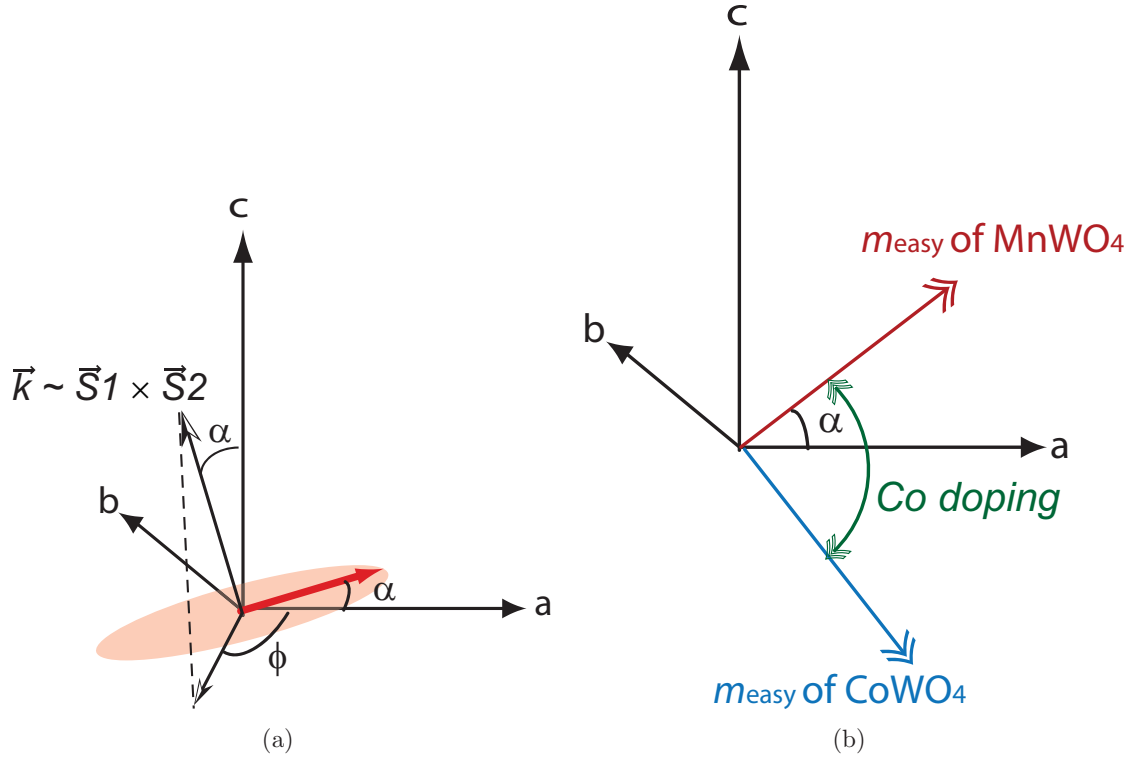


Figure 4.15: (a) Schematic diagram of normal vector $\vec{k}$ of the helical plane, the angle α between $\vec{k}$ and c -axis, and ϕ is the angle between the projection of $\vec{k}$ onto the $a-b$ plane with the a -axis. (b) Magnetic easy axis of MnWO_4 and CoWO_4 , and the curve arrow indicates the rotation of the magnetic easy axis upon Co doping.

equivalent to the long and short half axis of the magnetic ellipse, respectively.

In order to derive a general expression for the FE polarization, we need to calculate the vector product of the two magnetization vectors at the pair of atomic sites coupled by the magnetic exchange interaction. The result for nearest neighbor spins within a chain along the c -axis is

$$\vec{m}(\vec{R}_{i2}) \times \vec{m}(\vec{R}_{i1}) = \vec{m}_{\parallel} \vec{m}_{\perp} \sin(q_z c/2) \vec{k}, \quad (4.2)$$

where $\vec{k}$ is the normal vector of the helical plane (length 1), as depicted in Fig. 4.15(a).

As mentioned above, the coupling between spins exclusively within the chains (c -axis) cannot explain the observed P_c polarization in the FE phase II region. Magnetic exchange interactions between different chains contributes to the P_c polarization. The exchange coupling constants of MnWO_4 are experimentally investigated by inelastic neutron scattering work [34], which leads to an estimate of the Heisenberg exchange constants for different pairs of spins along and between the chains. The magnetic exchange between spins along b -direction was generally very weak, and however, sizable exchange constants had been determined for neighboring spins along the c - as well as a -axes. Therefore, it appears conceivable to include contributions to the polarization due to the spin-spin interactions along the a -axis:

$$\vec{m}(\vec{R}_{i+1,l}) \times \vec{m}(\vec{R}_{il}) = \vec{m}_{\parallel} \vec{m}_{\perp} \sin(q_x a) \vec{k}, \quad (4.3)$$

where $\vec{R}_{i+1,l}$ and $\vec{R}_{il}$ refer to two magnetic ions in neighboring chains displaced along the a -axis.

The electrical polarization can now be expressed as the vector product of the Eqn. 4.2 and 4.3 with the corresponding average position vectors connecting the spins in each case. Using spherical coordinates, we express the normal vector $\vec{k} = \sin(\alpha)\cos(\varphi)\vec{e}_x + \sin(\alpha)\sin(\varphi)\vec{e}_y + \cos(\alpha)\vec{e}_z$, where α is the angle of $\vec{k}$ with the z -axis and φ denotes the angle of the $x - y$ -plane projection of $\vec{k}$ with the x -axis (Fig. 4.15(a)). $\vec{e}_i$ are the unit vectors along the i th cartesian coordinate ($i = x, y, z$). For simplicity, we will consider $\vec{e}_x$ parallel to $\vec{a}$ and $\vec{e}_z$ parallel to $\vec{c}$ (the angle between $\vec{a}$ and $\vec{c}$ is nearly 90°), with $\vec{e}_y$ parallel to $\vec{b}$. The polarization in terms of α and φ due to the intrachain exchange is

$$\overrightarrow{P^{(1)}} = C^{(1)} \vec{m}_{\parallel} \vec{m}_{\perp} \sin(q_z c/2) [-\sin\alpha \sin\varphi \vec{e}_x + \cos\varphi \vec{e}_y], \quad (4.4)$$

A similar expression is obtained for the interchain exchange along the a -axis:

$$\overrightarrow{P^{(2)}} = C^{(2)} \vec{m}_{\parallel} \vec{m}_{\perp} \sin(q_x a) [-\cos\alpha \vec{e}_y + \sin\alpha \sin\varphi \vec{e}_z], \quad (4.5)$$

$C^{(1)}$ and $C^{(2)}$ are constants that are independent of α or φ . Supposedly, $|C^{(2)}| < |C^{(1)}|$ is because of the larger distance between the chains along the a -axis and the weaker magnetic exchange. The signs of q_z and q_x determine the helicity of the spiral spin modulation.

In MnWO_4 , the helical plane is perpendicular to the $a - c$ -plane forming an angle of about 34° with the a -axis, corresponding to the spin easy axis in the collinear AF1 and AF3 phases [33]. Accordingly, the orientation of the helix is defined by $\alpha = 34^\circ$ and $\varphi = 180^\circ$ (Fig. 4.15(b)). This results in a b -axis polarization from both Eq. 4.4 and Eq. 4.5. Whether the two contributions to P_b are additive or subtractive depends on the helicities of the spin spiral and the signs of the pre-factors in Eq. 4.4 and Eq. 4.5, i.e. the microscopic details of the magnetic interactions.

We consider a general spin helix as a function of (α, φ) , which is in arbitrary direction as shown in Fig. 4.15(a), and also the magnetic exchange interaction along the a -axis. On the other hand, the magnitude of the FE polarization, P_b , depends on the angle α discussed by Sagayama *et al.* [48], considering only the contribution due to nearest neighbors along the c -axis, i.e. Eq.4.4. However, due to the second contribution from Eq. 4.5, the angular dependent behavior of $P_b(\alpha, \varphi)$ is more complex.

For the next, we would like to qualitatively discuss how the complex x -dependent FE polarization is related to the possible changes of the spin helix induced by Co substitution. By Eq. 4.4 and Eq. 4.5, we will focus on angular dependence, the expressions in the square brackets, although the possible changes of the pre-factors with x may cause additional changes of the magnitude of $\vec{P}$. The reorientation of the helical plane was recently observed for Co concentrations between 0.05 and 0.1 (Fig. 4.10 and [42]). The driving mechanism behind will be discussed.

It seems conceivable that the change of the average magnetic anisotropy upon Co doping plays a major role. The magnetic easy axis of the transition metal (T) spin in TWO_4 strongly depends on the T-ion [50]. For CoWO_4 , it was observed that the angle of the easy axis with the a -axis is $\alpha = -46^\circ$ [46] in the $a - c$ plane, a difference of 80° with respect to MnWO_4 , as shown in Fig. 4.15(b). Therefore, one could expect that the Co substitution tends to rotate the easy axis and the helical plane in the multiferroic phase of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ into the direction of the spin easy axis of CoWO_4 , as schematically indicated by the curved arrow in Fig. 4.15(b). This rotation was indeed observed in neutron scattering experiments for small $x \leq 0.05$ [42, 43, 47]. The decrease of α from 34° ($x = 0$) to 5° ($x = 0.075$) results in a reduction of the FE polarization without changing its orientation, as shown in Fig. 4.10.

However, the decrease of P_b is energetically unfavorable because the multiferroic state gains energy from the coupling of the polarization to the magnetic order parameter. The free energy expansion that couples the electric polarization P and magnetization M is derived based on a continuum field theory of the Ginzburg-Landau type by Mostovoy *et al.* [13]. It is invariant upon the time reversal and spatial inversion symmetry operations and has the mathematical form of a Lifshitz invariant: $\Phi_{em}(P, M) \sim \gamma \vec{P} \cdot [\vec{M}(\nabla \cdot \vec{M}) - (\vec{M} \cdot \nabla)\vec{M}]$. Because the free energy is proportional to the polarization, the gain of free energy in the multiferroic state scales accordingly

with the magnitude of the polarization. If the spin helix rotates closer to the a -axis (the decrease of α angle in Fig. 4.15(a)), the polarization and energy gain of the multiferroic state will further decrease as long as φ is unchanged. From the energy point of view, we can, therefore, expect an instability at a concentration x_{c1} when α decreases below a critical value ($\alpha_c \sim 5^\circ$ from $x = 0.075$ data in Fig. 4.10) and the multiferroic AF2 state cannot gain enough energy to be stable compared to other competing states.

The multiferroic state has to find another way out to gain more energy, which is a flop of the helical plane allowing for larger values of the FE polarization. Therefore, the system rotates the helical plane toward the $a-c$ -plane (for $\varphi = 90^\circ$ and $\alpha = 90^\circ$). Based on Eq. 4.4 and 4.5, this causes rotation of $\vec{P}$ into the $a-c$ -plane, where the two components P_a and P_c arise from Eq. 4.4 and 4.5, respectively. It is interesting to note that how the P_a and P_c components depend on the (α, φ) angles is exactly the same, implying a similar temperature or magnetic field dependent behavior with scaled magnitudes of the polarization values (depending on the different pre-factors in Eq. 4.4 and 4.5).

The P_a induced from ac helix state is realized in the AF5 phase between $x_{c1} = 0.075$ and $x_{c2} = 0.135$ (Fig. 4.3(b) and 4.3(c)). The first sign of the polarization flop from our experimental data of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ is observed at $x = 0.075$ (Fig. 4.3(b)). P_a reaches the largest values around 9 K, even higher than the values for $x = 0.1$ (Fig. 4.3(b) and previous reports [43, 44]). With further cooling, however, P_a passes through a maximum and decreases again. This unusual behavior may indicate a temperature-dependent tilt of the ac helical plane below 8 K away from the optimal orientation, supported by magnetization data. The c -axis component exactly mimics the temperature-dependent behavior of P_a at a smaller scale, expected from Eq. 4.4 and 4.5. Due to this low-temperature tilt, maximum polarization cannot be obtained

for $x = 0.075$ in zero magnetic field. A magnetic field applied along the b -axis inhibits the rotation at low temperature and reveals the maximum value of $P_a > 120 \mu\text{C}/\text{m}^2$ at 4.5 K, which appears to be the upper limit for the MnWO_4 system. The high-field data are included in Fig. 4.3(b) (dashed line) and will be discussed more in Fig. 4.21(a).

P_a and P_c then decrease quickly between x_{c1} and x_{c2} without any sizable b -axis polarization observed. In this doping range, the P_a of $x = 0.1$ is consistent with previous reports [43, 44]. Therefore, the observed decrease of the polarization indicates the possibility of another rotation of the spin helix so that $\alpha < 90^\circ$ and/or $\varphi < 90^\circ$ and $\sin\alpha\sin\varphi < 1$, as sketched Fig.4.15(a), or the deformation of the spin helix. Then, it would be interesting to discuss how the helical plane is rotated so that no sizable b -axis polarization is observed. If α, φ systematically decrease with x , both Eq. 4.4 and 4.5 are expected to also give rise to a significant component P_b , which was not experimentally observed. However, the neutrons scattering results shows no trace of AF2 phase in $x = 0.12$ (Fig. 4.11(a) and (b)) and very weak scattering at $x = 0.135$ (Fig. 4.11(c) and (d)) near the wavevector $\vec{q}_{2/4} = (0.225, 0.5, -0.45)$ that is identified to be the AF2/4 in the $x > 0.15$ doping range (as in Fig. 4.13). In other words, the α angle is too small for the system to give rise to P_b polarization, similar to low temperature $x = 0.075$ case, and small value of $(m_{\parallel}m_{\perp})$ of the spin helix reduces the pre-factor in Eq. 4.4 and 4.5. This only explains how the AF5 ac helix rotates without inducing P_b in the FE phase II, but the nature of why this AF5 ac helix rotates so fast and finishes the rotation in such a narrow doping range is still a open question. This fast decrease of polarization could be due to increase of the helicity, which makes the product of $m_{\parallel}m_{\perp}$ smaller for the same amount of total spin moments.

However, the quick decrease of P_a and P_c also diminishes the stabilizing energy of the multiferroic ac helical state from the magnetoelectric coupling term in free energy

expansion. Therefore, another instability causes the polarization to flop back toward the b -axis (for $x \geq 0.15$). However, because of the strong anisotropy induced by Co, the planar helix cannot be formed so the low temperature phase forms a conical spin structure, which corresponds to the AF2/4 conical phase. The onset of the AF2/4 phase with x is actually $x = 0.135$ (in Fig. 4.11(c)), and yet, both the AF2/4 and AF5 phase in $x = 0.135$ are premature to regain the energy to stabilize either multiferroic state. With further increasing x up to 0.30, the AF2/4 conical phase is realized so that the multiferroic state is stabilized to induce P_b polarization. The further decrease of P_b at higher x is driven by the stabilization of the commensurate paraelectric AF4 phase that extends to lower temperatures and coexists with the helical phase below T_C . The phase boundary is right at $x = 0.15$, as shown in Fig. 4.12, and it reveals the coexistence of a sizable amount of AF5 phase with the arising AF2/4 phase (with b -axis polarization). The AF5 phase at $x = 0.15$ (the major phase at low temperatures) competes with the newly formed AF2/4 phase and the existing high temperature AF1 to cause another anomaly in the P_b data (in Fig. 4.3(d)). It is therefore interesting to observe how competition between AF5 and AF2/4 phase in $x = 0.15$ is changed in the magnetic fields.

4.1.3 Magnetic field effects on the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ compounds

The $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ system shows a complex phase diagram in the previous sections. The Co^{2+} ion substitution in the MnWO_4 causes continuous rotation of the magnetic easy axis due to nearly 80° difference of magnetic anisotropy. This makes the frustrated $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ a complex magnetic system. It would be interesting to see how the external field would affect these magnetic phases. In the following subsections, it is divided into four parts corresponding to three FE phases [I (Sec. 4.1.3.1), II (Sec. 4.1.3.2), and III (Sec. 4.1.3.3)], and the special case [$x = 0.15$ (Sec.

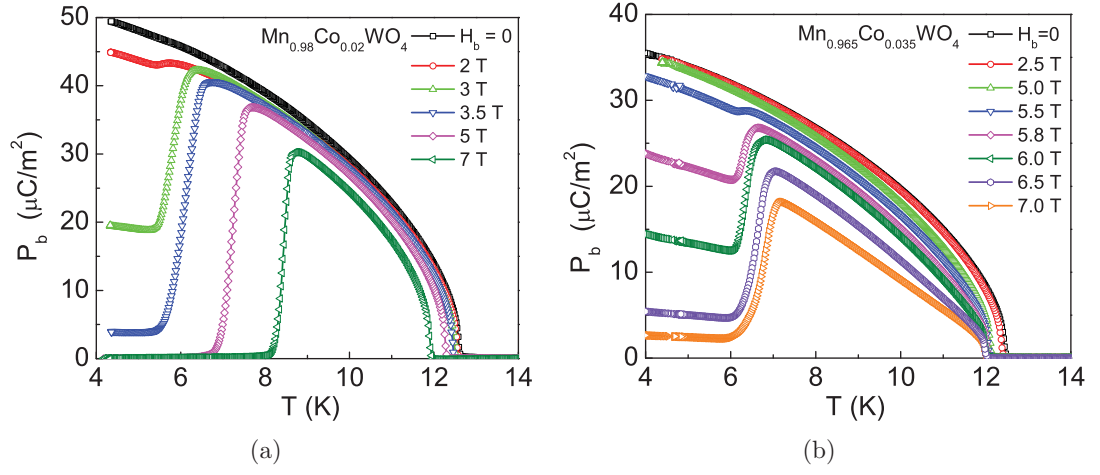


Figure 4.16: Ferroelectric polarization of (a) $\text{Mn}_{0.98}\text{Co}_{0.02}\text{WO}_4$ and (b) $\text{Mn}_{0.965}\text{Co}_{0.035}\text{WO}_4$ in external magnetic fields oriented along the b -axis

4.1.3.4)].

4.1.3.1 Magnetic field effects on phase diagram of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ ($x \leq 0.05$)

For the Co doping level less than 0.05, the $\vec{P}(T)$ of the FE phase I [AF2 (spiral) phase] was found along b -axis. $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ ($0.02 \leq x \leq 0.05$) at zero field show two phase transitions into AF3 and AF2 phases because the commensurate $\uparrow\uparrow\downarrow$ AF1 phase, ground state of the parent compound MnWO_4 , is suppressed by at least 2% of Co substitution.

Fig. 4.16(a) show the b -axis polarization (P_b) of $\text{Mn}_{0.98}\text{Co}_{0.02}\text{WO}_4$ with application of magnetic field along b -axis. At $H_b = 2$ T, P_b starts to show a small polarization drop below 6K. The P_b drop increases with higher H_b , and P_b reaches to zero at lock-in transition T_L around 6K in 3.7 T, indicating that a field-induced $\uparrow\uparrow\downarrow$ AF1 phase is formed as seen in the parent compound MnWO_4 . The sharp decrease of P_b

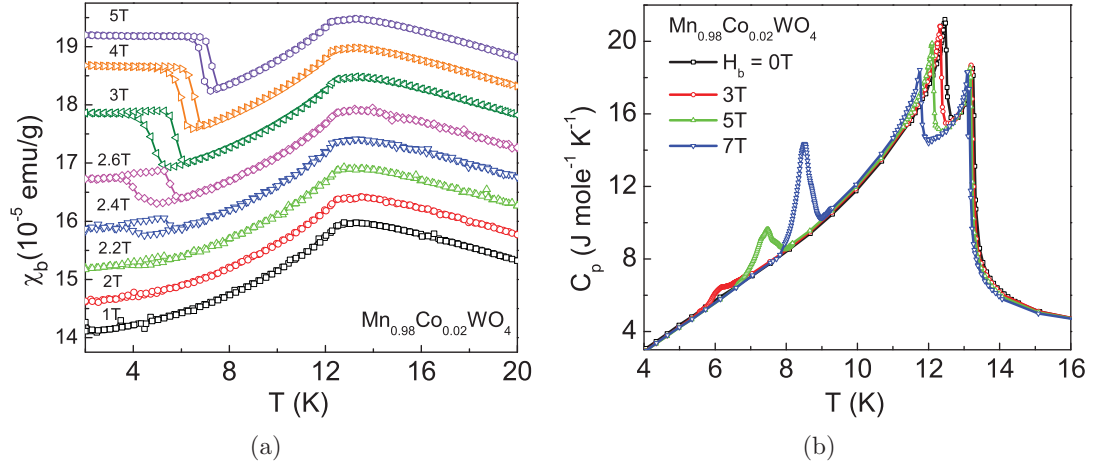


Figure 4.17: (a) Magnetic susceptibility and (b) specific heat of $\text{Mn}_{0.98}\text{Co}_{0.02}\text{WO}_4$ in external magnetic field oriented along the b -axis.

(signature of AF1 phase transition) exhibits strong thermal hysteresis, characteristic of a first-order phase transition. The width of the hysteresis decreases with increasing H_b from 1.8 K (2 T) to 0.25 K (7 T). When the Co content increases to $x = 0.035$, the critical H_b to form the field-induced AF1 phase shifts higher to 5 T, as shown in Fig. 4.16(b). P_b shows no change up to $H_b = 5$ T and decreases continuously above $H_b = 5.5$ T. At $H_b = 7$ T data, the P_b exhibits a finite value at lowest temperature instead of zero, indicating that the AF1 phase is not fully restored. Although the H_b would induce AF1 phase in this Co concentration interval, the compound with higher Co doping requires higher H_b to fully stabilize the induced AF1 phase. The mixed AF1/AF2 phase is similar to (2%) Zn doped MnWO_4 compound [41].

Fig. 4.17(a) and 4.17(b) show the magnetic susceptibility and specific heat data of $\text{Mn}_{0.95}\text{Co}_{0.05}\text{WO}_4$ with the application of magnetic field H_b . At 2.2 T, the low temperature magnetic susceptibility around 5 K starts to develop a small thermal hysteresis loop. With increasing H_b , the susceptibility data forms a step-like fast increase, and the lock-in transition shifts to higher temperature. The response of both

magnetic susceptibility and polarization (Fig. 4.16(a)) indicate that the increase of magnetic field stabilizes the $\uparrow\uparrow\downarrow\downarrow$ AF1 phase by increasing the ratio of AF1:AF2 in the low-temperature phase separation state. This is further supported by the specific heat measurements. The peak at T_L is not detectable at zero magnetic field, but it increases continuously with higher H_b along with an upward shift of T_L . Since only the AF1 phase out of the mixed AF1/AF2 phases shows a peak in the presence of H_b fields, this allows us to correlate the field-induced entropy change from AF1 phase transition peak area with the change of the AF1 phase fraction in the AF1:AF2 ratio. The calculated entropy difference due to the AF1 phase transition peak increases from $\Delta S = 0$ J/mole/K at $H_b = 0$ Tesla to $\Delta S = 0.259$ J/mole/K at $H_b = 7$ Tesla, indicating the volume increase of AF1 state at higher magnetic field.

At the upper limit of the FE phase I ($x = 0.042$ and 0.05), the b -axis magnetic fields (H_b) up to 7 Tesla are no longer able to induce AF1 phase. At zero magnetic field, the major component of polarization is along the b -axis (in Fig. 4.18(b)) with a small amount of a -axis component (Fig. 4.18(a)). With increasing H_b , P_b decrease continuously but P_a increase quickly. Furthermore, P_a in the H_b fields shows an interesting temperature dependence. At H_b field of 3 Tesla, the P_a polarization increases sharply around T_C , passes through a maximum, and then, decreases to a much lower value at low temperature. Above 5 T, P_a increases gradually and reaches its maximum $\approx 90 \mu C/m^2$ at 4.2 K in 7T. This value is nearly identical to the zero-field P_a of higher doping sample at $x = 0.1$ (Fig.4.3(b)). Therefore, H_b rotates the macroscopic FE polarization of $Mn_{0.95}Co_{0.05}WO_4$ continuously from b -axis toward to a -axis with an associated increase of the polarization magnitude from $30 \mu C/m^2$ to $90 \mu C/m^2$.

Fig. 4.19(a) shows the magnetic susceptibility with the application of magnetic field H_b . The low field susceptibility (χ_b) remains almost unchanged up to 2 Tesla. At larger fields, $\chi_b(T)$ is significantly enhanced below the FE transition $T_C = 12.2$ K,

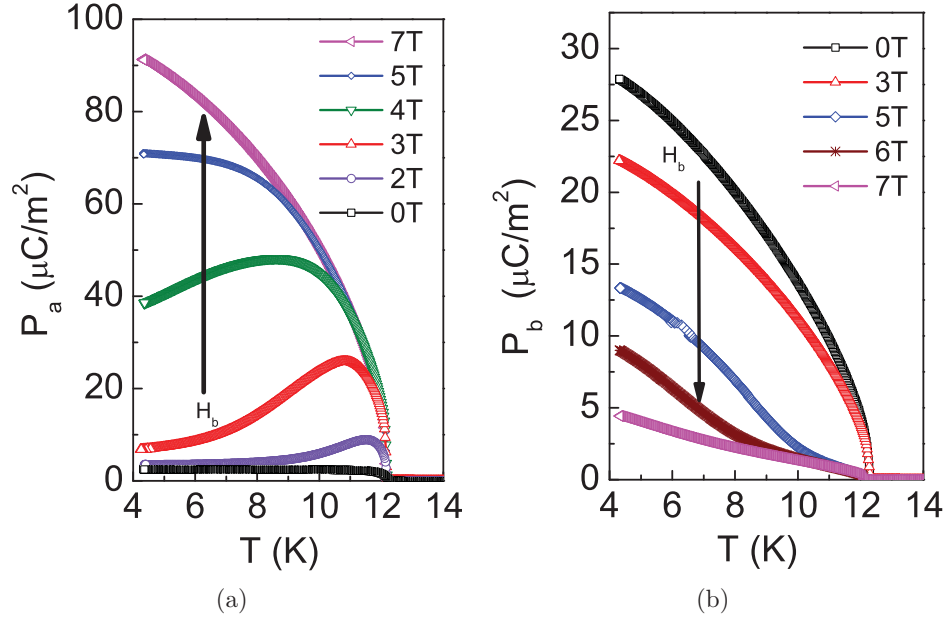


Figure 4.18: Ferroelectric polarization of $\text{Mn}_{0.95}\text{Co}_{0.05}\text{WO}_4$ in external magnetic fields oriented along the b -axis. (a) a -axis component and (b) b -axis component.

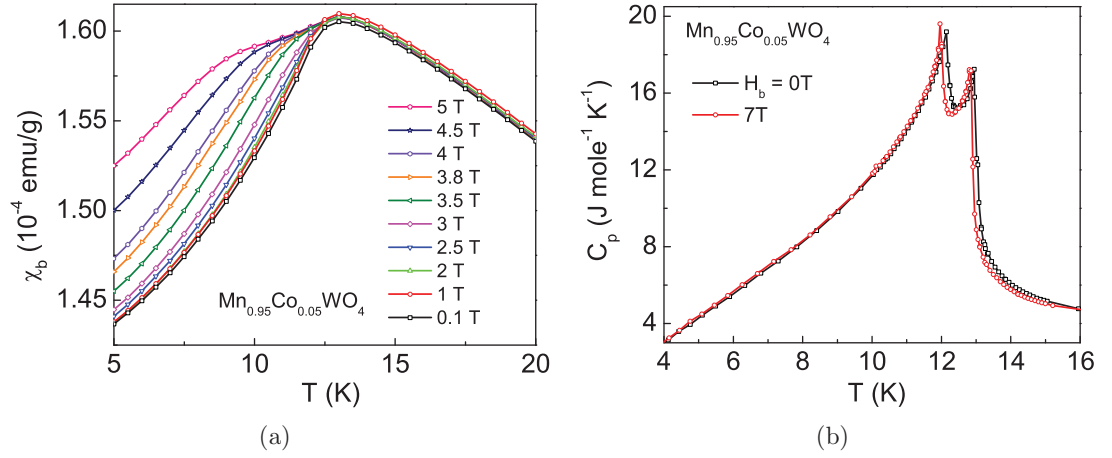


Figure 4.19: (a) Magnetic susceptibility and (b) specific heat of $\text{Mn}_{0.95}\text{Co}_{0.05}\text{WO}_4$ in external magnetic fields oriented along the b -axis.

indicating that the external H_b has an effect onto the magnetic spiral structure. No change of $\chi_b(T)$ is found in the sinusoidal AF3 phase between T_C and T_N , indicating that the field-induced enhancement of the susceptibility is related to the above observed polarization anomalies (P_a increase and P_b decrease with H_b fields). The magnetic field-dependent specific heat data (Fig. 4.19(b)) show no additional anomaly below the FE transition T_C and the AF3 transition. In the temperature range where the anomalies happen, only the magnetic response shows an enhancement without any phase transition peak in the specific heat data.

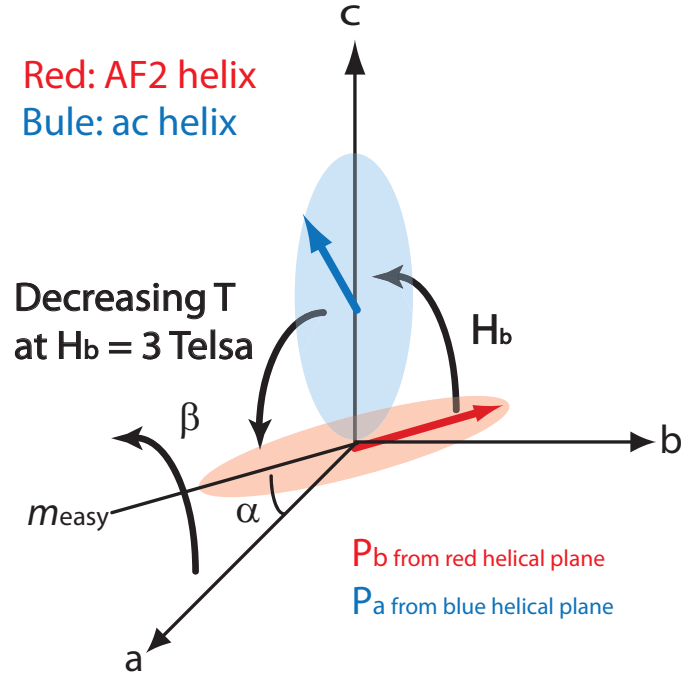
To see more insight of the field-dependent polarization anomalies, the origin of the continuous change of FE polarization between a - and b -axes in magnetic fields requires a more detailed discussion. The immediately raised question is whether P_a and P_b are two components of the same polarization vector of a single magnetic phase or they originate from a phase separation into two helical phases with different orientations of the helical plane. Preliminary neutron data for $\text{Mn}_{0.95}\text{Co}_{0.05}\text{WO}_4$ in high magnetic fields have not shown evidence for a phase separation into two magnetic structures [51]. It is therefore justified to attribute the two components P_a (Fig. 4.18(a)) and P_b (Fig. 4.18(b)) to the a - and b - components of one vector $\vec{P}$. This could be concluded that the b -axis magnetic field rotates the spin helical plane by 90° closer to the $a - c$ plane at the maximum field of 7 Tesla in the whole temperature range of the ferroelectric phase. From the single-crystalline neutron scattering measurements, I. Urcelay-Olabarria *et al.* [44] claimed that the applied external magnetic field tends to flip the spin spiral plane into the direction where is perpendicular to the external field. A similar spiral plane rotation due to magnetic field effect can be concluded from our $P_a(H_b)$ and $P_b(H_b)$ data. As shown in Fig. 4.20(a), the H_b field rotates the spiral plane of AF2 phase toward the $a - c$ plane about the magnetic easy axis to be perpendicular to the b -axis. So far, we can only qualitatively explain the $P_a(H_b)$

increase and $P_b(H_b)$ decrease as a consequence of the rotation of the spin helical plane, but in order to resolve why the 3 Tesla P_a data show a maximum around 11 K and decreases at low temperature we need to further analyze our polarization data to study the temperature-dependent rotation of the spin spiral plane.

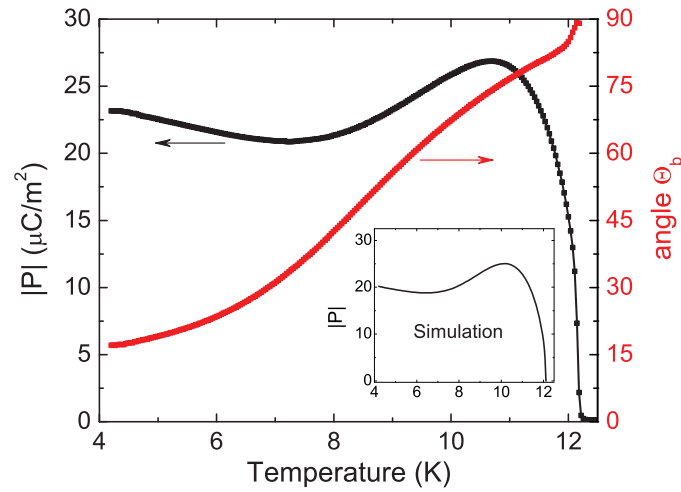
The magnitude of this vector ($|P| = \sqrt{P_a^2 + P_b^2}$) and its angle with the b -axis (Θ_b) can be calculated as a function of temperature and magnetic field by the experimental data for P_a and P_b . The results of $|P|$ and Θ_b measured at a constant field of 3 Tesla as a function of temperature are shown in Fig. 4.20(b). The magnitude of the polarization rises quickly below T_C and shows a pronounced maximum at about 11 K. At lower temperature, $|P|$ tends to saturate at a value of $23 \mu\text{C}/\text{m}^2$ after passing through a shallow minimum. At the same time, the $\Theta_b(T)$ smoothly decreases from 90° at T_C to about 15° at 4 K. The ferroelectric polarization is first aligned with the a -axis at T_C but it rotates back to the b -axis with decreasing temperature.

The complex temperature-dependent $|P(T)|$ and $\Theta_b(T)$ data (as shown in Fig. 4.20(b)) could be explained by the rotation of the helical plane related to the magnetic order of the Mn spins. The rotation of the spin helix about the magnetic easy axis is quantitatively described by the angle β of the helical plane with the b -axis as shown in Fig. 4.20(a). At the field of 3 Tesla, the spin helix at T_C apparently lies in the $a-c$ plane ($\beta(T_C) = 90^\circ$) and the polarization is along the a -axis. At lower temperature, β decreases and the helical plane tilts away from the $a-c$ plane. At the same time, the magnitude of the polarization ($|P(T)|$) increases as expected when temperature is further decreased below T_C . The unusual temperature dependence of $|P(T)|$ at 3 Tesla (Fig. 4.20(b)) with a maximum at 11 K must be a combined effect of both the increase of $|P(T)|$ with decreasing T and the rotation of the polarization vector from the a -axis to the b -axis.

In order to derive an empirical equation to describe the field-dependent rotation



(a)



(b)

Figure 4.20: (a) Schematic diagram of the field dependent rotation of the spin spiral plane (red helical plane) about magnetic easy axis at 3 T and (b) magnitude and orientation of the polarization vector of $\text{Mn}_{0.95}\text{Co}_{0.05}\text{WO}_4$ at 3 T. Θ_b is the angle of the polarization vector with the b -axis. The inset shows the polarization magnitude calculated from Eq. 4.9.

of polarization and unusual temperature-dependent phenomenon in the 3 T data, we have to add the polarization change due to the rotation of the spin helical plane about the magnetic easy axis by β angle to the above-mentioned Eq. 4.4. Because here we want to connect the rotation of $\vec{P}$ between b - and a -axis with the rotation of the spiral plane about the magnetic easy by β angle. For simplicity, we only consider the main exchange interaction along the c -axis, and choose to start from the pure b -axis polarization in the Cartesian coordinate system so that the $\varphi = 0$ because $\vec{P}$ is aligned with the b -axis at zero field. Therefore, from Eq. 4.4, the expression can be written as

$$\vec{P} = C^{(1)} \sin(q_c c / 2) \vec{m}_{\parallel} \vec{m}_{\perp} \sin \alpha \vec{b} \quad (4.6)$$

where $\vec{a}$, $\vec{b}$, and $\vec{c}$ are the unit vectors along the a -, b -, and c -axis, respectively. $\vec{m}_{\parallel}$ and $\vec{m}_{\perp}$ are the two orthogonal components of the magnetic moment vector along the b -axis and the easy axis, respectively, defining the ellipticity of the helical spin order and q_c is the c -axis component of the magnetic modulation vector. $C^{(1)}$ is a constant related to the structural details.

The calculation is done as follows: First transform the Cartesian coordinate into $(\vec{e}_{\text{easy}}, \vec{b}, \vec{k})$ coordinate system, where the main axes are magnetic easy axis, b -axis and normal vector of the spiral plane in the AF2 phase. Then, we rotate the whole spiral plane about the $\vec{e}_{\text{easy}}$ by β angle toward the $a - c$ plane. The last step is to transform the current coordinate back to Cartesian coordinate as

$$\vec{P} = C^{(1)} \sin(q_c c / 2) \vec{m}_{\parallel} \vec{m}_{\perp} (\sin(\beta) \vec{a} + \cos(\beta) \sin(\alpha) \vec{b}) \quad (4.7)$$

where $\vec{a}$ and $\vec{b}$ are the unit vectors along the a - and b -axis. Now, we can use Eq.

4.7 to describe the rotation between P_a and P_b in term of β angle. Note that for a comparison some simplifying assumptions have to be made. The angle α is chosen as 16° (consistent with neutron scattering results [43, 34]), and no change of this angle with magnetic field is considered. Furthermore, we assume that the product $\vec{m}_\parallel \vec{m}_\perp$ does not change in external magnetic fields. Up to this point, Eq. 4.7 describes the H_b field-induced rotation of the polarization from the b -axis ($\beta=0$) to the a -axis ($\beta=90^\circ$). In the following, we want to add the temperature-dependent factors in the Eq. 4.7 to discuss the unusual temperature-dependent phenomenon of $|P|$ in the 3 T data. First, focusing on the angular dependence (β, α) , Eq. 4.7 can be written as

$$\vec{P} = P_0(T)(\sin(\beta)\vec{a} + \cos(\beta)\sin(\alpha)\vec{b}) \quad (4.8)$$

where for the temperature-dependent order parameter $P_0(T)$, we assume the mean field function $P_0(T) = P_0(0)\sqrt{1 - T/T_C}$, with $P_0(0) = 90\mu C/m^2$.

The rotation angle of the helical plane β is related to the measured polarization angle Θ_b through $\tan(\beta) = \tan(\Theta_b)\sin(\alpha)$. Eq. (4.8) should qualitatively describe the data shown in Fig. 4.20(b). The magnitude of the polarization vector can now be expressed as

$$|P(T)| = P_0(T)\sqrt{(\sin^2(\beta) + \cos^2(\beta)\sin^2(\alpha))} \quad (4.9)$$

We use the temperature-dependent Θ_b (Fig. 4.20(b)) from our experiments as input to equation (4.9) so the magnitude of the polarization could be calculated and shown in the inset of Fig. 4.20(b) (labeled "Simulation"). The characteristic features of $|P(T)|$, including the maximum of $|P(T)|$ below T_C , are in fact very well reproduced. A more quantitative evaluation does require additional input from high-field

neutron scattering experiments such as the possible field and temperature dependence of the parameters defining the helical spin structure ($\alpha, m_{\parallel}, m_{\perp}$, etc.) and a low-temperature correction to the mean field formula for $P_0(T)$. However, the good agreement of the experimental data with the simple formula for the polarization (equation 4.9) prove that the orientation of the spin helical plane is the major parameter determining the magnitude and orientation of $\vec{P}(T)$.

4.1.3.2 Magnetic field effects on phase diagram of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ ($x \leq 0.075 \leq 0.135$)

For the Co doping level between $x = 0.075$ and 0.135 , the $\vec{P}(T)$ of the FE phase II [AF5 (spiral) phase] was found in the $a-c$ -plane because the Mn spins form an $a-c$ helical plane. In the FE phase II, there are two Co concentration interval $x \leq 0.1$ and $x > 0.1$ due to the formation of high temperature AF1 phase. When $x \leq 0.1$, magnetic spins form sinusoidal AF3 order at the T_N , and it is then transformed into AF5 phase below T_C . The high temperature AF1 phase was first found significant in the $x = 0.12$ compound along with the development of AF4 phase at higher temperature, and therefore, the phase sequence with decreasing temperature for $x = 0.12$ is AF4, AF3, AF1, and AF5.

Fig. 4.21(a) and 4.21(b) show the b -axis (H_b) and c -axis (H_c) magnetic field-dependent a -axis polarization of $\text{Mn}_{0.925}\text{Co}_{0.075}\text{WO}_4$. At zero field, P_a sharply increases to a maximum around 9 K, and drops at lower temperature, indicating that the $a-c$ spin spiral structure was first formed at T_C and rotates away from the $a-c$ plane about the a -axis (or an axis at a small angle with the a -axis) toward the $a-b$ plane at low temperature, as shown as "Low-T & H_c " in Fig. 4.21(d). The application of H_b and H_c fields shows opposite results. With increase of H_b , the $P_a(T)$ at low temperature shows a significant enhancement, which means that the H_b stabilizes

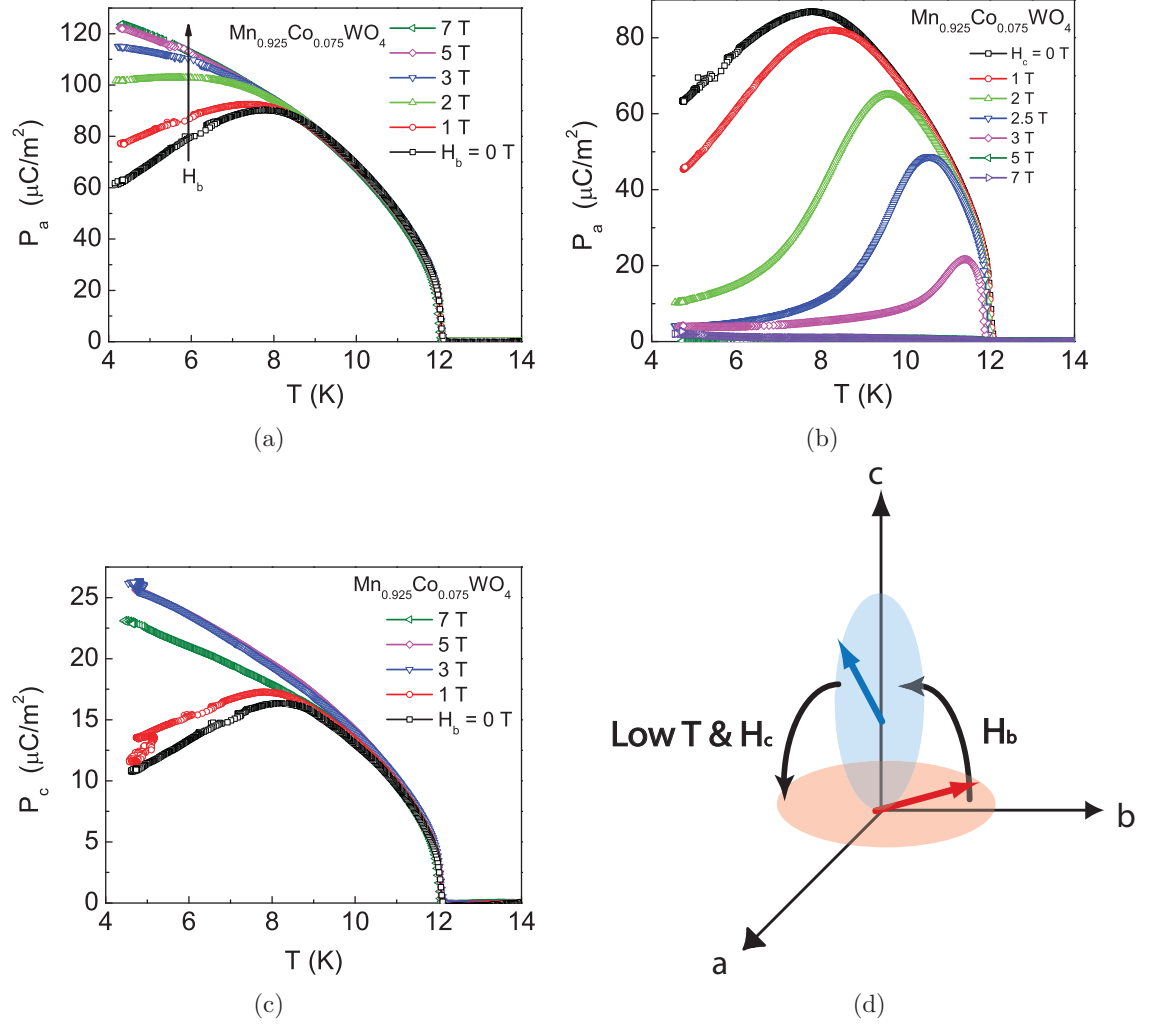


Figure 4.21: Ferroelectric polarization of $\text{Mn}_{0.925}\text{Co}_{0.075}\text{WO}_4$ in external magnetic fields. (a) a -axis component in b -axis magnetic fields $P_a(H_b)$, (b) a -axis component in c -axis magnetic fields $P_a(H_c)$, (c) c -axis component in b -axis magnetic fields $P_c(H_b)$ (d) schematic diagram of the temperature-dependent (Low-T) and field-dependent (H_b or H_c) rotation of the helical plane.

the $a - c$ helical structure. The enhancement effect of the P_a reaches to maximum at $H_b = 5$ T, where the a -axis polarization at lowest temperature increases from $60 \mu\text{C}/\text{m}^2$ at 0 Tesla to $120 \mu\text{C}/\text{m}^2$ at 5 Tesla. It should be noted that this value is the highest measured in any doped or undoped MnWO_4 compound, and it exceeds the maximum b -axis polarization of MnWO_4 by a factor of two. On the contrary, 1 Tesla of c -axis magnetic field is already high enough to reduce P_a , meaning that the magnetic structure tilts away from an optimal $a - c$ helical plane. The further increase of H_c continuously decreases a -axis polarization, and the P_a drops to zero above $H_c = 5$ T. As mentioned above [44], the applied external magnetic field tends to flip the spin spiral plane into the direction where it is perpendicular to the external field. The rotation of the spiral plane due to the application of external magnetic fields allows us to explain what happen to our $P_a(H_b)$ and $P_a(H_c)$ data. When the external magnetic field is along the b -axis, the $a - c$ spiral plane of the AF5 phase is forced to be perpendicular to b -axis, as shown in Fig. 4.21(d). With the help of H_b , the $\text{Mn}_{0.925}\text{Co}_{0.075}\text{WO}_4$ compound could better stabilize the $a - c$ spin spiral structure at low temperature so P_a does decrease. On the contrary, the H_c fields force the $a - c$ spin spiral structure to rotate into $a - b$ plane, which is detrimental to the P_a . The increase of P_a by H_b and decrease of P_a by H_c behavior is not limited to the $\text{Mn}_{0.925}\text{Co}_{0.075}\text{WO}_4$ sample but to all the FE II phases ($x = 0.075, 0.1, 0.12$ and 0.135) and the $x = 0.15$.

The c -axis polarization P_c due to the interchain magnetic interactions along a -axis in the b -axis magnetic field (Fig. 4.21(c)) increases with increasing H_b , which is similarly to the $P_a(H_b)$ data. Since the $P_a(H_b)$ and $P_c(H_b)$ scale well with each other, this provides an additional prove for the Eq. 4.3. Fig. 4.22(a) and 4.22(b) shows the b -axis (χ_b) and c -axis (χ_c) components of magnetic susceptibility of $\text{Mn}_{0.925}\text{Co}_{0.075}\text{WO}_4$. The presence of b -axis or c -axis magnetic field shows no notable anomaly at sinusoidal

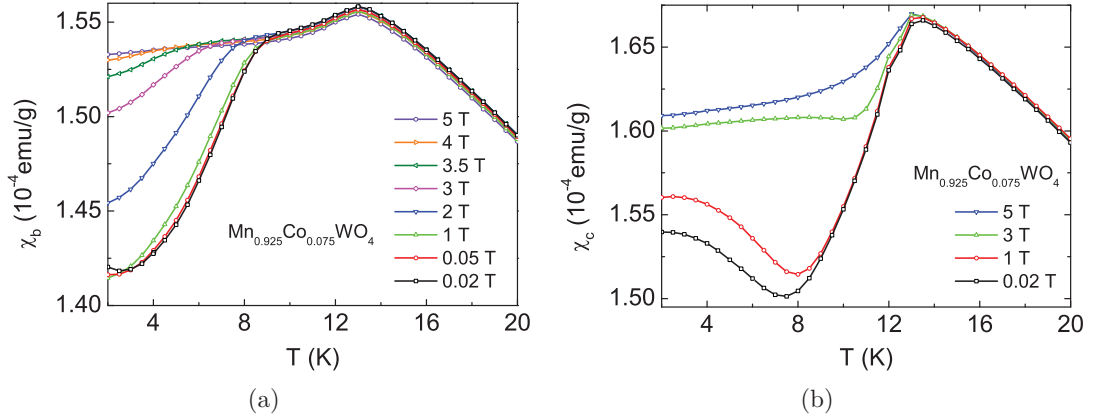


Figure 4.22: Magnetic susceptibility of $\text{Mn}_{0.925}\text{Co}_{0.075}\text{WO}_4$ in external magnetic fields oriented along the (a) b -axis and (b) c -axis.

AF3 phase transition. Below the T_C , both χ_b and χ_c show an increase of magnetic susceptibility with the application of magnetic fields, which could be related to the spin flops to be perpendicular to the external field.

With increasing x up to 0.1, the P_a in b -axis magnetic field (Fig. 4.23(a)) behaves slightly different from the $x = 0.075$ case. The a -axis polarization of $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$ shows no change even if the magnetic field H_b increase up to 7 Tesla, indicating that the spin spiral structure of $x = 0.01$ compound forms a perfect $a - c$ spin spiral. Fig. 4.23(b) shows the a -axis polarization in the presence of c -axis magnetic field. However, it takes as high as magnetic field $H_c = 2$ T to observe the decrease of P_a . Increasing the H_c further decreases P_a and almost completely eliminates the P_a in the 4 T of H_c . The H_c field flips the $a - c$ spin helical plane into $a - b$ plane so that the P_a decreases, as shown in Fig. 4.23(d). The $P_a(H_b)$ and $P_a(H_c)$ two data is qualitatively consistent with the previous reports [43, 44]. The interchain magnetic interactions along a -axis also results in the c -axis polarization of $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$. Furthermore, the application of c -axis magnetic field also decreases the c -axis polarization as shown in Fig. 4.23(c).

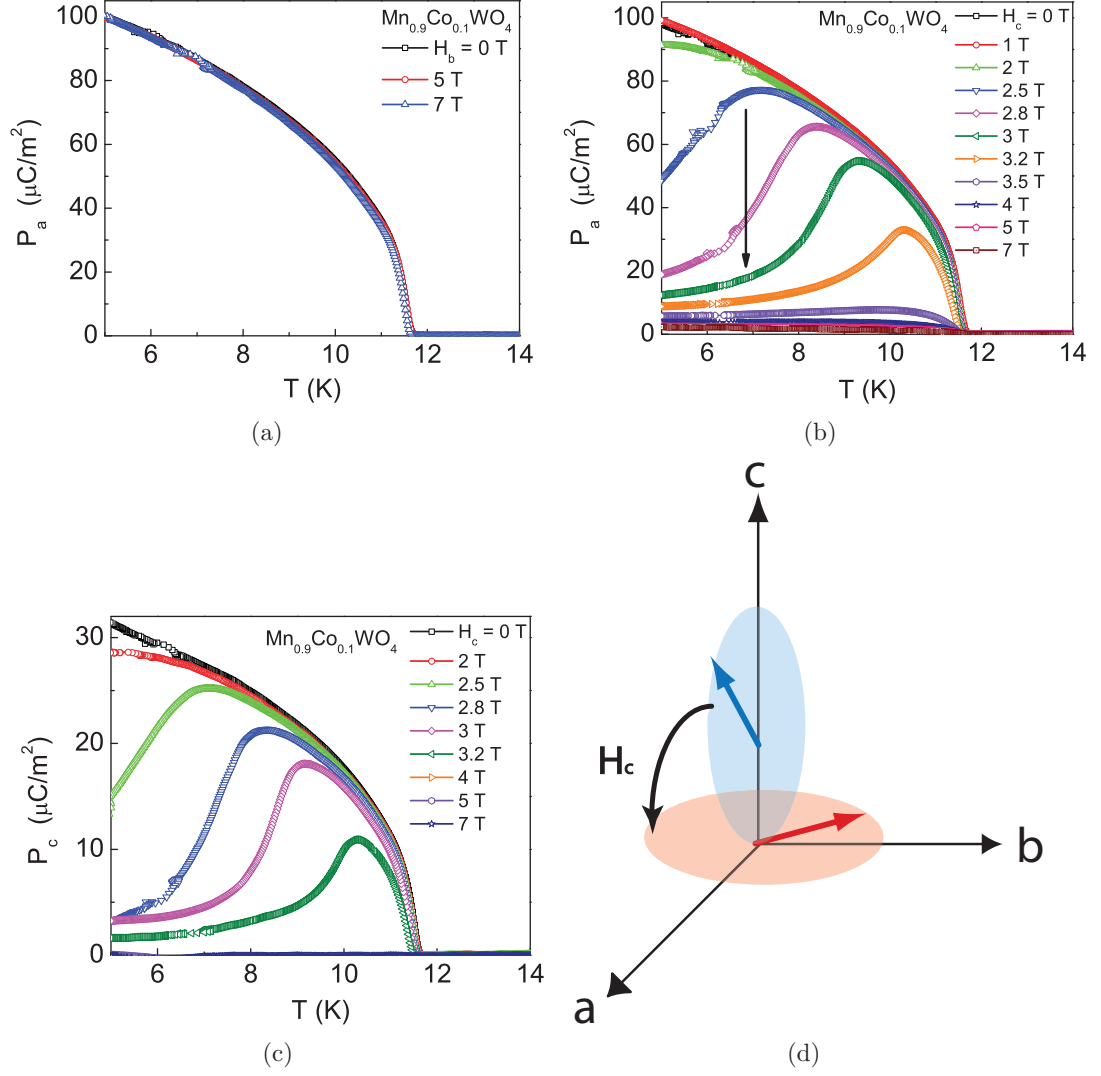


Figure 4.23: Ferroelectric polarization of $\text{Mn}_{0.9}\text{Co}_{0.1}\text{WO}_4$ in external magnetic fields. (a) a -axis component in b -axis magnetic fields $P_a(H_b)$, (b) a -axis component in c -axis magnetic fields $P_a(H_c)$, (c) c -axis component in c -axis magnetic fields $P_c(H_c)$ (Note: The $P_c(H_c)$ in the field of $H_c \geq 4$ Tesla are very small) and (d) schematic diagram of the field-dependent rotation of the spin helical plane.

At this point, the claim that the applied external magnetic field tends to flip the spin spiral plane into the direction where it is perpendicular to the external field from I. Urcelay-Olabarria *et al.* [44] is well-supported by our experiment data from $x = 0.05$ up to 0.1. However, the physical picture of the rotation forced by the external magnetic field is not discussed yet. The easiest way to argue this magnetic field effect is to consider two antiparallel spins with application of magnetic field in the direction of one of the spin. Although the spin parallel to the external magnetic field is able to gain energy to be stable, the other spin, however, is suffered in the presence of the magnetic field due to no energy gain. The way to stabilize both antiparallel spins is for them to align perpendicular to the external magnetic field so that both spins still keep antiferromagnetic exchange energy and are stable under magnetic field.

However, the magnetic structure of the multiferroic phase (AF2 or AF5) of our system is not a simple case with a upward spin and a downward spin. The derivation by using Ginzburg-Landau theory on how the spins helix structure react to the external magnetic field is performed in the Ref. [13]. As shown in the Fig. 4.24, the application of external magnetic field first enhances those spins parallel to the field and reduces those antiparallel spins so that the whole spin helical structure is distorted and causes the decrease of the ferroelectric polarization. Whenever the external magnetic field is big enough, those spins antiparallel to the external field flip toward the direction of the field and form a wide spin conical structure with small amount of magnetic moment component in the direction the magnetic field (the third picture of each row in Fig. 4.24). With further increase of magnetic field, the angle of the cone decreases, and eventually, the conical structure will be collapsed so that all spins are aligned to the direction of the external field. For the induced polarization from the spin helix, the polarization is proportional to the cross product of c -axis unit vector and $\vec{k}$ vector (cross product of two neighbor spins). Therefore, when a

conical structure is formed due to the magnetic field effect, it would be important to find out the angle between c -axis unit vector and $\vec{k}$ vector (spiral plane normal vector) to understand how the polarization is changed accordingly. The $\vec{k}$ vector of the ac helix generated by the conical structure in the first row of the Fig. 4.24 is perpendicular to the c -axis so that large amount of P_a is induced, and this is why P_a of $x = 0.05$ and 0.75 compounds is around $100 \mu C/m^2$ at 7 Tesla. On the contrary, with application of c -axis magnetic field on the ac helix, the ab helix generated from the conical structure is parallel to the ab plane, and the $\vec{k}$ vector is parallel to the c -axis so that there is no P_b induced. In summary, the external magnetic field forces the spin helix to form a conical structure so that the spins are surrounding the external field. The rotation of the polarization due to the magnetic fields is the result of the change of magnetic structure from the ac helix (blue area in Fig. 4.24) to conical structure with the spiral plane on the top flat plane (red area in Fig. 4.24) of the spin conical structure.

When $x \geq 0.12$ as shown in phase diagram Fig. 4.8, the presence of high temperature AF1 phase reduces critical temperature of T_C , and the transition is strong first order phase transition with thermal hysteresis about 1K at the zero field Fig. 4.25(a) and 4.25(b) display the a -axis polarization of $Mn_{0.88}Co_{0.12}WO_4$ in the magnetic field of H_b and H_c , respectively. As typical AF5 helical phase under H_b and H_c , the $P_a(H_b)$ increase with higher H_b fields, whereas the $P_a(H_c)$ decreases with increasing H_c fields. The ac helix in $x = 0.12$ compound is not optimal, similar to low temperature part of $x = 0.075$ as shown Fig. 4.21(d), and the field H_b makes the spin helix favor the $a - c$ plane; therefore, the $P_a(H_b)$ is increased. On the other hand, the H_c field tilts the spin helix away from the $a - c$ plane so that the $P_a(H_c)$ decrease with H_c field. This is well-understood from the above discussion.

However, the b -axis polarization with application of c -axis magnetic field shows

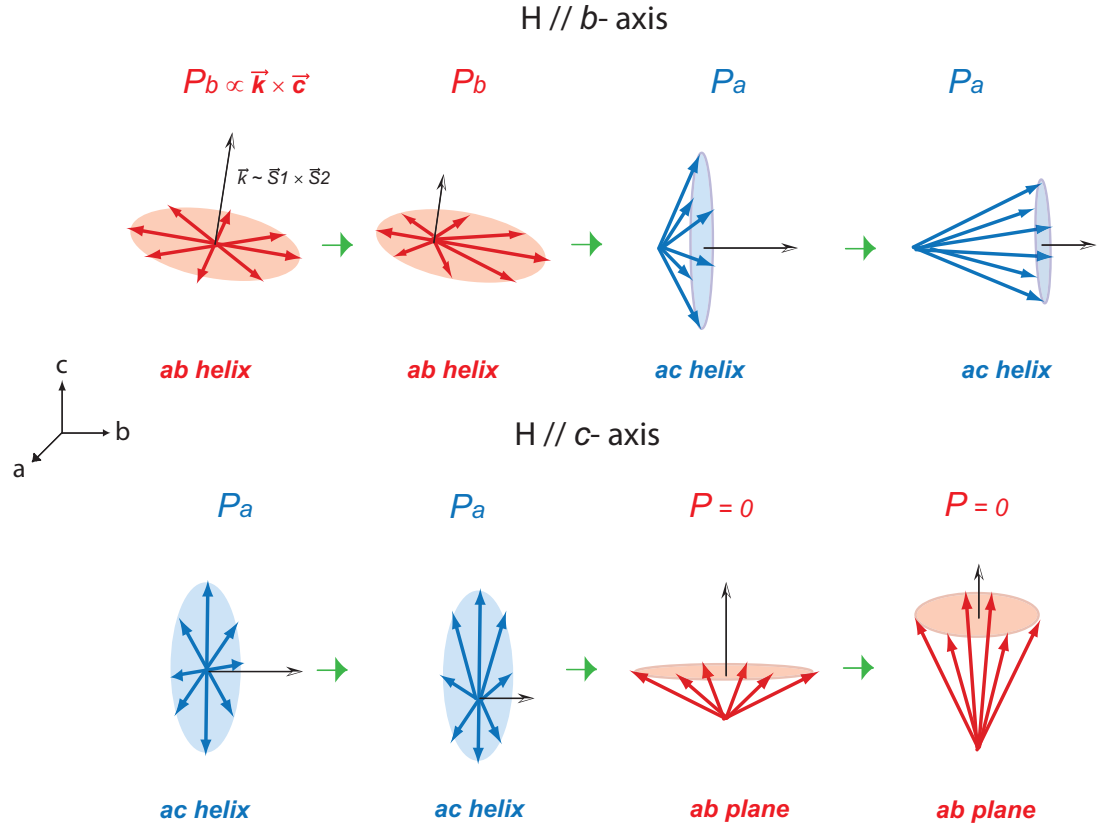


Figure 4.24: Schematic diagram of the field-dependent (H_b or H_c) rotation of the *ab* and *ac* spin helix.

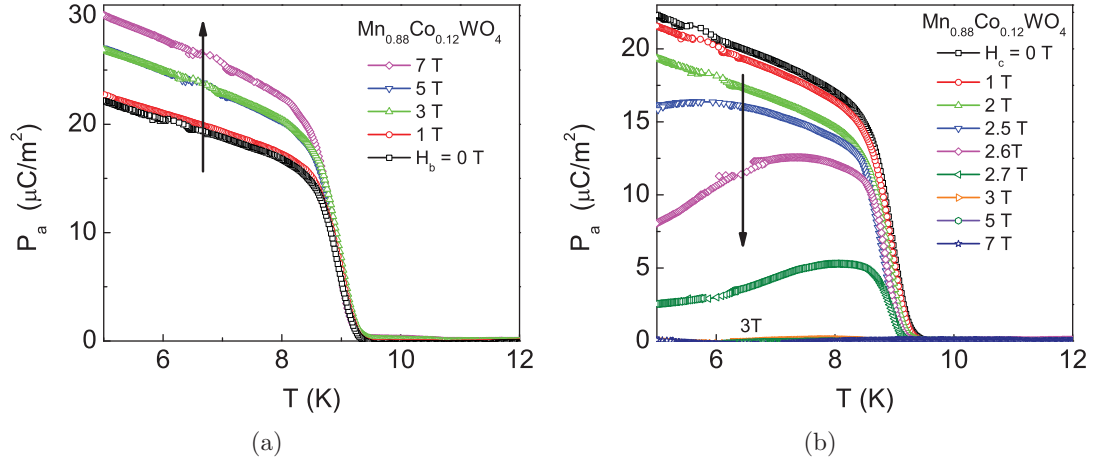
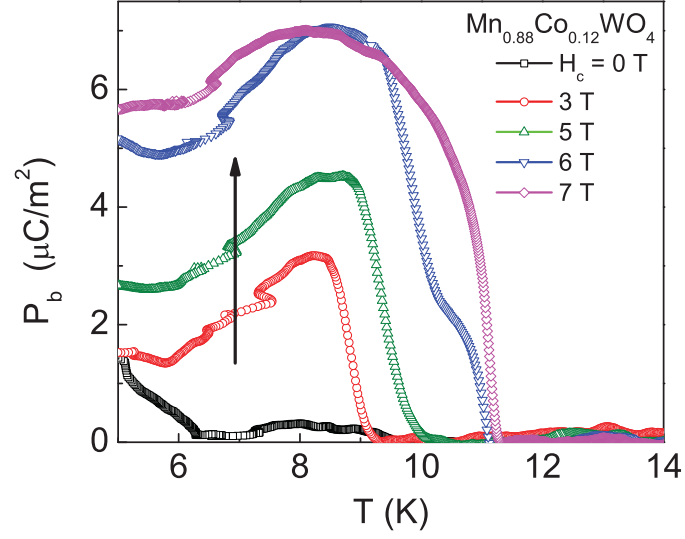


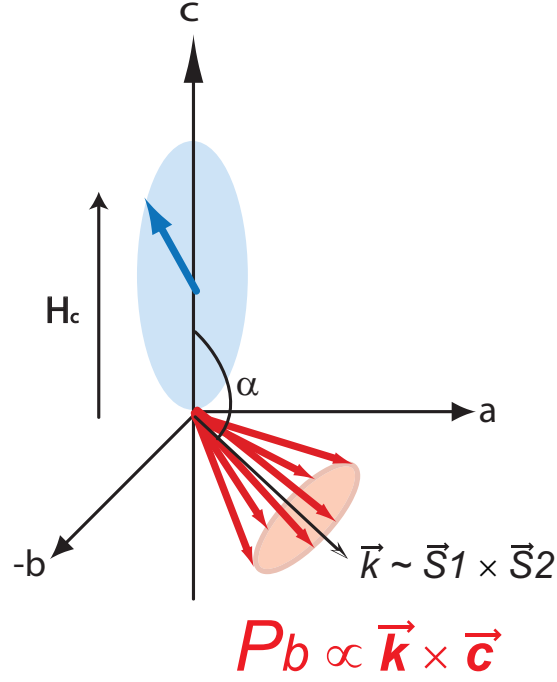
Figure 4.25: Ferroelectric polarization of $\text{Mn}_{0.88}\text{Co}_{0.12}\text{WO}_4$ in external magnetic fields. (a) a -axis component in b -axis magnetic fields $P_a(H_b)$ and (b) a -axis component in c -axis magnetic fields $P_a(H_c)$ (Note: The $P_a(H_c)$ in the field of $H_c \geq 3$ Tesla are very small).

a new type of field-dependent behavior in the Co doped MnWO_4 system, as shown in Fig. 4.26(a). At zero field, b -axis polarization is barely observable within the resolution of the pyro-electric measurements. The presence of c -axis magnetic fields stabilizes the b -axis polarization of $\text{Mn}_{0.88}\text{Co}_{0.12}\text{WO}_4$. At the field of $H_c = 3$ T, the b -axis polarization shows a sharp increase at around $T_C = 9$ K, reaches to its maximum $\approx 3 \mu\text{C}/\text{m}^2$, and then decreases at lower temperature. Increasing c -axis magnetic field further increases b -axis polarization. At the same time, the T_C of $P_b(H_c)$ shift toward higher temperature, indicating that the stability in the temperature range of the ferroelectric phase increases on the expense of the AF1 phase, where the AF1 phase is discussed in Fig. 4.8 and 4.11.

To further investigate the effects of c -axis magnetic fields to the $x = 0.12$ compound, H_c dependence of magnetic susceptibility and specific heat data is shown in Fig. 4.27(a) and 4.27(b). At zero field, the four phase transitions of $x = 0.12$ with the order of decreasing temperature are AF4, AF3, AF1, and AF5. The increase of



(a)

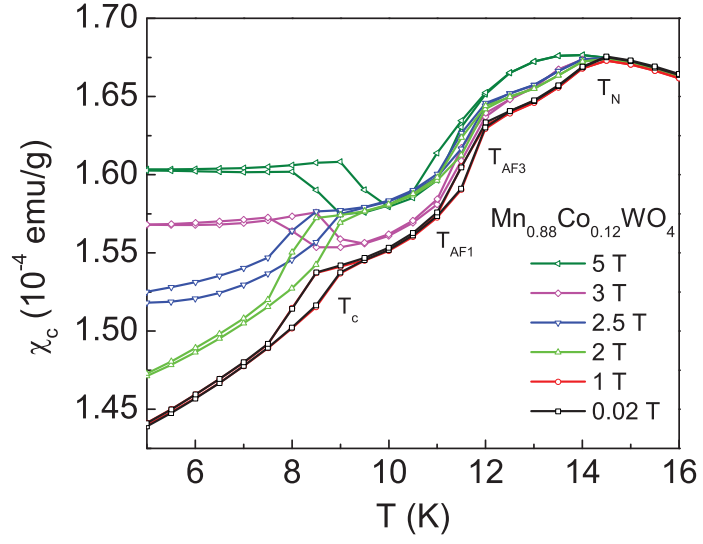


(b)

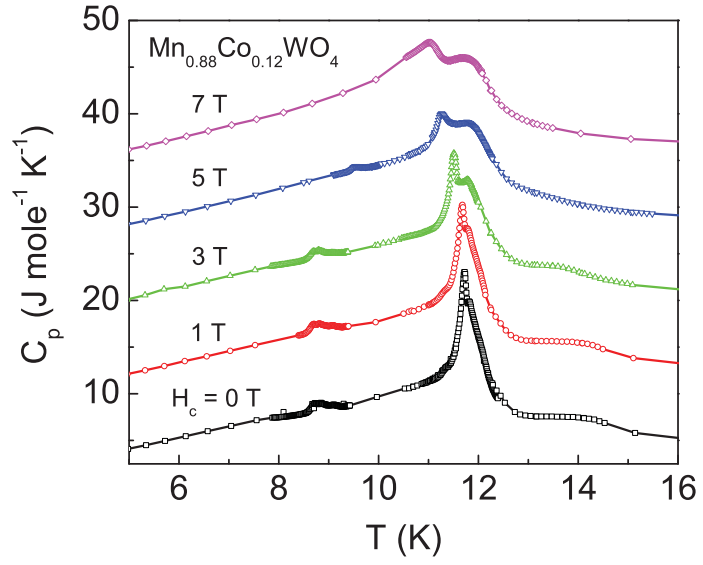
Figure 4.26: (a) Ferroelectric polarization along the b -axis of $\text{Mn}_{0.88}\text{Co}_{0.12}\text{WO}_4$ in external magnetic fields oriented along the c -axis $P_b(H_c)$ and (b) schematic diagram of the field-dependent (H_c) rotation of the spin helical plane

H_c first causes the enhancement of the low temperature magnetic susceptibility, and the low temperature χ_c develops a step-like of sharp increase above $H_c = 3$ Tesla. Although this step-like sharp increase is similar to that of the ground state of the pure MnWO_4 , the sharp increase seen here could be related to the induced $P_b(H_c)$ at the low temperature or the decrease of $P_a(H_c)$. Furthermore, the thermal hysteresis of the AF5 phase transition at T_C shifts to higher temperature, indicating the shrinkage of AF1 phase. The temperature shifting anomaly is confirmed by the specific heat measurements. The small peak due to the first-order phase transition at T_C shifts to higher temperature, and it corresponds to the development of the step-like magnetic susceptibility (χ_c) and upward shift to higher temperature of the T_C of the P_b . Combining the $P_b(H_c)$, χ_c , and c -axis magnetic field specific heat data, it is confirmed that H_c induces the AF2 phase on the expense of the high temperature AF1 phase.

It is worth to note that the induced $P_b(H_c)$ is not observed in $x = 0.075$ and 0.1 compounds. While the H_c is forcing the $a - c$ spin helical plane to rotate into $a - b$ plane, it may be due to the strong magnetic anisotropy of the specific magnetic system in the $x = 0.12$ compound that causes the center of the spin conical structure away from the c -axis, and therefore, the normal vector $\vec{k}$ of the spiral plane has a finite angle α with the c -axis to induce P_b polarization, as shown in Fig. 4.26(b). On the other hand, the other possibility is that the spin helical plane is in the $a - b$ plane (α angle in Fig. 4.26(b) is zero with $\vec{k} = \vec{c}$) after the field-induced rotation, and the main spin-spin interaction is now along the a -axis so the propagation vector is oriented with a -axis because the magnetic exchange interaction along c gives to no polarization in this configuration. Since the direction of polarization is determined by the vector product of the normal vector $\vec{k} (= \vec{c})$ and propagation vector ($\vec{a}$) of the spiral plane, the polarization in the presence of H_c is, therefore, along the b -axis. This part requires further magnetic field dependent neutron scattering measurements



(a)



(b)

Figure 4.27: (a) Magnetic susceptibility and (b) specific heat of $\text{Mn}_{0.88}\text{Co}_{0.12}\text{WO}_4$ in external magnetic fields oriented along the c -axis.

to get a better microscopic understanding.

4.1.3.3 Magnetic field effects on phase diagram of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ ($0.17 \leq x \leq 0.3$)

For the Co doping level $x > 0.15$ as shown in Fig. 4.8, the $\vec{P}(T)$ of the FE phase III was aligned along the b -axis due to the recovery of the AF2 spiral phase (so called AF2/4 conical phase) from a two $\vec{k}$ modulation vector of the spin conical structure [47]. At zero magnetic field, the simple modulation AF4 type of magnetic structure forms at the T_N temperature and followed by the AF2/4 conical phase at lower temperature. The recovered b -axis polarization decreases with higher Co replacement and drops to zero when the x is greater than 0.3.

The b -axis polarization of the FE phase III ($0.17 \leq x \leq 0.3$) with the application of b -axis magnetic field is shown in Fig. 4.28. When the Co concentration $x = 0.17$, the value of P_b at zero field is $\sim 28 \mu\text{C}/\text{m}^2$ at 5 K and drops to $21 \mu\text{C}/\text{m}^2$ in 7 Tesla with the T_C shifting to lower temperature. The effect of H_b for $x = 0.2$ becomes more significant, and the P_b decreases by half in the presence of 7 Tesla. By further increasing x to 0.25, the b -axis magnetic field of 7 Tesla is able to completely suppress the P_b . From these polarization data, we can conclude that the H_b fields simply destroy the magnetic conical structure by first decreasing the angle of the conical structure so that the spin cone becomes narrower. Then, the H_b fields further rotate spin toward the magnetic easy axis as shown in Fig. 4.28(d). At the same time, because the spins of the AF4 phase are also in the $a - c$ plane, the AF2/4 conical structure in the H_b fields is likely transformed into the AF4 phase by collapsing cone to a line oriented along the spin easy axis, as shown in Fig. 4.28(d).

Fig. 4.29(a) shows the magnetic susceptibility in the b -axis magnetic field. At zero

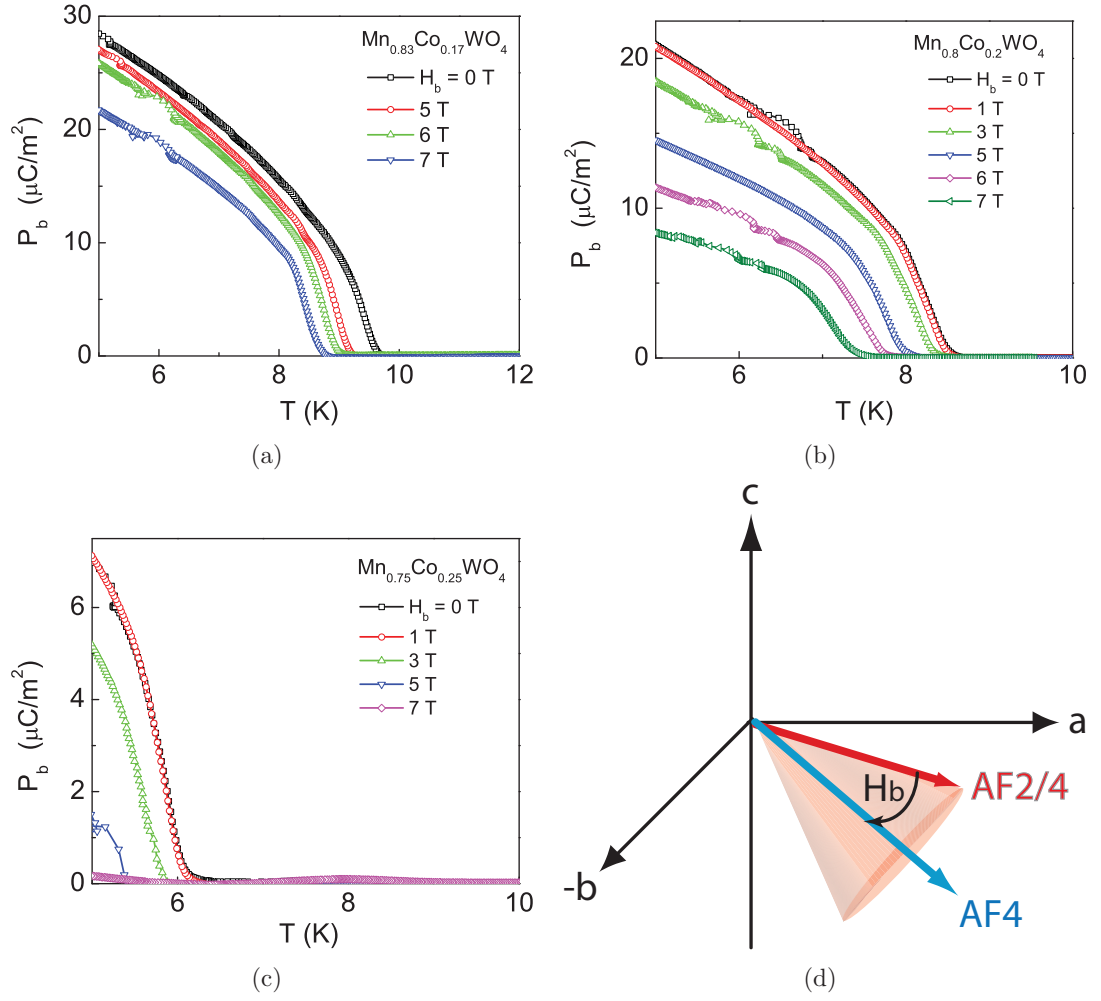
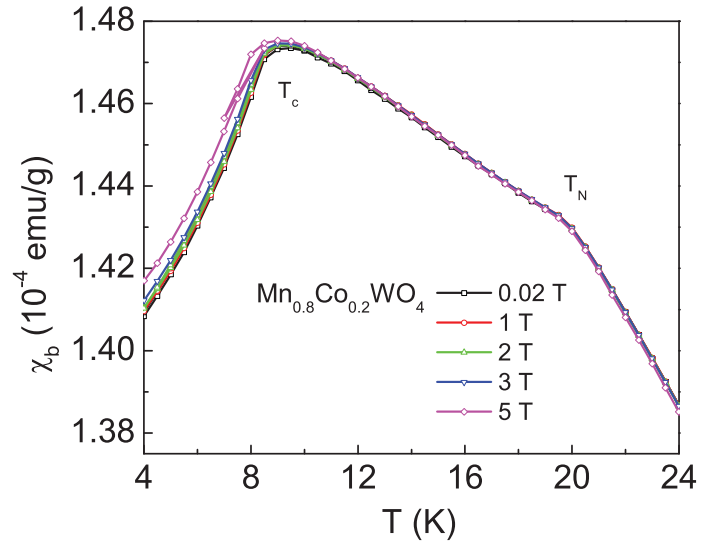
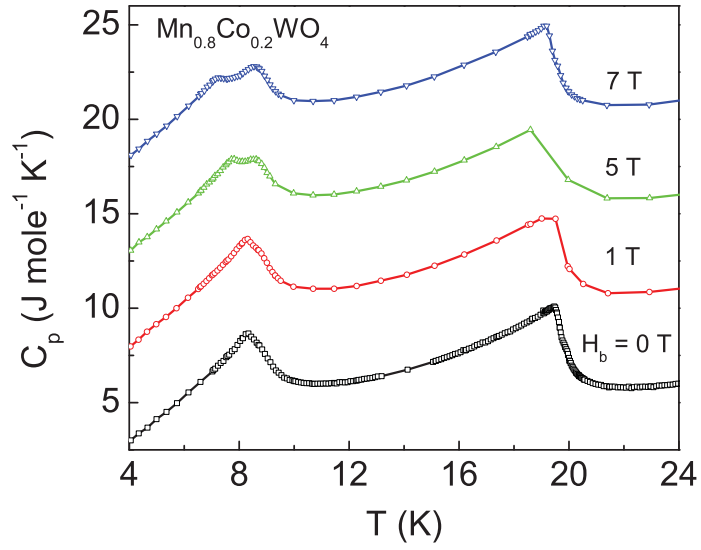


Figure 4.28: Ferroelectric polarization along the b -axis in the external magnetic oriented along the b -axis of (a) $\text{Mn}_{0.83}\text{Co}_{0.17}\text{WO}_4$, (b) $\text{Mn}_{0.8}\text{Co}_{0.2}\text{WO}_4$ and (c) $\text{Mn}_{0.75}\text{Co}_{0.25}\text{WO}_4$. (d) schematic diagram of the field-dependent (H_b) rotation of the spin conical structure.



(a)



(b)

Figure 4.29: (a) Magnetic susceptibility and (b) specific heat of $\text{Mn}_{0.8}\text{Co}_{0.2}\text{WO}_4$ in external magnetic fields oriented along the b -axis.

field, the T_N near 20 K shows the AF4 phase transition, and, at low temperature, the drop of magnetic susceptibility is the AF2/4 phase transition. The presence of high magnetic field $H_b = 5$ T causes a slight increase of the magnetic susceptibility in the AF2/4 phase. The magnetic field effect on the phase boundary is more pronounced in the specific heat data as shown in Fig. 4.29(b). With increasing b -axis magnetic field, the AF4 phase transition peak shifts to lower temperature and the peak of AF2 phase transition separates into two peaks, but it is not clear on why the low temperature peak splits into two peaks in high magnetic field.

4.1.3.4 Field-induced spontaneous polarization reversal of $\text{Mn}_{0.85}\text{Co}_{0.15}\text{WO}_4$

At the Co doping $x = 0.15$, this is right at the phase boundary of FE phase II and III as shown in Fig. 4.8. The FE polarization was found aligned with the b -axis, and no pyro-electric current along a -axis could be found within the experimental resolution. The single-crystalline neutron scattering measurements [45] show that four phases (AF4, AF2, AF1, and AF5) coexist at low temperature. The complex phase coexistence could be thought in an easier way as the phase separation into the FE phase II (AF5 ac helical phase) and III (AF2/4 conical phase). In the following, we want to discuss some interesting field-dependent behavior of this complex phase coexistence.

Fig. 4.30(a) shows the a -axis polarization of $x = 0.15$ sample with magnetic field applied in the b -axis. At zero field, the pyro-electric current could be barely detected, and however, the P_a could be induced at magnetic field of $H_b = 3$ T. With increasing H_b field, the P_a continuously increases to $\sim 11 \mu\text{C}/\text{m}^2$ at 5 K at $H_b = 4$ Tesla, and then, the P_a drops to $4.6 \mu\text{C}/\text{m}^2$ in 7 Tesla. The induced P_a behavior is similar to what we saw in the FE II (AF5) phase, where the H_b field could stabilize the $a - c$ plane helical phase. The higher magnetic field $H_b > 4$ Tesla is high enough to collapse

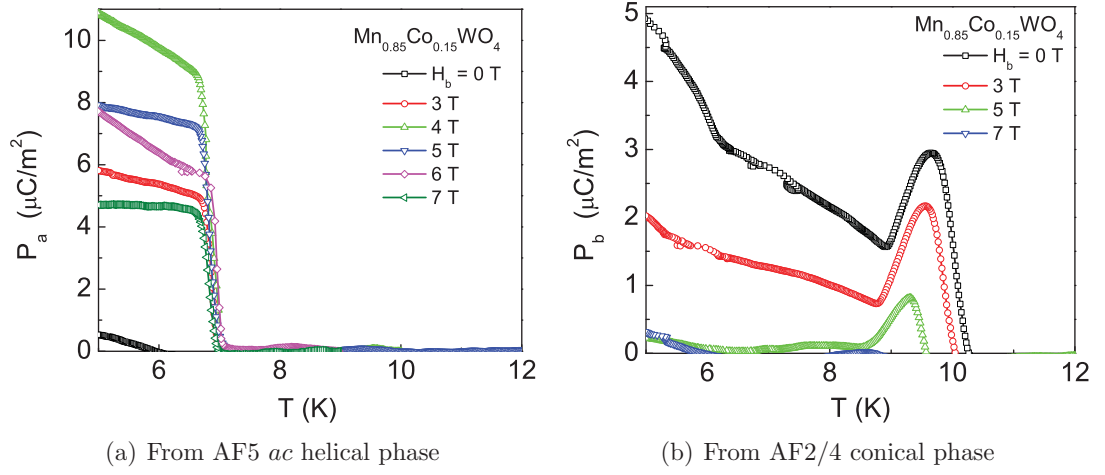


Figure 4.30: Ferroelectric polarization of $\text{Mn}_{0.85}\text{Co}_{0.15}\text{WO}_4$ in external magnetic fields oriented along the b -axis. (a) a -axis component and (b) b -axis component.

the $a - c$ plane helical structure and causes the decrease of the P_a . On the other hand, Fig. 4.30(b) shows the b -axis polarization P_b in the presence of b -axis magnetic field. With the 3 T H_b applied, the P_b drops to less than $2 \mu\text{C}/\text{m}^2$ at 5 K from $5 \mu\text{C}/\text{m}^2$ at zero field, and the P_b is completely destroyed at the field $H_b = 7$ T. The decrease of $P_b(H_b)$ corresponds to the case in the FE III AF2/4 conical phase, where the H_b collapses the spin cone to a line oriented along the spin easy axis and causes the drop of the P_b . It is then confirmed that there is coexistence of the AF5 ac helical phase and AF2/4 conical phase. With application of H_b fields, these two coexisting phases react to the H_b fields accordingly.

What we have learned from the $x = 0.12$ (Fig. 4.26(a)) is that the c -axis magnetic field induces the b -axis polarization P_b . It is because the AF5 ac helix is rotated by the H_b field and adding the strong magnetic anisotropy causes the induced P_b polarization. In the $x = 0.15$ case, it is more complex because it coexists with the AF2/4 conical phase that responds to the H_b fields significantly as seen in the $x = 0.20$ compound (Fig. 4.28). Since we saw both $P_a(H_b)$ from AF5 phase and $P_b(H_b)$ from AF2/4

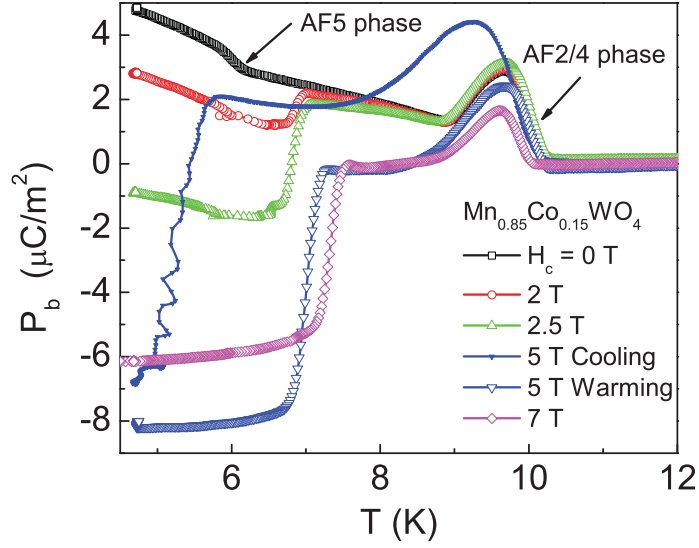


Figure 4.31: Ferroelectric polarization along the b -axis of $\text{Mn}_{0.85}\text{Co}_{0.15}\text{WO}_4$ in external magnetic fields oriented along the c -axis $P_b(H_c)$.

conical phase behavior in the sole $x = 0.15$ compound, the c -axis field effect has to be considered for the two coexisting phases, the high temperature AF2/4 conical phase and low temperature AF5 phase, separately.

Fig. 4.31 displays c -axis magnetic field dependence of the b -axis polarization P_b . The zero field P_b data first shows a sharp increase at T_C due to the AF2/4 conical phase and increases again at the AF5 phase transition. In the c -axis magnetic field H_c of 2 Tesla, the P_b of the AF2/4 phase does not change yet; however, at low temperature, the P_b from the AF5 phase starts to decrease instead of increase of P_b as seen in the zero field data. With increasing H_c fields, the high temperature P_b of the AF2/4 slightly decreases, whereas the low temperature P_b from AF5 phase decreases relatively significantly and develops negative polarization. The drop of P_b that causes negative P_b polarization at low temperature appears at ~ 6.5 K at $H_c = 2$ Tesla and continuously shifts to 7.5 K in 7 Tesla. In order to test if the negative polarization is intrinsic, the 5 Tesla data collected during the cooling are poled by a

positive electric field. The interaction that causes the negative P_b at low temperature is strong enough to overcome the positive electric field so that the cooling 5 T data still show negative polarization value at low temperature. The phase transition into the negative polarization is a strong first-order transition and shows a around 2 K wide thermal hysteresis at 5 T. The negative P_b effect reaches its maximum at 5 Tesla with P_b around $-8 \mu C/m^2$, and then, the P_b drops to $-6 \mu C/m^2$ at 7 Tesla.

The main question is why the P_b polarization changes its sign. Once the positive P_b polarization from the AF2/4 conical phase is established, P_b is forced to be negative in the low temperature AF5 phase range on the expense of AF1 phase. Similar to the $x = 0.12$ case, the ac helix of the AF5 phase in H_C fields is rotated toward the $a-b$ plane to generate P_b polarization. However, the generated P_b from the AF5 phase interacts with the existing b -axis polarization domains from the AF2/4 conical phase in a way that the AF5 phase gives rise to negative P_b . There is a strong magnetoelectric coupling in between the domain boundaries of the AF2/4 phase domains and AF5 phase domains. The strong competition between AF2/4 phase and AF5 phase in the domain walls results in negative P_b in the temperature range where the AF5 phase dominates. Future work on the domain wall investigation of this x compound is necessary to get more insight of the nature of the intrinsic negative magnetoelectric effect.

Fig. 4.32(a) represents the c -axis magnetic susceptibility of $Mn_{0.85}Co_{0.15}WO_4$. The magnetic response of $Mn_{0.85}Co_{0.15}WO_4$ develops a step-like sharp increase of magnetic susceptibility in the presence of c -axis magnetic field. At the field of 2.5 Tesla, the χ_c first shows the sharp increase with decreasing temperature, and then, keeps flat to form like a plateau at low temperature. The 5 Tesla data further show a significant enhancement of the magnetic susceptibility below the T_N , similar to the $x = 0.2$ data in Fig. 4.29(a). At the same time, similar to $x = 0.12$ compound, the

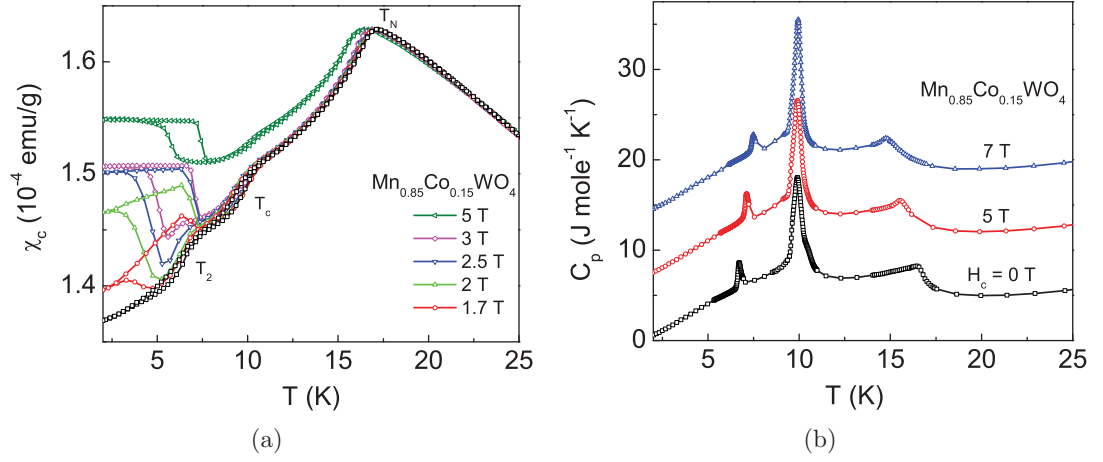


Figure 4.32: (a) Magnetic susceptibility and (b) specific heat of $\text{Mn}_{0.85}\text{Co}_{0.15}\text{WO}_4$ in external magnetic fields oriented along the c -axis.

thermal hysteresis of the T_2 shifts to ~ 7 K at the field of 5 Tesla, which corresponds to the transition temperature shift of the negative P_b . The magnetic susceptibility shows a related magnetic field effect on reaction of both AF5 phase and AF2/4 conical phase. The specific heat data (Fig. 4.32(a)) confirm the temperature shift of T_2 to ~ 7.5 K at 7 Tesla.

4.1.4 Multiferroic properties of $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$

The triclinic (space group $P\bar{1}$) crystal structure of CuWO_4 is different from the monoclinic b -axis structure of MnWO_4 . Furthermore, the spin value $S=1/2$ of Cu^{2+} in CuWO_4 is smallest among all the 3d transition metals. The low spin makes the quantum fluctuations more important at low temperature, and therefore, causes the lowest T_N of CuWO_4 among all the TWO_4 ($T = \text{Fe, Co, Ni, and Cu}$) with ground state of AF4 phase, as shown in Fig. 4.9(e). The replacement of Mn by Cu ions will affect the original magnetic exchange coupling and anisotropy resulting in change of magnetic and ferroelectric properties. The chemical doping effects of Cu ions and magnetic field effects of the system will be discussed in the subsections.

4.1.4.1 Zero magnetic field multiferroic properties of $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$

The polarization along the b -axis for the $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$ ($x = 0, 0.05, 0.1, 0.2$ and 0.3) by the pyro-electric current measurements is shown in Fig. 4.33(a). The data gives us information about ferroelectric AF2 phase and the transition from AF2 to paraelectric AF1 phase. 5% of Cu replacement causes slightly higher T_C , smaller maximum value of the P_b and non-zero polarization value at low temperature. The drop of P_b in the $x = 0.05$ at about 7 K extends over a wider temperature interval compared to the almost vertical drop of MnWO_4 . At $x = 0.1$, maximum value of P_b shows further decrease, and the polarization drop due to AF1 transition has a broader transition but the low temperature of P_b increases. The finite value of P_b at low temperature of $x = 0.05$ and 0.1 indicates the mixture of AF1 and AF2 phase, where the increase of the lowest temperature polarization value with increasing Cu content means the increase fraction of ferroelectric AF2 phase. With further increasing Cu content to $x = 0.2$, the AF2 phase becomes the ground state, and the polarization

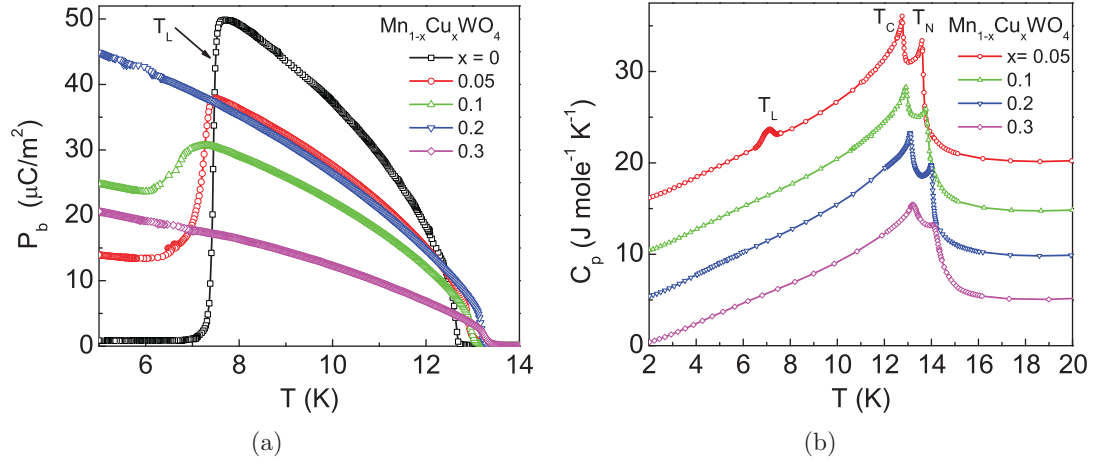


Figure 4.33: (a) Ferroelectric polarization and (b) specific heat of $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$ ($x = 0, 0.05, 0.1, 0.2$ and 0.3). Specific heat data are vertically offset for better clarity.

value keeps increasing to the lowest temperature. The maximum value of the P_b increases compared to the $x = 0.1$ data, but the maximum value of P_b decreases again at $x = 0.3$.

The information of the phase boundary could be checked more carefully by the specific heat measurements as shown in Fig. 4.33(b). The T_N (~ 14 K) and T_C (~ 12.5 K) shift to higher temperature with increasing Cu content, whereas the first-order AF1 phase transition peak moves toward low temperature, which is consistent with the polarization data. From $x = 0.05$ to $x = 0.1$, the AF1 phase transition peak becomes broader and its magnitude decrease significantly to barely observable, whereas the polarization data show a more clearly broad transition near 6.5 K.

The polarization data in Fig. 4.33 define the FE phases of the $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$ and the AF1 phase transition into the paraelectric states. The specific heat data could help defining the paraelectric AF3 phase, and therefore, the phase diagram of $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$ from $x = 0$ up to 0.3 could be construct in Fig. 4.34. The main FE phases are the AF2 phases, and no rotation of polarization could be found. The Cu

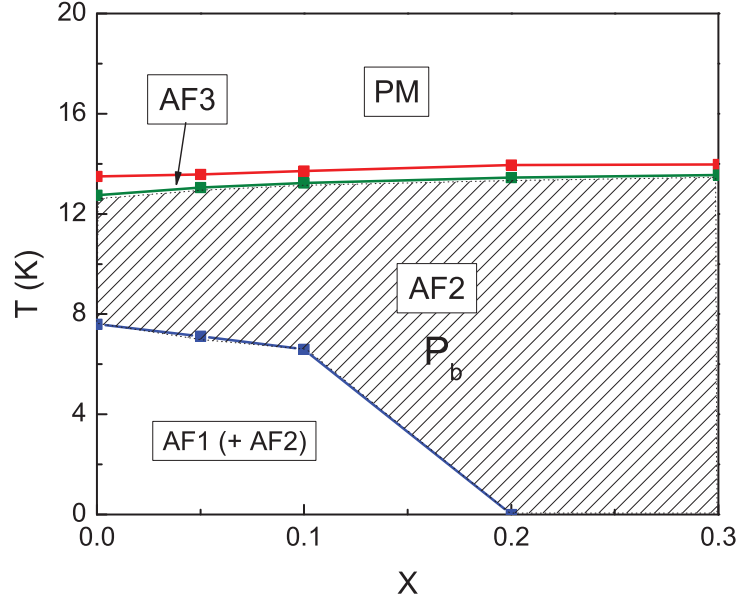


Figure 4.34: Phase diagram of $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$ derived from polarization and specific heat data.

replacement simply suppresses the $\uparrow\uparrow\downarrow$ AF1 phase and slightly increases the T_C of the AF2 phase and the T_N of the sinusoidal AF3 phase, where the increase of T_C and T_N makes the Cu doping effect different from Zn doping effect [41].

4.1.4.2 Field-dependent multiferroic properties of $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$

In the previous section, it was shown that the magnetic and multiferroic properties of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ system could be controlled by external magnetic fields. For the $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$ system, it is interesting to see how the AF2 phase and the mixture of AF1 + AF2 phase are affected by magnetic fields.

The b -axis magnetic field dependence of polarization and specific heat data of $\text{Mn}_{0.95}\text{Cu}_{0.05}\text{WO}_4$ are shown in Fig. 4.35. The finite polarization value at low temperature below T_L is first found diminished in the presence of H_b (Fig. 4.35(a)).

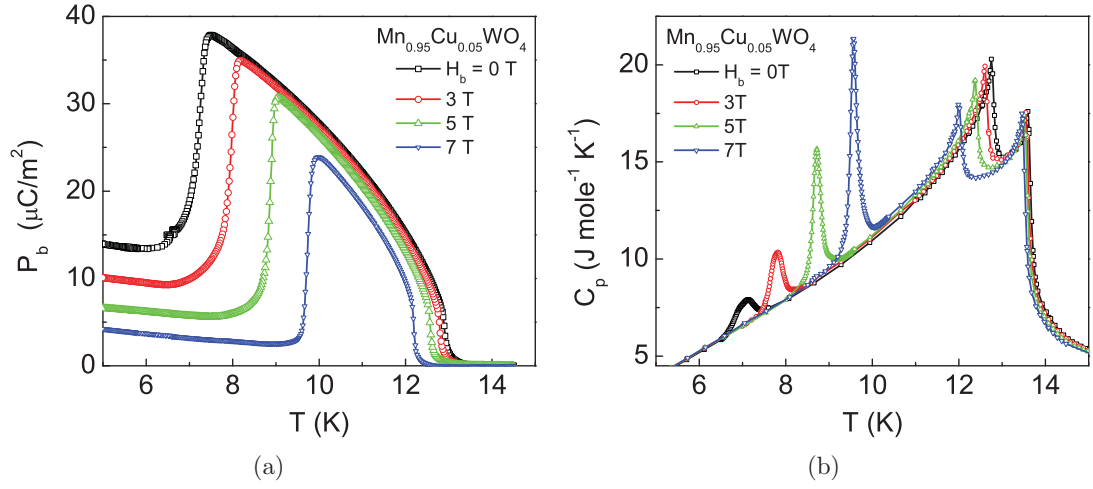


Figure 4.35: (a) Ferroelectric polarization and (b) specific heat of $\text{Mn}_{0.95}\text{Cu}_{0.05}\text{WO}_4$ in external fields oriented along the b -axis.

With increasing H_b , both the low temperature part of polarization and the maximum polarization value keep decreasing. At the same time, the lock-in transition temperature T_L shifts to high temperature, whereas the T_C moves toward low temperature. These indicate the stabilization of AF1 phase by increasing the portion of AF1 phase compared to the AF2 phase. At the H_b as high as 7 Tesla, the AF1 state is not completely restored because the polarization value at low temperature remains non-zero. The AF1 phase stabilized by H_b is further supported by the specific heat data in Fig. 4.35(b). The AF1 phase transition peak shifts to higher temperature with increasing of H_b , and the corresponding peak area increases at the same time. Since only the AF1 phase out of the mixture AF1 and AF2 phases shows a peak with the application of H_b fields, this allows us to correlate the field-induced entropy change from AF1 phase transition peak area with the change of the AF1 phase fraction in the AF1:AF2 ratio. Fig. 4.36 shows the field-dependent b -axis polarization at 5 K (Fig. 4.35(a)) as a function of entropy difference calculated from specific data (Fig. 4.35(b)). The entropy difference due to the AF1 phase transition peak increases from

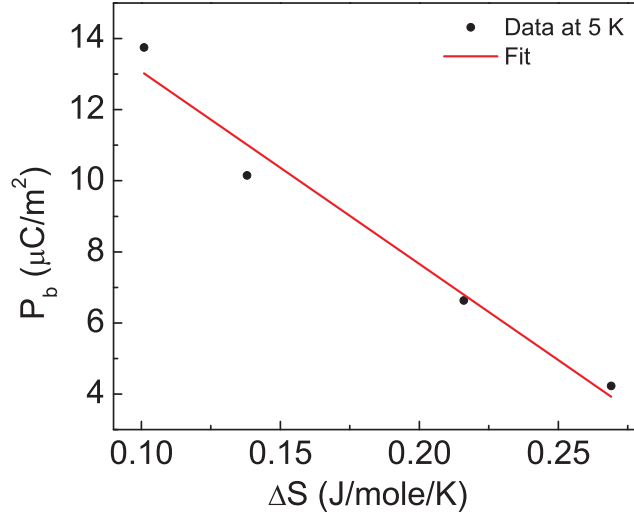


Figure 4.36: Ferroelectric polarization measured along b -axis as a function of function of calculated entropy difference from specific heat data.

$\Delta S = 0.101$ J/mole/K at $H_b = 0$ Tesla to $\Delta S = 0.269$ J/mole/K at $H_b = 7$ Tesla. It indicates the volume of AF1 state increases at higher magnetic field, and it causes the decrease of b -axis polarization. It is also interesting to note that the b -axis the polarization almost linearly decreases with the entropy difference due to the presence of the AF1 phase.

A similar trend of how AF1 dominates in AF1/AF2 mixture phases by application of H_b is observed in $\text{Mn}_{0.9}\text{Cu}_{0.1}\text{WO}_4$ (Fig. 4.37). At zero field, the content of AF1 phase is minor compared to the AF2 phase as mentioned above, and it is shown more clearly in the polarization data (Fig. 4.37(a)) as a small drop of polarization at low temperature. With the increase of H_b , the low temperature part of P_b decreases faster and the transition becomes sharper. For the specific heat data (Fig. 4.39), the zero field data barely show the first-order transition peak of the AF1 phase; however, at $H_b = 3$ Tesla, they show a small and very broad peak. With increasing H_b , this peak shifts to higher temperature and increases its peak area along with slight decrease of

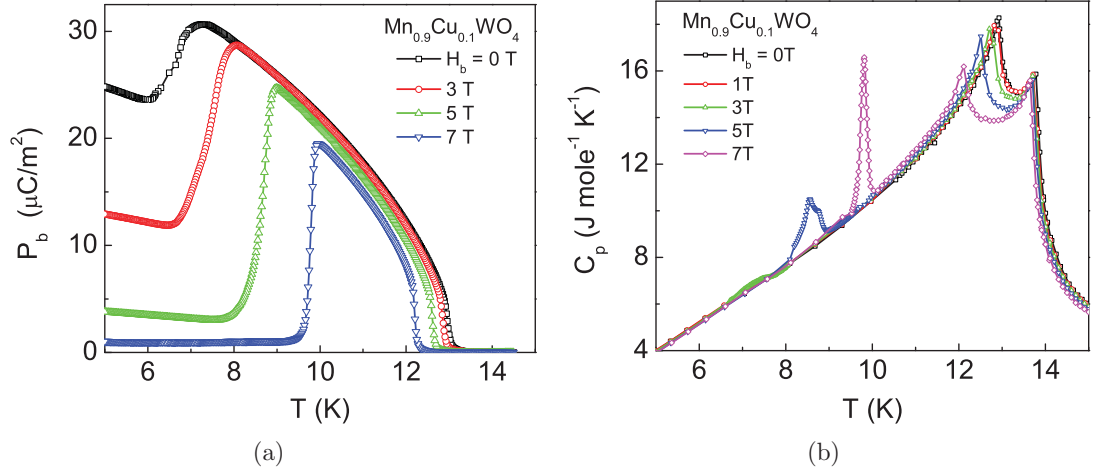


Figure 4.37: (a) Ferroelectric polarization and (b) specific heat of $\text{Mn}_{0.9}\text{Cu}_{0.1}\text{WO}_4$ in external fields oriented along the b -axis.

temperature of the AF2 and AF3 phase transitions.

The b -axis magnetic field is perpendicular to the spin easy axis in the $a - b$ spiral plane with an α angle of 34° with respect to the a -axis. Fig. 4.38 show the b -axis polarization data of $\text{Mn}_{0.95}\text{Cu}_{0.05}\text{WO}_4$ and $\text{Mn}_{0.9}\text{Cu}_{0.1}\text{WO}_4$ with the magnetic field applied along the magnetic easy axis. When the magnetic field is aligned in the direction of easy axis, the effect to the mixture of AF1:AF2 is completely opposite to the effect of H_b . The FE polarization data of both doping samples at low temperature increase smoothly with magnetic field. Above a critical field, the low temperature polarization shows no T_L transition. Therefore, the magnetic easy-axis fields stabilize the AF2 phase to become the ground state by eliminating the AF1 state.

When the copper content increase to $x = 0.2$, at zero field, even the P_b data (Fig. 4.39(a)) shows no signature of the AF1 phase, indicating that the AF1 phase is completely suppressed by the 20 percent of Cu doping. At the H_b of 5.5 Tesla, both the P_b and T_C decrease, but the ground state is still the AF2 phase. However, with application of $H_b = 6$ Tesla, a field-induced AF1 phase is observed around 9

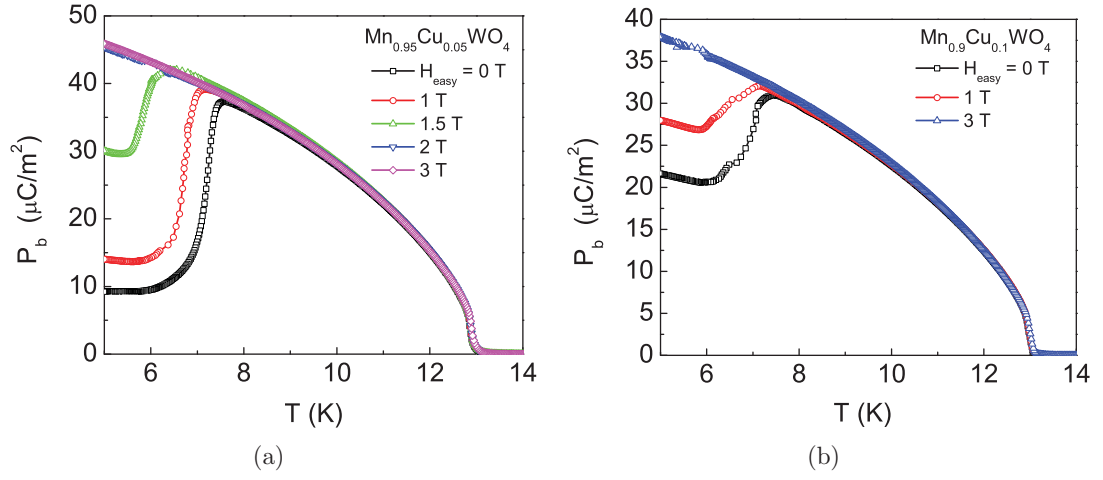


Figure 4.38: Ferroelectric polarization of $\text{Mn}_{0.95}\text{Cu}_{0.05}\text{WO}_4$ and $\text{Mn}_{0.9}\text{Cu}_{0.1}\text{WO}_4$ in external magnetic fields oriented along the magnetic *easy* axis.

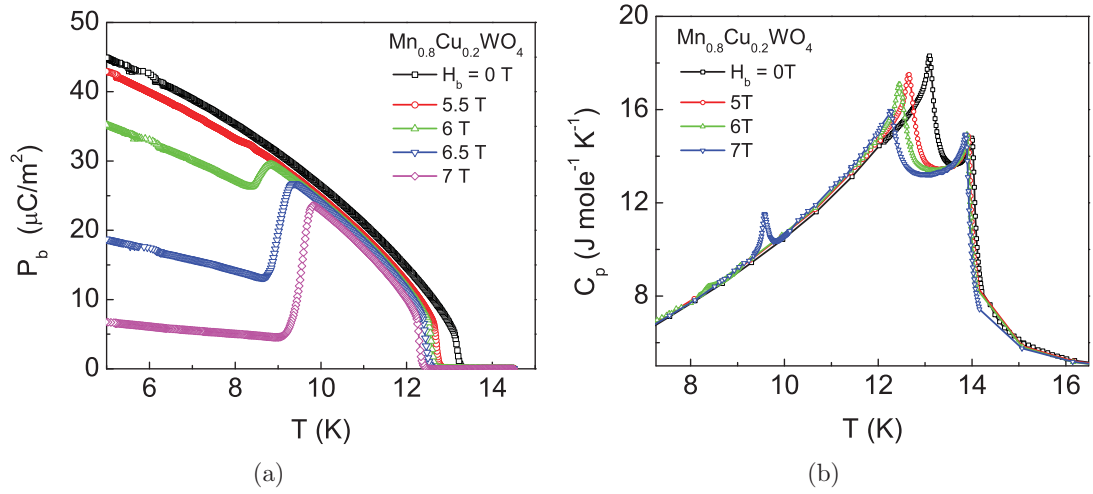


Figure 4.39: (a) Ferroelectric polarization and (b) specific heat of $\text{Mn}_{0.8}\text{Cu}_{0.2}\text{WO}_4$ in external fields oriented along the *b*-axis.

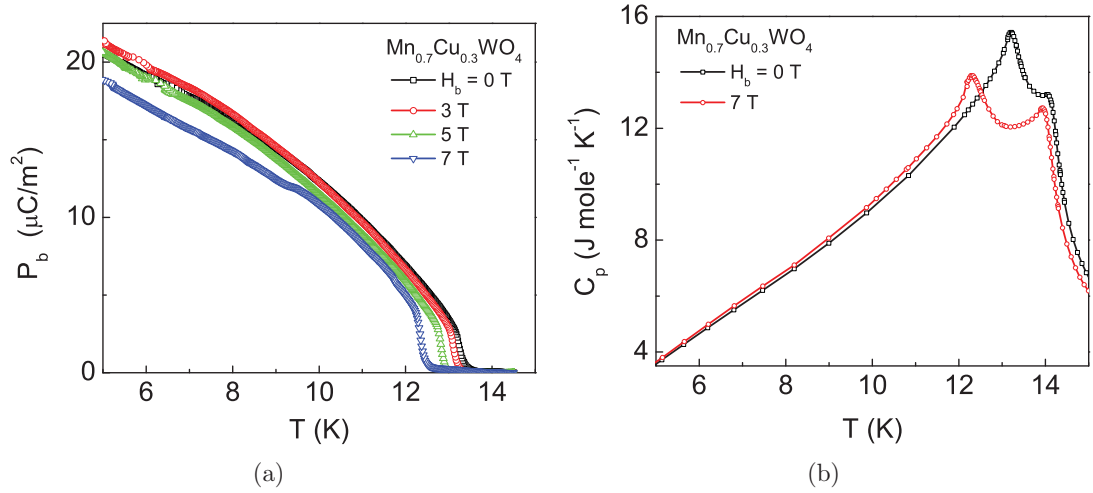


Figure 4.40: (a) Ferroelectric polarization and (b) specific heat of $\text{Mn}_{0.7}\text{Cu}_{0.3}\text{WO}_4$ in external fields oriented along the b -axis.

K. With further increasing H_b , the AF1 phase is clearly stabilized so that the ratio AF1:AF2 continuously increases quickly. The magnetic field dependent specific heat data further confirm the decrease of T_N and T_C . The peak of AF1 phase transition shows up at the H_b of 7 Tesla.

At the copper content of $x = 0.3$, the b -axis polarization shows no T_L transition at the H_b up to 5 Tesla as shown in Fig. 4.40(a). Even so, at $H_b = 7$ Tesla, the P_b data show a very tiny polarization drop around 9.5 K. Similar to $x < 0.3$, the T_C shifts toward lower temperature with increase of H_b . The shifting of T_C is confirmed by the specific data along with the slight down shift of T_N . However, no indication of AF1 phase transition could be observed in Fig. 4.40(b).

In summary, with small amount Cu ions replacement, the ground state (AF1 phases) of the parent compound MnWO_4 is suppressed slowly, and therefore, for those $x < 0.2$ compounds, the ground state is a mixture of AF1 and AF2 with certain ratio. The ratio of AF1:AF2 decreases with higher Cu content and becomes zero at

$x = 0.2$. The b -axis magnetic field tends to stabilize the AF1 phase, whereas the easy-axis fields suppress the AF1 phase.

4.2 Magnetoelectricity in the system $R\text{Al}_3(\text{BO}_3)_4$ ($R = \text{Tb}, \text{Er}, \text{Tm}, \text{Tm}_{0.9}\text{Yb}_{0.1}, \text{Yb}, \text{Ho}_{0.5}\text{Tm}_{0.5},$ $\text{Ho}, \text{ and } \text{Ho}_{0.5}\text{Y}_{0.5}$)

The $R\text{Fe}_3(\text{BO}_3)_4$ compounds crystallize in the trigonal huntite structure (Fig. 4.41), space group $R32$ (No. 155) [52]. There is a known structural transition $R32 \rightarrow P3_121$ (No. 152) at T_S with sizable anomalies in dielectric constant [53] and specific heat [54]. The structural transition temperatures of $R\text{Fe}_3(\text{BO}_3)_4$ compounds correlates with ionic radius of the rare earth R elements, with T_S decreasing from 430 K ($R = \text{Ho}, \text{Y}$) to 90 K of the larger ionic radius $R = \text{Eu}$.

The FeO_6 octahedra form edge-sharing helical chains along c -axis so that the magnetic exchange interactions between Fe moments are established through super-exchange interactions along the c -axis chain. Between different chains, it is possible for Fe moments in different chains to form super-super exchange interactions through BO_3 units (Fig. 4.41). With further decreasing temperature below T_S , the Fe moments form antiferromagnetic order at $T_N < 40$ K. However, the magnetic R ions are embedded between the FeO_6 octahedra, and therefore, the f -moments couple strongly with the d -moments. The strong magnetic anisotropy of the R -moments causes spin rotation transitions of Fe-moments, resulting in complex phase diagram of the $R\text{Al}_3(\text{BO}_3)_4$ compounds [53, 32]. The magnetoelectric (ME) effects of $R\text{Fe}_3(\text{BO}_3)_4$ compounds are well-investigated [55]. For example, the largest ME effect in the $R\text{Fe}_3(\text{BO}_3)_4$ reported was $\text{NdFe}_3(\text{BO}_3)_4$, showing strong ME effect up to 20 Tesla. Another example in the $\text{HoFe}_3(\text{BO}_3)_4$ and the mixed $\text{Ho}_{1-x}\text{Nd}_x\text{Fe}_3(\text{BO}_3)_4$ system, the wealth of magnetic interactions between R -moments and Fe-moments coupling to the lattice really causes very complex ME effect [32, 56]. Therefore, it is difficult to clarify the physical picture

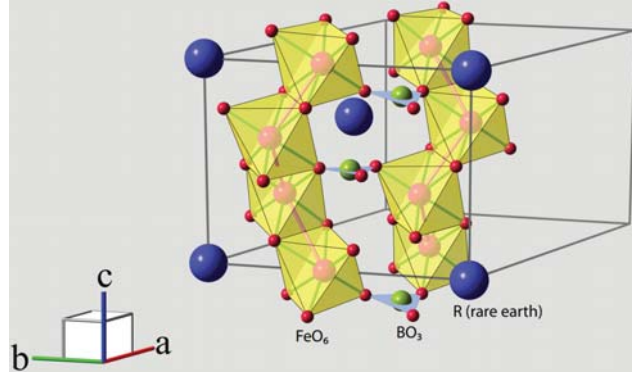


Figure 4.41: Crystal structure of $R\text{Fe}_3(\text{BO}_3)_4$.

of the relationship between the ME effect, the magnetic properties of the system and the role of Fe spins and R moments.

To simplify the problem, the single-crystalline $R\text{Al}_3(\text{BO}_3)_4$ compounds, iso-structural with $R\text{Fe}_3(\text{BO}_3)_4$ systems, were synthesized through a collaboration with Bezmaternykh *et al.* from Russian Academy of Sciences. The replacement of Fe ions by Al ions make the rare earth R ions the only magnetic ions in the system. In the following, we want to see how the magnetic properties of the $R\text{Al}_3(\text{BO}_3)_4$ system change and how the ME effects are affected by removal of the d -electron spins.

4.2.1 Magnetic susceptibility of $R\text{Al}_3(\text{BO}_3)_4$

Since the rare earth ion is the only magnetic contribution, the magnetic anisotropy of the $R\text{Al}_3(\text{BO}_3)_4$ compound is determined by the properties of the rare earth element. Here, we choose the Cartesian coordinate (x, y, z) , where the x - and z -axis are corresponding to a - and c -axis of the crystallographic axis, respectively, and the y -axis is just perpendicular to both other axis.

TbAl₃(BO₃)₄ and ErAl₃(BO₃)₄

Fig. 4.42 shows the magnetic susceptibility for the TbAl₃(BO₃)₄ and ErAl₃(BO₃)₄ along x and z directions. The χ_z data of TbAl₃(BO₃)₄ displays a paramagnetic type of temperature dependence without any magnetic phase transition, indicating no magnetic order. It also reveals the strongest uniaxial anisotropy among all $R\text{Al}_3(\text{BO}_3)_4$ samples, and the χ_z exceeds the in-plane χ_x by more than a factor of 132 at low temperature (Fig. 4.42(a)). In contrast, ErAl₃(BO₃)₄ shows the largest easy plane anisotropy, followed by TmAl₃(BO₃)₄. For quantitative comparison, table 4.1 shows measured magnetic anisotropy at 5 K [10], the effective magnetic moments from a *Weiss* fit of the high-temperature inverse susceptibility data and calculated effective magnetic moments in the unit of μ_B . Since the magnetic data show paramagnetic temperature dependence, and the effective moments from *Weiss* fit and calculated are close, it means that the Al ion replacement did simplify the magnetic correlations of the system and the rare ions are relatively independent due to 6 Å distance between two R ions.

Table 4.1: Magnetic anisotropy and effective magnetic moment of $R\text{Al}_3(\text{BO}_3)_4$ at 5 K, where $R = \text{Tb}$ and Er .

Rare earth ion	Tb	Er
χ_z/χ_x	132	0.041
$\mu_{eff} (\mu_B)$	9.30	9.55
Calculation (μ_B)	9.72	9.59

TmAl₃(BO₃)₄, YbAl₃(BO₃)₄, and Tm_{0.9}Yb_{0.1}Al₃(BO₃)₄

Fig. 4.43 shows the magnetic susceptibility for the TmAl₃(BO₃)₄ and YbAl₃(BO₃)₄

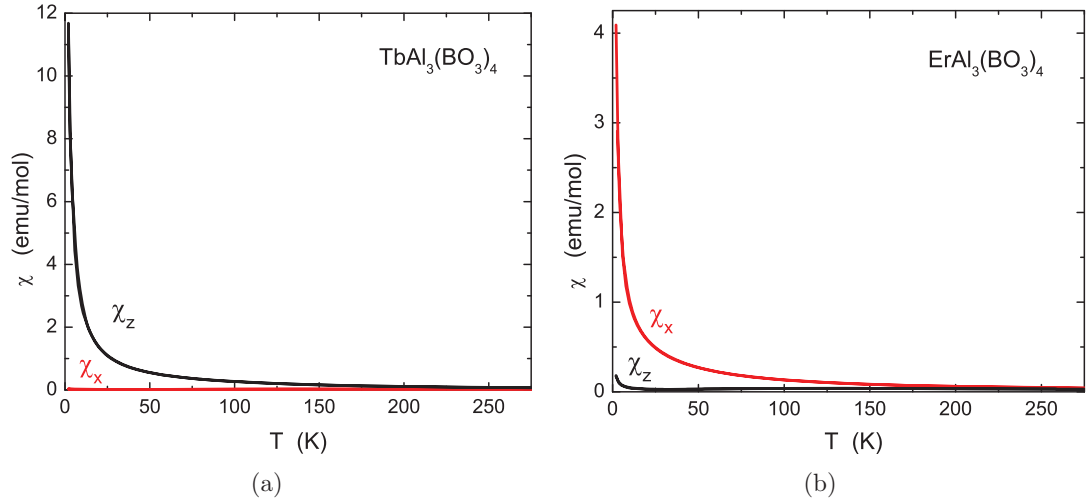


Figure 4.42: In-plane (χ_x) and c -axis (χ_z) magnetic susceptibilities of $R\text{Al}_3(\text{BO}_3)_4$, where $R =$ (a) Tb and (b) Er.

with the mixed compound of these two as $R = \text{Tm}_{0.9}\text{Yb}_{0.1}$ along x and z directions. These three magnetic susceptibility data all show paramagnetic type of temperature-dependent behavior and easy plane anisotropy. However, the Yb compound shows an intersection of the χ_z and χ_x , indicating that there is a change of magnetic anisotropy of the sample from uniaxial anisotropy at high temperature and to easy plane anisotropy at low temperature, as shown in the inset of Fig. 4.43(c). The magnetic anisotropy of $\text{YbAl}_3(\text{BO}_3)_4$ is closer to isotropic than magnetic anisotropy of $R = \text{Tm}$ sample, which can be compared quantitatively in table 4.2. It should be also noted that the Yb moment has the smallest value $\sim 5 \mu_B$, almost half of other measured compounds. Since there is only 10% of Yb doped in the $R = \text{Tm}_{0.9}\text{Yb}_{0.1}$ compound, the magnetic anisotropy of the mixture compound is relatively close the Tm case, and the effective moment is in between the values of Tm and Yb moments as expected.

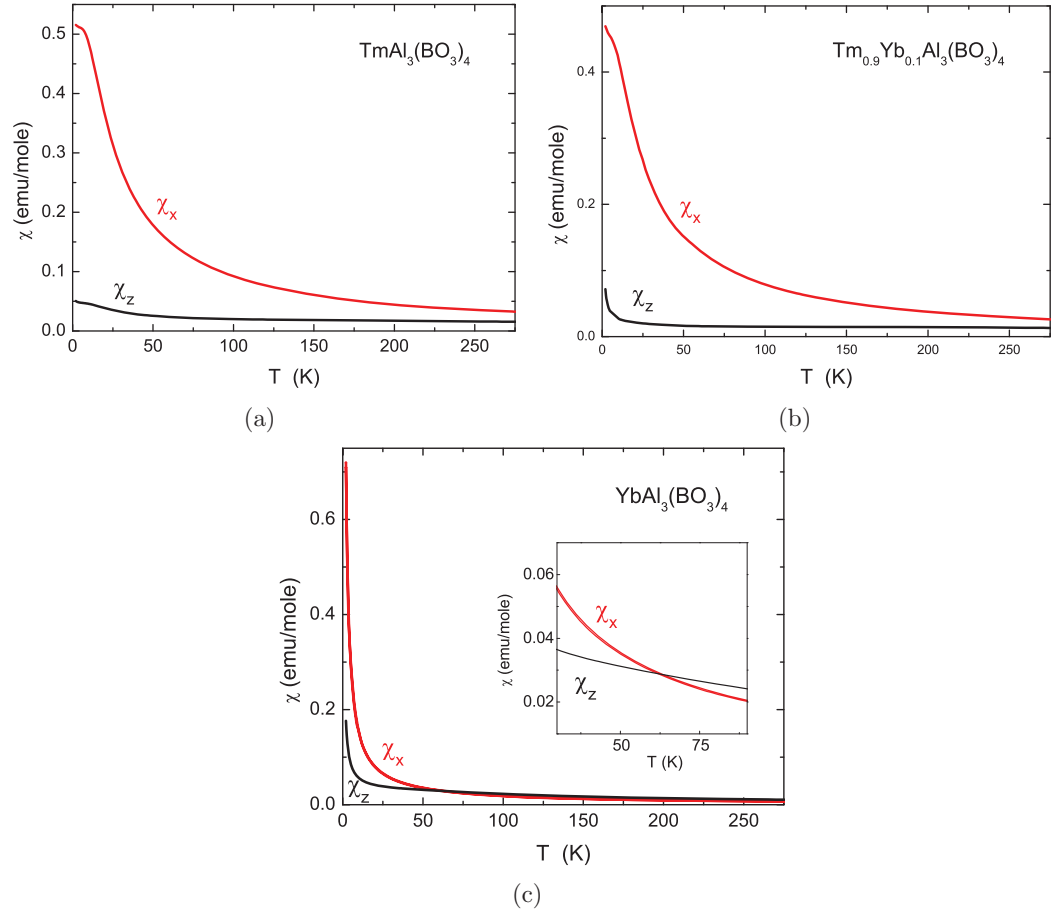


Figure 4.43: In-plane (χ_x) and c -axis (χ_z) magnetic susceptibilities of $RAl_3(BO_3)_4$, where $R =$ (a) Tm, (b) $Tm_{0.5}Yb_{0.5}$, and (c) Yb. Inset of (c) shows the intersection of χ_x and χ_z .

Table 4.2: Magnetic anisotropy and effective magnetic moment of $R\text{Al}_3(\text{BO}_3)_4$ at 5 K, where $R = \text{Tm}$, $\text{Tm}_{0.9}\text{Yb}_{0.1}$, and Yb .

Rare earth ion	Tm	$\text{Tm}_{0.9}\text{Yb}_{0.1}$	Yb
χ_z/χ_x	0.092	0.086	0.292
$\mu_{eff} (\mu_B)$	8.23	7.74	5.23
Calculation (μ_B)	7.57	7.21	4.54

$\text{HoAl}_3(\text{BO}_3)_4$, $\text{Ho}_{0.5}\text{Tm}_{0.5}\text{Al}_3(\text{BO}_3)_4$, and $\text{Ho}_{0.5}\text{Y}_{0.5}\text{Al}_3(\text{BO}_3)_4$

$\text{HoAl}_3(\text{BO}_3)_4$ is nearly magnetic isotropic with a minute preference of the z -axis (or c -axis) (Fig. 4.44(b)). The anisotropy ratio of χ_z/χ_x is 1.2 over a large temperature range and increases slightly to about 3 at the lowest temperature. With 50 % replacement of Tm ions on Ho sites, there is an intersection of the χ_z and χ_x observed at around 10 K, which is an exchange of magnetic anisotropy of the sample from uniaxial anisotropy and to easy plane anisotropy at low temperature, and the magnetic anisotropy reversal also causes the magnetic anisotropy of $\text{Ho}_{0.5}\text{Tm}_{0.5}\text{Al}_3(\text{BO}_3)_4$ slightly less than 1 as shown in the inset of Fig. 4.44(a) due to the smaller χ_z/χ_x ratio of Tm ions. In the $R = \text{Ho}_{0.5}\text{Y}_{0.5}$ (Fig. 4.44(c)) case, the nonmagnetic Y ions dilute the Ho ions in the compound so, compared to $R = \text{Ho}$ compound, it shows similar magnetic anisotropy ($\chi_z/\chi_x = 1.9$) with smaller amount of effective moments ($7.14 \mu_B$) per formula unit, as shown in table 4.3. The $\text{HoAl}_3(\text{BO}_3)_4$ result (> 14.5 K) is consistent with an earlier report [57], and both experimental data do not show a reversal of χ_z/χ_x above 2 K in contrast to the theoretical prediction [57].

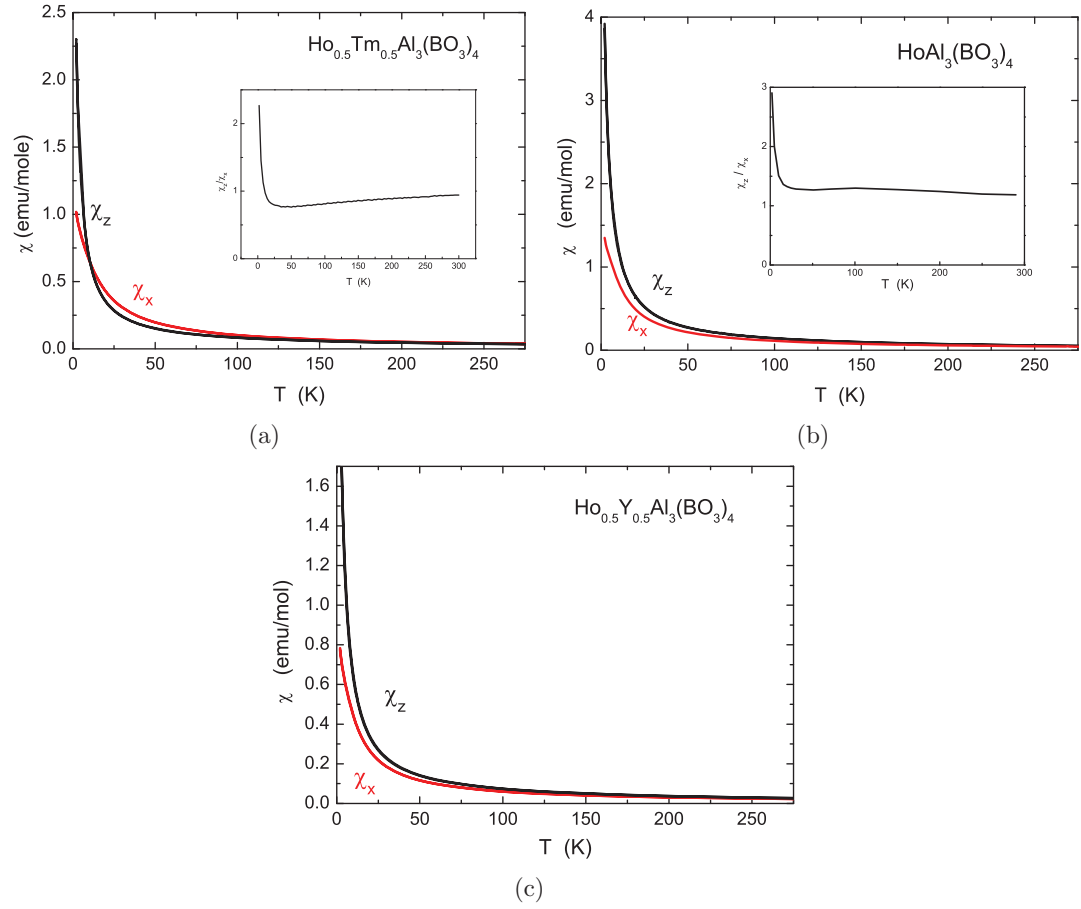


Figure 4.44: In-plane (χ_x) and c -axis (χ_z) magnetic susceptibilities of $R\text{Al}_3(\text{BO}_3)_4$, where $R =$ (a) $\text{Ho}_{0.5}\text{Tm}_{0.5}$, (b) Ho , and (c) $\text{Ho}_{0.5}\text{Y}_{0.5}$. The insets reveal the nearly isotropic magnetism of $\text{Ho}_{0.5}\text{Tm}_{0.5}\text{Al}_3(\text{BO}_3)_4$, and $\text{HoAl}_3(\text{BO}_3)_4$.

Table 4.3: Magnetic anisotropy and effective magnetic moment of $R\text{Al}_3(\text{BO}_3)_4$ at 5 K, where $R = \text{Ho}$, $\text{Ho}_{0.5}\text{Tm}_{0.5}$, and $\text{Ho}_{0.5}\text{Y}_{0.5}$.

Rare earth ion	$\text{Ho}_{0.5}\text{Tm}_{0.5}$	Ho	$\text{Ho}_{0.5}\text{Y}_{0.5}$
χ_z/χ_x	1.452	1.9	1.904
$\mu_{eff} (\mu_B)$	9.16	10.6	7.14
Calculation (μ_B)	9.21	10.6	7.49

4.2.2 Magnetoelectric (ME) properties of $R\text{Al}_3(\text{BO}_3)_4$

The magnetoelectric (ME) properties of the system $R\text{Al}_3(\text{BO}_3)_4$ is related to the coupling between the magnetic properties (due to the crystal field splitting of the f -orbital moments and the occupation of spin moments in the f -levels) and the lattice. Because the noncentrosymmetric space group $R32$ is a non-polar structure, any ME effect is due to a field-induced polar distortion to give rise to a macroscopic electrical polarization. In the following, we want to see whether or not the ME effect is possible at all with weak coupling of f -moments in the $R\text{Al}_3(\text{BO}_3)_4$ system. If it shows some ME effect, then, we want to check if the ME polarization can correlate with magnetic data.

$\text{TbAl}_3(\text{BO}_3)_4$

Magnetoelectric current measurements with either longitudinal or transverse magnetic fields swept up to 70 kOe of $\text{TbAl}_3(\text{BO}_3)_4$ along the in-plane x - and out-of-plane z -directions do not show any magnetoelectric signal within the experimental resolution. This indicates that the compound with the largest uniaxial anisotropy, $R = \text{Tb}$, is either not magnetoelectric or the ME effect is very small. In the isostructural

$R\text{Fe}_3(\text{BO}_3)_4$ system, no ME effect was observed for the strong uniaxial anisotropy of the rare earth moment compound, and it was attributed to the small in-plane components of the f -moments for $R=\text{Pr}$, Tb , Dy [55]. Although the $R\text{Fe}_3(\text{BO}_3)_4$ system is more complex due to complex coupling interactions between Fe ions, rare earth elements and the lattice, it appears conceivable that the phenomenological model derived from the rare earth iron borates could also qualitatively explain the missing ME effect in $\text{TbAl}_3(\text{BO}_3)_4$.

In contrast, the nearly isotropic magnets ($R = \text{Ho}$) and those easy-plane magnets ($R = \text{Er}$, Tm and Yb) have been sizable magnetoelectric polarization. Interestingly, among all the $R\text{Al}_3(\text{BO}_3)_4$ that we have measured, the largest ME effect is in the transverse field orientations with the electric polarization $P_x(H_y)$ measured along x -axis and the applied magnetic field oriented y -axis. At the same time, the sign of $P_x(H_y)$ is always opposite to $P_x(H_x)$, where the longitudinal polarization $P_x(H_x)$ is chosen to be positive as reference.

$\text{ErAl}_3(\text{BO}_3)_4$

In the search for a correlation between magnetic anisotropy and ME effects, we started from the ME current measurements of $\text{ErAl}_3(\text{BO}_3)_4$ in the longitudinal H_x and transverse field H_y up to 70 kOe so that the polarization change in the fields can be determined by integrating the ME current, as shown in Fig. 4.45. Both $P_x(H_x)$ and $P_x(H_y)$ ME polarization still show sizeable value at the temperature as high as 100 K and smoothly increase with temperature, which distinguishes this system from the $R\text{Fe}_3(\text{BO}_3)_4$ system (ME effect appears only below $T_N < 40$ K). Furthermore, $P_x(H_y)$ shows slightly higher ME polarization value of $\sim -150 \mu\text{C}/\text{m}^2$ compared to the $P_x(H_x)$.

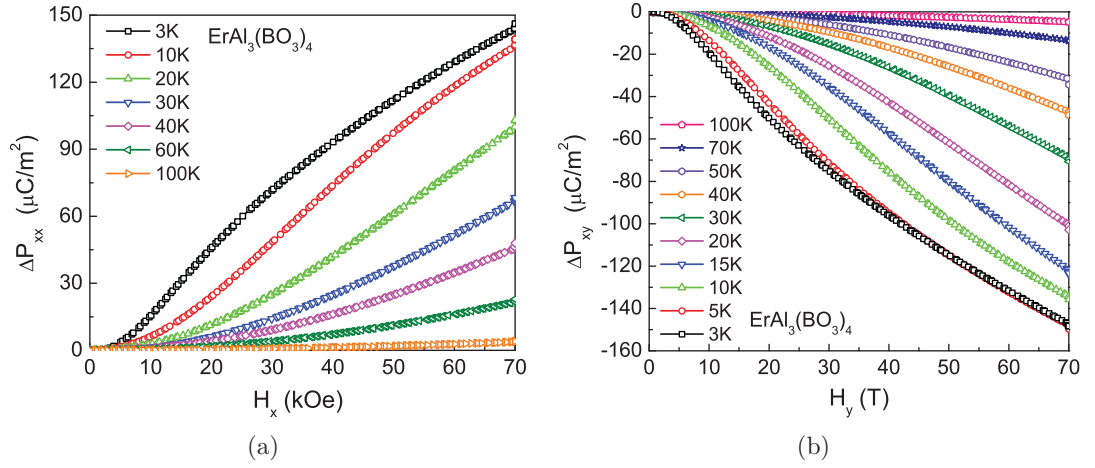


Figure 4.45: (a) Longitudinal and (b) transverse magnetoelectric polarizations $P_x(H_x)$ and $P_x(H_y)$ of $\text{ErAl}_3(\text{BO}_3)_4$.

$\text{TmAl}_3(\text{BO}_3)_4$, $\text{YbAl}_3(\text{BO}_3)_4$, and $\text{Tm}_{0.9}\text{Yb}_{0.1}\text{Al}_3(\text{BO}_3)_4$

As shown in the tables 4.1 and 4.2, the magnetic anisotropy of $\text{TmAl}_3(\text{BO}_3)_4$ is 2.2 times larger the $R = \text{Er}$ case, and it shows even larger ME polarization change $P_x(H_x)$ and $P_x(H_y)$, as shown in Fig. 4.46(a) and 4.46(b), respectively. The value of $P_x(H_y)$ in $R = \text{Tm}$ compound is $\sim -750 \mu\text{C}/\text{m}^2$ in the transverse field of 70 kOe. At this point, it appears that the decrease of easy plane anisotropy toward magnetic isotropy might cause higher ME effect. However, when the R is replaced by Yb ions, it exhibits a much smaller ME polarization in Fig. 4.46(d) although the χ_z/χ_x of the $R = \text{Yb}$ compound is indeed closer to one than $R = \text{Er}$ and Tm cases. In fact, the ME effect of $\text{YbAl}_3(\text{BO}_3)_4$ is the smallest among all the samples that we investigated, and the polarization magnitude of is $\sim -46 \mu\text{C}/\text{m}^2$ at the lowest temperature of 3 K and at a field H_y of 70 kOe. Even so, the ME polarization values of $R\text{Al}_3(\text{BO}_3)_4$ exceed the ME polarization obtained at the same magnetic fields from the $R\text{Fe}_3(\text{BO}_3)_4$ system significantly. Fig. 4.46(c) shows the ME polarization data of $R = \text{Tm}_{0.9}\text{Yb}_{0.1}$ sample. The maximum value is $\sim -490 \mu\text{C}/\text{m}^2$ at temperature of 5 K and at a field

H_y of 70 kOe, which does not scale with the doping ratio between with $R = \text{Tm}$ and Yb compounds. This excludes the phase separation of $R = \text{Tm}$ and Yb phases, confirming the assumption that Yb ions are randomly distributed in the Tm sites. This results in a more complex magnetic response and ME polarization.

$\text{HoAl}_3(\text{BO}_3)_4$, $\text{Ho}_{0.5}\text{Tm}_{0.5}\text{Al}_3(\text{BO}_3)_4$, and $\text{Ho}_{0.5}\text{Y}_{0.5}\text{Al}_3(\text{BO}_3)_4$

In the nearly isotropic magnet $\text{HoAl}_3(\text{BO}_3)_4$, it displays an extremely large ME effect. The longitudinal polarization $P_x(H_x)$, in Fig. 4.47(a), rises to $1900 \mu\text{C}/\text{m}^2$ at 3 K and 70 kOe field. The transverse ME polarization turns to be even larger in magnitude as $-3600 \mu\text{C}/\text{m}^2$ in Fig. 4.47(b). At low magnetic fields, in the inset of Fig. 4.47(b), the ME polarization of $\text{HoAl}_3(\text{BO}_3)_4$ is proportional to H^2 , indicating that the ME effect is bilinear up to 10 kOe. The polarization then continuously increases in higher order with high magnetic fields. The maximum of $3600 \mu\text{C}/\text{m}^2$ in magnitude of $\text{HoAl}_3(\text{BO}_3)_4$ appears to top the reported field-induced polarizations in the known magnetoelectric compounds and multiferroics, e.g. DyMnO_3 ($P_{\text{max}} = 2500 \mu\text{C}/\text{m}^2$) [58], before the single-crystalline $\text{CaBaCo}_4\text{O}_7$ compound ($\Delta P_{65\text{K}} = 9000 \mu\text{C}/\text{m}^2$ at 70 kOe) was reported [6].

Fig. 4.47(c) and 4.47(d) show the transverse polarization measurements of $R = \text{Ho}_{0.5}\text{Tm}_{0.5}$ and $\text{Ho}_{0.5}\text{Y}_{0.5}$ samples, respectively. The $\text{Ho}_{0.5}\text{Tm}_{0.5}\text{Al}_3(\text{BO}_3)_4$ shows significantly smaller ME polarization value ($145 \mu\text{C}/\text{m}^2$ at 5K and 70 kOe). However, this can be explained by the inversion twinning effect for this particular sample, where two third of the volume faces on direction and the other one third faces in an opposite direction, found by our collaborator [59]. Even we multiply this value by a factor of 3, it is still too small to scale with $R = \text{Tm}$ and Ho compounds. The half of nonmagnetic Y ions replacement of Ho ions does decrease the ME polarization ($2000 \mu\text{C}/\text{m}^2$ at 3K

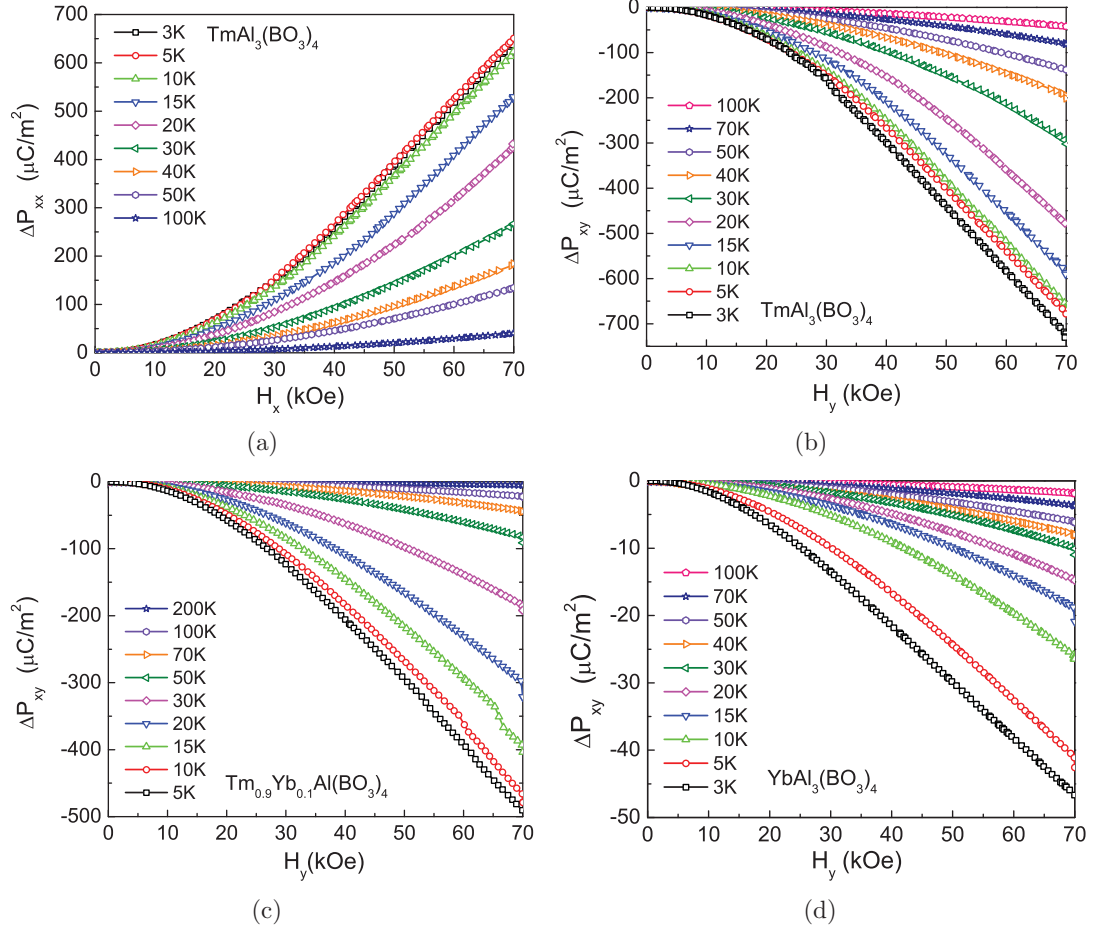


Figure 4.46: (a) Longitudinal magnetoelectric polarization $P_x(H_x)$ of $\text{TmAl}_3(\text{BO}_3)_4$. Transverse magnetoelectric polarization $P_x(H_y)$ of $R\text{Al}_3(\text{BO}_3)_4$, where $R =$ (b) Tm, (c) $\text{Tm}_{0.9}\text{Yb}_{0.1}$, and (d) Yb.

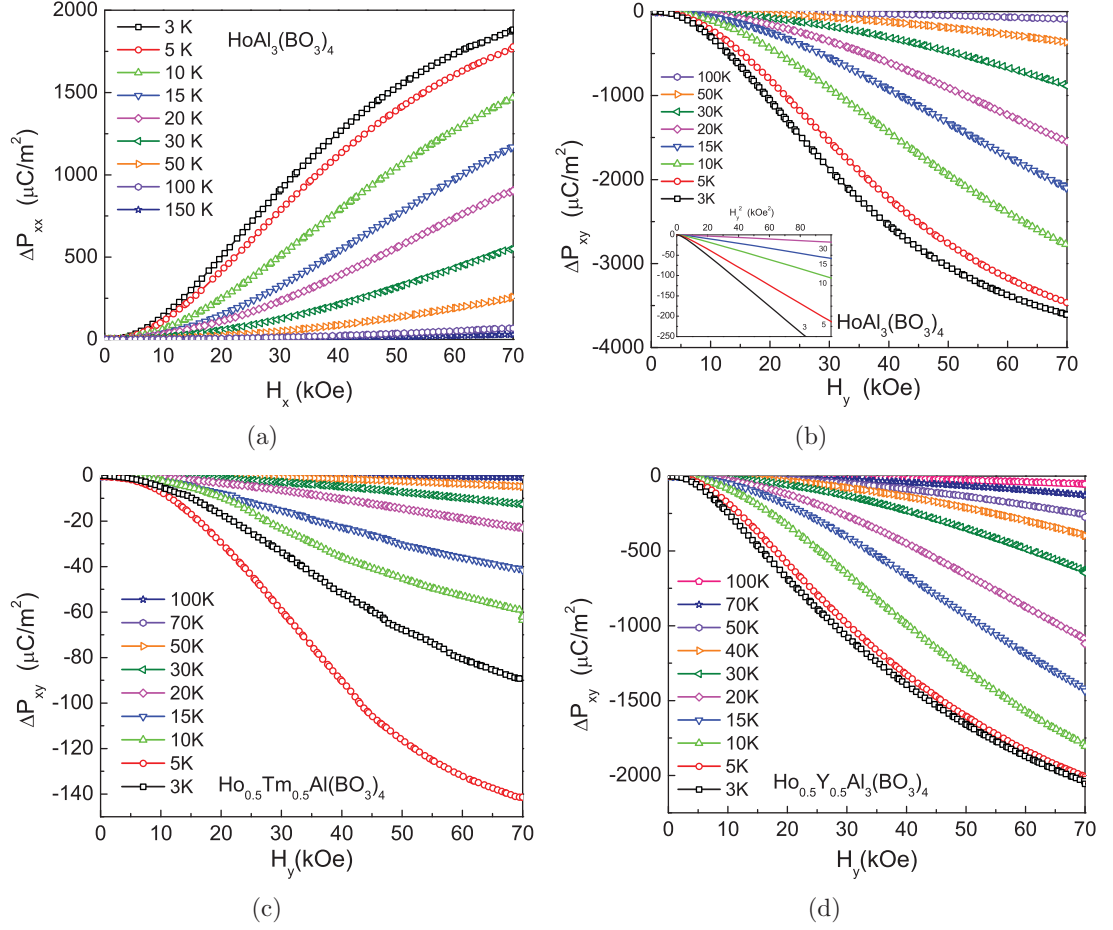


Figure 4.47: (a) Longitudinal magnetoelectric polarization $P_x(H_x)$ of $\text{HoAl}_3(\text{BO}_3)_4$. Transverse magnetoelectric polarizations $P_x(H_y)$ of $R\text{Al}_3(\text{BO}_3)_4$, where $R =$ (b) Ho, (c) $\text{Ho}_{0.5}\text{Tm}_{0.5}$, and (d) $\text{Ho}_{0.5}\text{Y}_{0.5}$. The inset of $\text{HoAl}_3(\text{BO}_3)_4$ shows the $\Delta P_{xy} \propto H^2$ scaling in the magnetic fields below 10 kOe.

and 70kOe), similar to the conclusion from the magnetic data shown in Fig. 4.44(c).

The fact that the ME polarization decreases smoothly with temperature in all of the ME $RAl_3(BO_3)_4$ compounds really distinguish the $RAl_3(BO_3)_4$ system from the $RFe_3(BO_3)_4$ where a sizable ME effect was only detected below the Néel temperature (~ 40 K) of the Fe spins [55]. This result leads us to conclude that the d -electron spin of the Fe ion in $RFe_3(BO_3)_4$ and the antiferromagnetic order does not facilitate the ME effect. It rather seems to be detrimental, preventing large field-induced polarization values.

If the Yb compound is excluded, there seems to be a relationship between magnetic anisotropy of the rare earth ion and the ME polarization. The magnetic anisotropy (χ_x/χ_z ratio) decreases in a sequence of Er, Tm, and Ho, and, at the same time, the transverse polarization $P_x(H_y)$ increases in the same sequence. At this moment, it is difficult to clarify whether Yb simply does not fit this tendency possibly because the f -moments is too small compared to others or the relationship of the magnetic anisotropy and ME effect is more complex. The ME effect is associated with a field-induced structural distortion to a polar structure since the zero-field space group $R\bar{3}2$ is non-polar. This macroscopic distortion was detected in the $RAl_3(BO_3)_4$ system through magnetostriction measurements and was found significant [60, 61]. Unfortunately, macroscopic magnetostriction data cannot explain the nature of the ME polarization, which requires microscopic investigation. The magnetic field effects on the microscopic structure and the nature of the distortions should be studied through scattering (X-ray, neutron) methods in magnetic fields. Those experiments will eventually lead to a more comprehensive understanding of the ME effects in the $RAl_3(BO_3)_4$ class of materials.

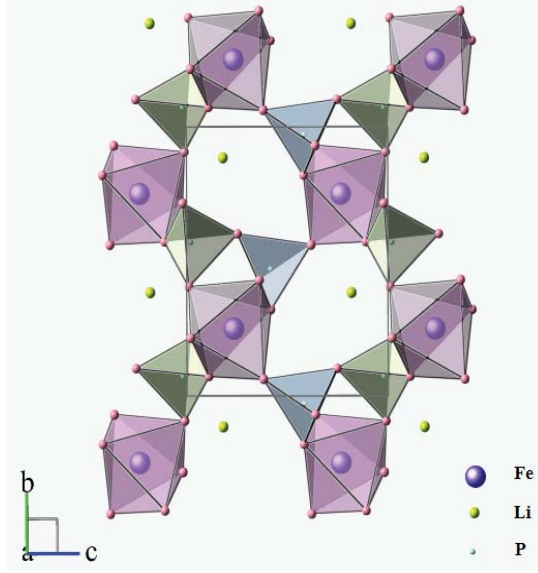


Figure 4.48: The crystal structure of the LiFeP_2O_7 .

4.3 Internal and external magnetoelectricity in LiFeP_2O_7

The LiFeP_2O_7 crystallizes in a polar structure with monoclinic b -axis unique space group $P2_1$ as shown in Fig. 4.48 [62, 63]. The magnetic Fe^{3+} ions form the super-super exchange interaction between two neighboring Fe^{3+} ions via two oxygen ions involving the stretched PO_4 tetrahedron [64, 4]. At low temperature, the super-super exchange interactions become significant to cause the antiferromagnetic (AFM) order of the Fe-moments at about $22 (\pm 5)$ K shown in earlier polycrystalline sample studies [62, 63]. The coexistence of the magnetic order and electrical polarization below the magnetic ordering temperature makes LiFeP_2O_7 an interesting compound to study the possible magnetoelectric coupling in the polar materials. In this section, the discussion will be focused on the possible interaction between magnetic order and electrical polarization in the LiFeP_2O_7 and how this interaction is affected by external magnetic field.

4.3.1 Magnetic susceptibility of LiFeP_2O_7

The single-crystalline LiFeP_2O_7 were synthesized through a collaboration with Zhang *et al.* [29] from the Department of Chemistry, University of Houston. The single crystals were in very good quality so that we can determine the orientations even from the crystal surface, and this permits us a more detailed investigation of the magnetic properties in different directions of the crystal. Fig. 4.49 displays the magnetic susceptibility at the field of 1000 Oe along the a, b and c crystallographic axes. The χ_a data decrease sharply at $T_N \sim 26.86$ K, confirming the antiferromagnetic (AFM) response of Fe moments as previous reports [62, 63]. However, χ_b shows the ferromagnetic response, and χ_c exhibits only a very minute anomaly at T_N and remains nearly constant in lower temperature region. The ferromagnetic response of χ_b data is in agreement with the previous report on the polycrystalline samples [65], and however, our single crystals allow us to distinguish a ferromagnetic response along b -axis and antiferromagnetic response along a -axis. The *Curie – Weiss* extrapolation of the inverse susceptibility reveals a negative Weiss temperature $\Theta \sim -50$ K with an effective magnetic moment of $\mu_{eff} \simeq 5.89 \mu_B$, close to the expected value for spin 5/2 ($\mu_{eff} \simeq 5.92 \mu_B$). The negative Weiss temperature implies that the antiferromagnetic interaction is dominating in the system, and the FM moment along the b -axis originates from the canted AFM order. A similar FM component due to canted antiferromagnetism is observed in a slightly different structure NaFeP_2O_7 system [66].

The FM moments shown in χ_b is further investigated in low fields (10 Oe) along the b -axis. Fig. 4.50(a) shows a sharp increase of the magnetic susceptibility at $T_N = 27$ K, contributed by the FM moments. The data collected during warming after cooling in zero magnetic field (ZFC) and cooling in a 10 Oe field (FC) are identical. Since the difference between ZFC and FC in ferromagnetic data comes from the formation of

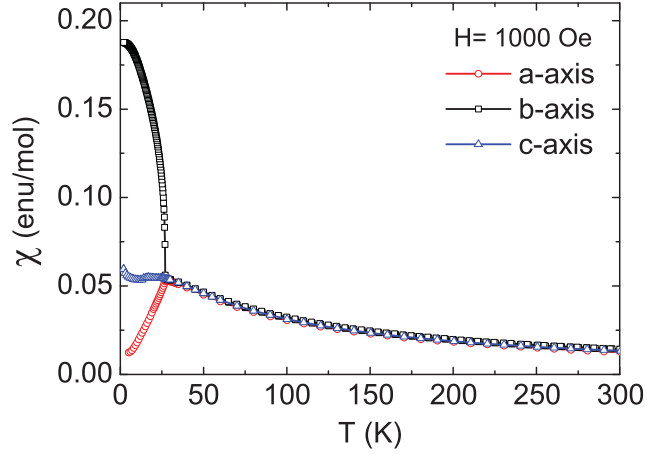


Figure 4.49: Susceptibility of LiFeP_2O_7 measured at 1000 Oe along a, b and c -axis.

ferromagnetic domains with opposite orientation of the magnetization, the identical ZFC and FC data suggest a single domain feature of the FM component in the b -axis. The inset of Fig. 4.50(a) shows the AC susceptibility χ_b (measured at 117 Hz with a field amplitude of 1 Oe) in the temperature range of 26.7 K and 27.1 K, near $T_N \sim 26.86$ K. The sharp peak at the second-order phase transition in χ_b shows a width of only 0.01 K, consistent with the critical temperature $T_N = 26.86$ K. Furthermore, the single domain state is further supported by $M - H$ hysteresis loop measurements in different temperatures (Fig. 4.50(b)). The FM hysteresis loops are indeed very sharp, even at 25 K, just below T_N . The reversal of the FM moment happens so instantaneous that no data point can be taken between the spin up and spin down state within experiment resolution. The field scale between two data points is as low as 10 Oe, and yet, no intermediate magnetization values could be detected near the coercive field, indicating the spontaneous FM moment flips at once from positive to negative values and vice versa, as the vertical dashed lines in Fig. 4.50(b). As long as the direction of the FM moments is determined, the b -axis susceptibility further increases linearly with the fields up to the maximum field of 50 kOe and shows the

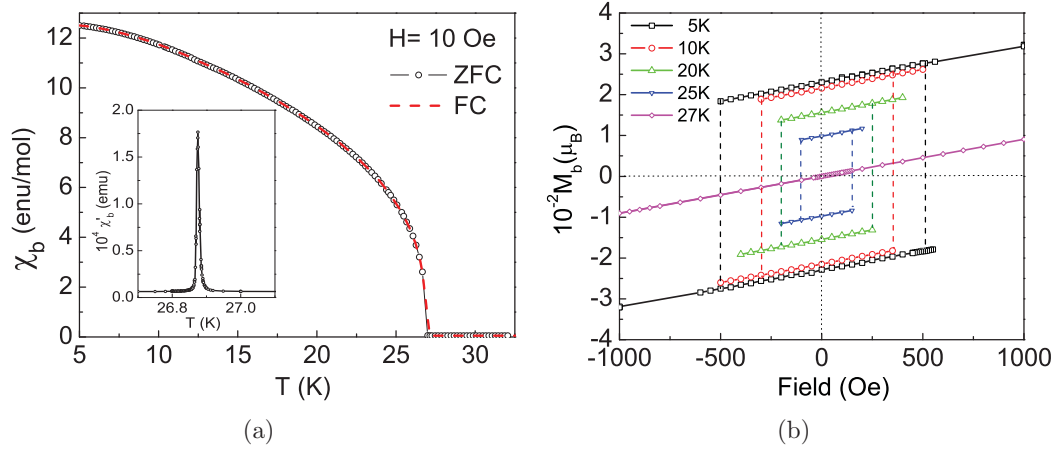


Figure 4.50: Temperature-depedent (a) b -axis susceptibility (χ_b) at 10Oe and (b) M_b of the LiFeP_2O_7 . Note that the perfect overlap of zero-field-cooled (ZFC) and field-collcd (FC) data in (a) indicates the single domain property of the magnetic moments. The inset in (a) shows the AC susceptibility near the phase transition.

spontaneous FM moment as small as $0.024 \mu_B/\text{Fe}$. The ferromagnetic hysteresis loops show a small asymmetry, whose origin is not yet clear. It could be due to the complex interactions of the FM order parameter M^Y with the AFM order parameters L^X, L^Z , and the polarization P^Y , as discussed in section 4.3.4 below.

The FM component due to the canted AFM order is allowed by symmetry. According to the powder neutron scattering data of LiFeP_2O_7 , the wavevector of the magnetic order is $\vec{q} = (0,0,0)$, and therefore, the magnetic representation of the little group of $\vec{q}$ can be decomposed into two irreducible representations, $\Gamma = 3(\Gamma_1 + \Gamma_2)$ [63]. Three basis vectors in the Γ_1 representation include two AFM components ($L^X = S_1^X - S_2^X$ and $L^Z = S_1^Z - S_2^Z$), both observed in neutron scattering data, and one FM component ($M^Y = S_1^Y + S_2^Y$), where S_1 and S_2 refer to the spins of two Fe ions in the unit cell. It is the M^Y order parameter that allows for the ferromagnetic moment along the b axis, as observed in the magnetic measurements. In fact, both FM (M_b) and AFM L_a anomaly occur at exactly the same temperature

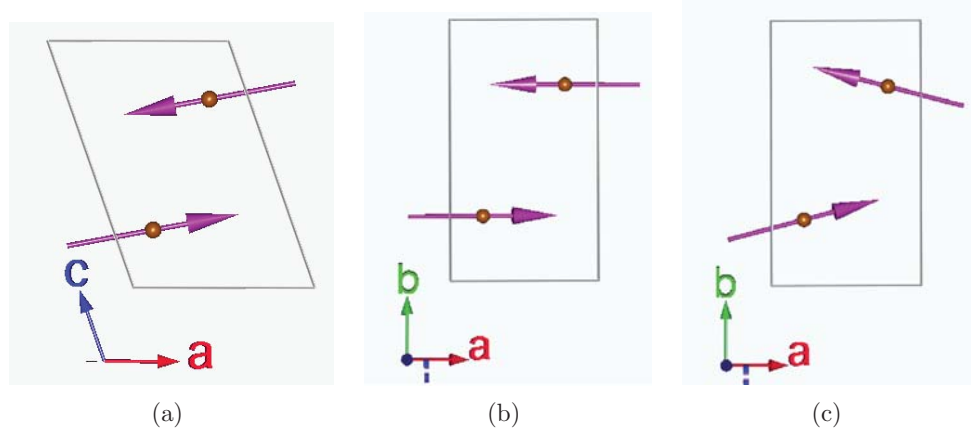


Figure 4.51: The magnetic structure of the LiFeP_2O_7 (a) in the a - c -plane and (b) in the a - b -plane. To better see how the spins are tilted, M^Y is shown 50 times larger in (c).

T_N , indicating that both are components of one single magnetic phase. Since the spontaneous FM moment measured at 5 K is as small as $0.024 \mu_B/\text{Fe}$, it is difficult for powder neutron scattering measurements to detect this size of magnetic moments. This is why people always compare both bulk and microscopic measurements side by side. Combining both data from our bulk measurement (b -axis component) and the refinement of powder neutron scattering data (a and c -axis components) [63], we can derive the microscopic picture of the magnetic order. The result is shown in Fig. 4.51 as the canted AFM magnetic structure. As shown in Fig. 4.51(b), the b -axis FM components are so small that it needs to be enlarge by a factor of 50 to see how the spins are canted to give rise to b -axis FM components in Fig. 4.51(c).

The smooth increase of the FM order parameter and single domain feature below T_N suggest that this is a second-order magnetic phase transition. This can be further supported by specific heat (C_p) measurements in Fig. 4.52. $C_p(T)$ exhibits a very sharp peak at T_N and a λ -shaped-like anomaly that is frequently observed near second-order phase transitions if critical fluctuations of the order parameter are significant.

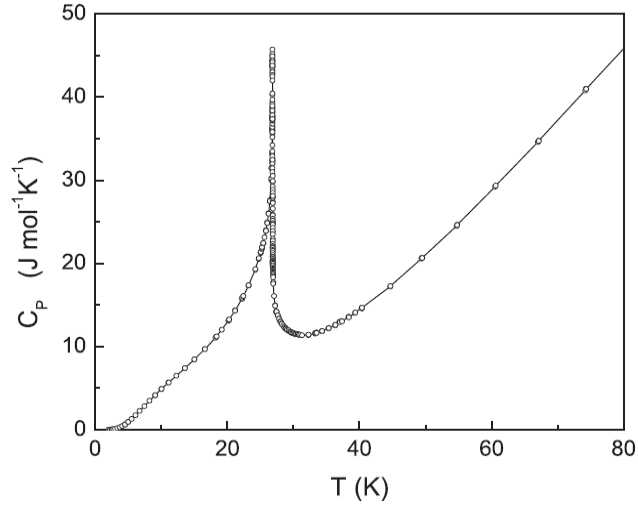


Figure 4.52: Heat capacity of LiFeP_2O_7 near magnetic transition temperature.

Since the magnetic phase transition is continuous, the expansion of the free energy with respect to the order parameters will provide a mean-field description of the magnetic phase transition, as discussed in Sec. 4.3.4.

4.3.2 Magnetoelectric effect of LiFeP_2O_7

A macroscopic electrical polarization exists at all temperatures below ambient due to the polar structure of LiFeP_2O_7 . However, it is not clear whether or not there is any structural and ferroelectric transition at certain critical temperature. No hysteresis in the $P(E)$ data is observed in the polarization measurements at the condition of ambient temperature in electric fields up to 24 kV/cm [29]. No high-temperature dielectric data for LiFeP_2O_7 is published possibly due to the finite conductivity of the LiFeP_2O_7 in high-temperature range. Magnetic data collected up to 700 K shows nothing to attribute to any additional anomaly that could be originated from a high-temperature phase transition [62]. Although high-temperature measurements of the ionic conductivity of LiFeP_2O_7 have shown a crossover near 700 K, differential thermal

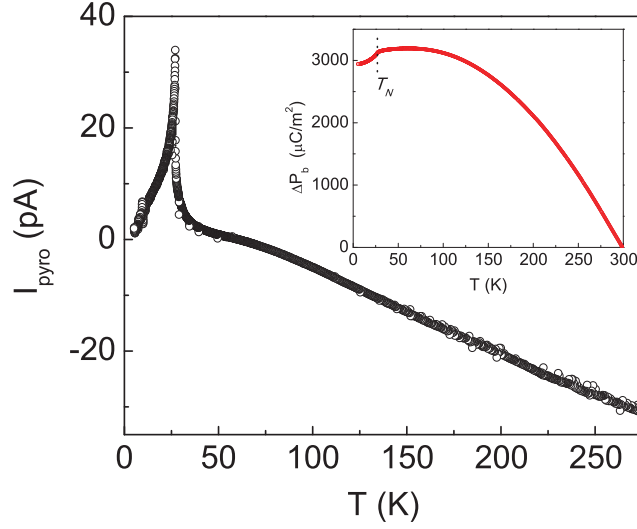


Figure 4.53: Pyroelectric current and polarization change (inset) as a function of temperature of LiFeP_2O_7 .

analysis data have not shown any notable anomaly that might suggest a structural or ferroelectric transition [67].

The single-crystalline samples for measurements have been found good insulators at and below ambient temperatures. Therefore, the pyroelectric current method can be applied to measure the change of electric polarization. Fig. 4.53 shows the pyroelectric current data as a function of temperature. The measured pyroelectric current is significant, and it reveals the strong increase of the polarization towards lower temperatures. The polarization change between ambient and low temperatures, $\Delta P_b(T)$, is obtained by integrating the pyroelectric current and dividing by the contact area, as shown in the inset of Fig. 4.53.

The most unusual feature in the pyroelectric current $I_p(T)$ is the sharp λ -shaped peak at $T_N = 27$ K, where the magnetic moments are transformed into canted AFM order, resulting in the drop of the polarization below T_N . This pronounced peak indicates a very strong coupling between the magnetic order parameters and the b -axis

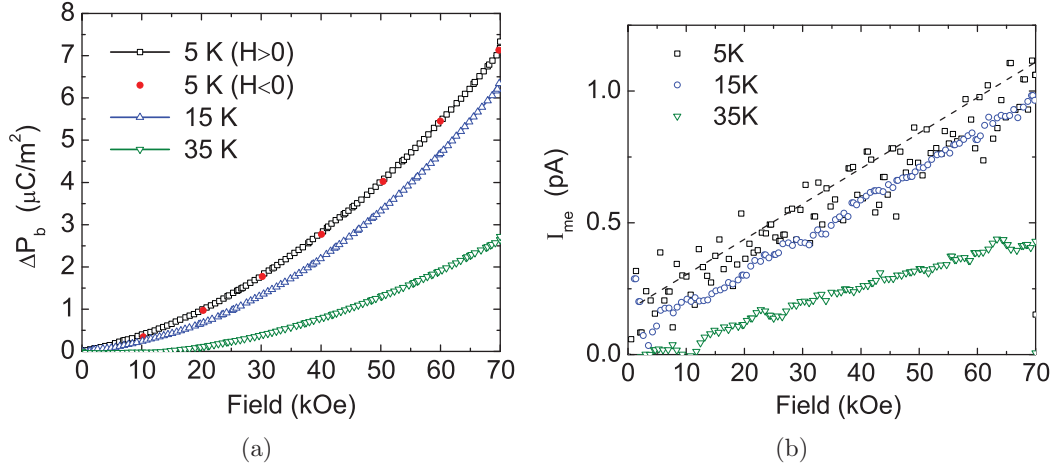


Figure 4.54: (a) Magnetolectric polarization change ($\Delta P_b(H)$) and (b) magnetolectric current, I_{me} at 5K, 15K and 35K. The bold circles in (a) show the polarization change in a negative magnetic field. The dash lines in (b) are a linear fit of the magnetolectric current data.

polarization, i.e., a large internal magnetolectric effect. To inspect the pyroelectric data closer, it also shows that $\Delta P_b(T)$ reaches its maximum ($I_p = 0$) at much higher temperatures of about $2T_N$, which corresponds to the onset of sizable magnetic fluctuations (note: Weiss temperature $\Theta \sim -50$ K) and their effect on the lattice. This is also in agreement with the heat capacity data that shows a significant enhancement of C_p on the top of the lattice contribution, starting at about 50 K (Fig. 4.52).

The external magnetolectric effects (the change of P_b due to applied external magnetic fields) were studied at different temperatures, as shown in Fig. 4.54. The b -axis polarization change increases in longitudinal fields H_b at the temperatures both below and above the magnetic transition temperature [35 K data in Fig. 4.54(a)]. However, the magnitude of $\Delta P_b(H)$ is relatively small at low magnetic fields, but it increases nonlinearly at higher fields. For temperatures below T_N , the $\Delta P_b(H)$ data appears to be linear at low field range. This is shown more clearly in the magnetolectric current I_{me} (Fig. 4.54(b)). I_{me} increases linearly with H_b at all

temperatures; however, only the data collected below T_N shows finite intercept with the vertical axis. The dashed line in Fig. 4.54(b) is a linear fit of the data, and it clearly shows the finite intercept only for the 5 K and 15 K data, but not in the 35 K data. Below T_N , I_{me} suddenly jumps to a finite value when the field just starts to increase. This is a clear indication of a linear magnetoelectric effect (intercept in current data) which is superimposed on the quadratic magnetoelectric coupling (I_{me} linear increase with H_b fields).

The superposition of linear and quadratic magnetoelectric effects below T_N is a result of the spontaneous magnetic moment that couples linearly to the field and to the polarization, which will be discussed in more detail in Sec. 4.3.4 below. It is also noted that the polarization change is symmetric with respect to the field orientations; the $\Delta P_b(H)$ data measured at 5 K in negative magnetic fields are shown as stars in Fig. 4.54(a). Similar measurements in a transverse magnetic field have not displayed any significant change of the b -axis polarization. The corresponding magnetoelectric current was an order of magnitude smaller and close to the resolution limit of the measurement.

4.3.3 Lattice anomalies at the magnetic transition

The observation on the internal magnetoelectric effect in Fig. 4.53 is a result of ionic displacements at the temperature range of magnetic ordering so that the electric polarization shows a corresponding change. The trigger is the strong spin-lattice coupling between magnetic order and the lattice polarization. The macroscopic distortion of the lattice below T_N is revealed through thermal expansion measurements. The relative length changes $\Delta L(T)/L_0$ of three orthogonal directions, b and c axes of the crystal and the orientation perpendicular to both axes, are shown in Fig. 4.55(a)

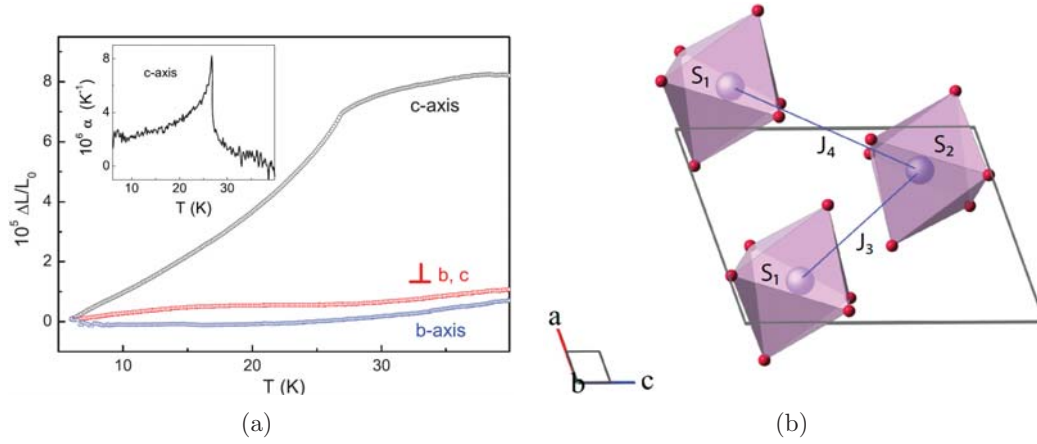


Figure 4.55: (a) Relative length change of b , c , and perpendicular ($\perp$) to b and c with reference to 6 K. The inset in (a) shows the c -axis thermal expansivity $\alpha(T)$ (b) schematic plot of the most relevant super-super exchange interactions, J_3 and J_4 , between different iron moments (only FeO₆ octahedra are shown) Ref. [4].

at low temperatures. It is remarkable that the crystal dimensions along b -axis, where the polarization shows anomaly, change very little when passing through the magnetic phase transition, and so does $\perp$ (b, c) direction. However, the crystal exhibits a significant contraction along the c axis at T_N , as the pronounced abnormal drop of the c -axis data in Fig. 4.55(a). The thermal expansivity of the c axis, $\alpha = \partial(\Delta c/c_0)/\partial T$, increases sharply near T_N and displays a λ -shaped-like peak, similar to the pyroelectric current and the specific data. This demonstrates the strong coupling of the magnetic orders and the polar lattice.

It is not clear at this point why the lattice response to the magnetic order is nearly uniaxial along the c direction only (Fig. 4.55(a)). From the structure of LiFeP₂O₇, the diphosphate group is partially oriented along the direction of contraction. It seems conceivable to assume that the magnetic order mainly distorts the diphosphate group to maximize the energy gain of the magnetic system. A decrease of the angle $P-O-P$ within the diphosphate group from 129° will also result in a contraction of

the c -axis. The distortion of the PO_4 tetrahedra further causes a change of the shape of the tunnels along the a -axis. As a result, Li ions would displace accordingly in the tunnels and give rise to the observed decrease of the polarization below T_N .

The distortion of the PO_4 units below the magnetic phase transition will also affect the super-super exchange interactions, which depend strongly on the $O - O$ distance in the exchange path of $\text{Fe} - O - O - \text{Fe}$ [64, 4]. The super-super exchange interactions gain more magnetic exchange energy through the elastic energy of the polar crystal, resulting in the contraction of the c -axis in the order phase. Theoretical estimates of the exchange coupling parameters [4] could give us a hint on how the super-super exchange interactions compete with elasticity of polar structure. The strongest coupling (J_3) is found between the two Fe spins $\vec{S}_1$ and $\vec{S}_2$ in the unit cell, and another sizable coupling (J_4) exists between $\vec{S}_1$ and $\vec{S}_2$ of two neighboring unit cells stacked along the a axis (here we use the same labels for the J_i as in the calculation of Ref. [4]). The corresponding exchange parameters are schematically shown in Fig. 4.55(b). The contraction along the c -axis will reduce the $O - O$ distance of these two (J_3 and J_4) super-super exchange pathways, increase the magnetic exchange constants, and maximize the energy gain in the magnetoelectric ordered state. This explains the magnetoelastic effect along the c -axis. While this discussion based on the macroscopic expansion anomalies can only be qualitative, high-resolution x-ray or neutron scattering experiments could resolve the microscopic details of the lattice distortion and lead to a more fundamental understanding of the observed effects.

4.3.4 Landau free energy expansion

The second-order characters of the magnetic phase transition are well-established through the magnetic (Fig. 4.50(a)) and thermodynamic (Fig. 4.52) measurements.

Within a mean-field description, the Landau free energy expansion can, therefore, be constructed in terms of magnetic order parameter and polarization. All possible couplings between different components of the magnetic order parameter and the lattice polarization will be included. Every term in the free energy expansion has to be invariant with respect to all symmetry operations of the crystal above T_N and the time reversal operation. The crystal space group $P2_1$ has only two symmetry elements, the identity and the screw-type operation (180° rotation about the b axis and a translation by $\vec{b}/2$). Based on previous and current data, the magnetic order parameters in the little group of $\vec{q} = (0,0,0)$ in the Γ_1 irreducible representation are (L^X, L^Z, M^Y) . The free energy expansion in terms of the magnetic order parameters and the electrical polarization is given by

$$\begin{aligned}
F(\vec{L}, \vec{M}, \vec{P}) &= F_0 + \frac{a}{2}L^2 + \frac{b}{4}L^4 + \frac{c}{2}M^2 + \frac{d}{4}M^4 \\
&+ \sigma_1 L^X L^Z + \sigma_2 L^X M^Y + \sigma_3 L^Z M^Y - \alpha P^Y + \frac{\beta}{2}(P^Y)^2 \\
&+ [\lambda_1 L^X L^Z + \lambda_2 L^X M^Y + \lambda_3 L^Z M^Y + \lambda_4 (L^X)^2 \\
&+ \lambda_5 (L^Z)^2 + \lambda_6 (M^Y)^2] P^Y + \dots
\end{aligned} \tag{4.10}$$

Eq. (4.10) includes the second and fourth orders of the magnetic order parameters $\vec{L}, \vec{M}$, and all other terms up to third order that are invariant under crystal and time reversal symmetry operations. The first two lines are related to different components of the magnetic order parameters in Γ_1 representation, and the energy of the polarized state. It is noted that the linear term in P^Y is symmetry allowed in the $P2_1$ polar structure. The σ_1, σ_2 , and σ_3 terms couple different components of the magnetic order parameter, and they are commonly of relativistic origin. Neutron scattering experiments [63] and our magnetization data (Fig. 4.49 and 4.50) show

that the major magnetization component in the ordered state is L^X whereas L^Z and M^Y are comparatively small. It then can be concluded that the primary order parameter is L^X , and the other two components are coupled to L^X through the bilinear terms σ_1 and σ_2 , causing the increase of all three components of the magnetic order parameter at the same critical temperature, T_N . This conclusion is supported by the magnetization data of Fig. 4.49. The a -axis magnetization shows a clear antiferromagnetic response below T_N , with a strong decrease at lower temperatures. However, the c -axis response is far more subtle and no significant decrease below T_N is found, indicating that the L^Z component of the order parameter is most probably induced by the weak coupling through the $\sigma_1 L^X L^Z$ term in Eq. (4.10). The third and fourth lines in Eq. (4.10) show the symmetry-allowed third-order terms which couple the magnetic order and the polarization.

By minimizing the free energy Eq. (4.10) with respect to L^X , L^Z , M^Y , and P^Y , the thermodynamically stable state and magnetic/dielectric orders can be defined as a function of temperature. However, because of the large number of unknown parameters such as $a, b, \dots, \sigma_i$, and λ_i , we will not attempt to fit a magnetic solution to the experimental data. The electrical polarization can be derived as

$$P^Y = \frac{1}{\beta} [\alpha - \lambda_1 L^X L^Z - \lambda_2 L^X M^Y - \lambda_3 L^Z M^Y - \lambda_4 (L^X)^2 - \lambda_5 (L^Z)^2 - \lambda_6 (M^Y)^2]. \quad (4.11)$$

Eq. (4.11) describes the b -axis polarization as a function of the magnetic order parameters. The first term, α/β , represents the temperature-dependent polarization in the paramagnetic state, as obtained by integrating the pyroelectric current above T_N (inset of Fig. 4.53). The remaining terms in Eq. (4.11) describe the coupling between electrical polarization and the magnetic order parameter, resulting in the

peak anomaly in the pyroelectric current and the decrease of the polarization P_b below T_N . Note that the significant change of the c -axis length below T_N , as shown in Fig. 4.55(a), is not considered in Eq. (4.10) and (4.11).

To include the symmetry-allowed terms that couple the magnetic order parameter to the lattice strain tensor ε_{ij} , we need to establish invariants of the lowest order in terms of L^X, L^Z, M^Y , and ε_{ij} . Since the lowest order terms have to be bilinear in the components of the magnetic order parameter to preserve the time reversal symmetry, they include all combinations of L^X, L^Z , and M^Y shown in the square brackets of Eq. (4.10). All those terms are also invariant with respect to the two symmetry elements of the space group, the identity and the screw operation. Therefore, only space-group-invariant components ε_{ij} of the strain tensor are allowed to couple in first order to the bilinear products of the magnetic order parameter components. Those elements are $\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}$, and ε_{xz} . The thermal expansion data shown in Fig. 4.55(a) indicate that the major lattice distortion is a compressive strain along the c -axis, ruling out any significant contributions from ε_{xz} (shear strain) and ε_{yy} (compression of the b -axis). The important terms are ε_{xx} and ε_{zz} that account for the observed c -axis compression below T_N .

The external magnetoelectric effects shown in Fig. 4.54 deserve a more detailed discussion. The coupling between the magnetic order parameters, the magnetic field, and the polarization is of interest. Any product combination of L^X, L^Z , and M^Y with the external field H^Y is invariant under the space group and the time reversal symmetry operations. The polarization P^Y is also an invariant. Therefore, the lowest order magnetoelectric effect is described by trilinear terms in the free energy expansion, for example $E_{me} \propto M^Y H^Y P^Y$. In the high-temperature phase ($T > T_N$), $M^Y = \chi^Y H^Y$ ($\chi^Y = dM^Y/dH^Y$ is the magnetic susceptibility), and the magnetoelectric response is quadratic in the external field,

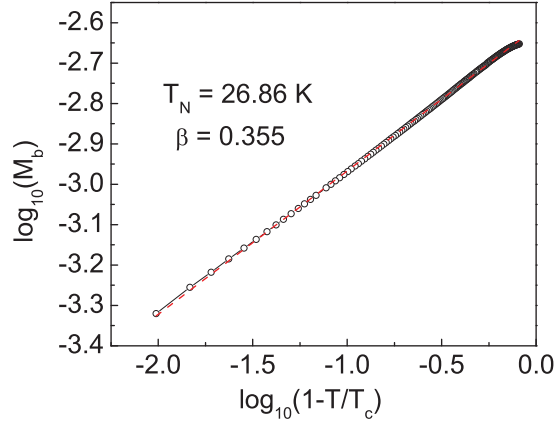


Figure 4.56: Scaling plot of the magnetization of LiFeP_2O_7 . The critical exponent β is determined by the slope (red dash line).

$$E_{me} \propto \chi^Y (H^Y)^2 P^Y \quad (4.12)$$

This is indeed observed above T_N ; see for example the 35 K data in Fig. 4.54. Below T_N , however, the existence of a spontaneous magnetization M^S adds an additional term to Eq. (4.12). With $M^Y = M^S + \chi^Y H^Y$

$$E_{me} \propto M^S H^Y P^Y + \chi^Y (H^Y)^2 P^Y \quad (4.13)$$

The existence of a spontaneous magnetization below T_N gives rise to a linear magnetoelectric response in addition to the quadratic effect, in perfect agreement with the experimental results shown in Fig. 4.54.

4.3.5 Critical scaling of magnetization

The mean-field theory cannot explain the λ -type anomaly of the heat capacity since the critical exponent of C_p in the Landau mean-field theory is zero. Spatial

fluctuations of the order parameter become essential when the system temperature approaches close to critical temperature T_N . Evidence for critical behavior is derived qualitatively from the λ -shaped anomaly of the specific heat and more quantitatively from the temperature-dependent magnetization [Fig. 4.50(a)]. $M(T)$ is expected to follow the relation $M(T) = M_0(1 - T/T_N)^\beta$ near the critical temperature. $\beta = 1/2$ is the critical exponent for the order parameter magnetization in a mean-field description; however, a more realistic model description that takes the spatial fluctuations of the order parameter into consideration leads to different values of β depending on the model, the spatial dimension, and the specific order parameter [68]. The double logarithmic plot in Fig. 4.56 shows a significant range where the scaling formula for $M(T)$ is fulfilled, as indicated by the dashed line. The estimated critical temperature $T_N = 26.86$ K in Fig. 4.56 agrees well with the T_N determined from the sharp ac susceptibility peak. The critical exponent $\beta = 0.355$ is clearly smaller than the mean-field value, but it is consistent with values obtained for typical spin models (Ising or Heisenberg) when critical fluctuations are allowed [68]. This shows the limits of the mean-field theory in describing the second-order magnetic phase transition. A more advanced description has to take into account the spatial fluctuations of the order parameter and the critical behavior as well as the details of the magnetic order (L^X, L^Z, M^Y) and the microscopic interactions.

Chapter 5

Summary

In the study of multi-interactions in solids, the main focus of this work is on the multiferroic and magnetoelectric materials. We have investigated the multiferroic properties of Co doped as well as Cu doped MnWO_4 , where the frustrated magnetic structures break the spatial inversion symmetry and induce ferroelectric polarization. Furthermore, the magnetoelectric (ME) properties of the $R\text{Al}_3(\text{BO}_3)_4$ system was studied, and, in the noncentrosymmetric but non-polar structure, magnetic fields induce polar distortion and give rise to ME polarization. Last but not least, we investigated single-crystalline LiFeP_2O_7 , a polar crystal with magnetic order of Fe spins at low temperature, and the magnetic ordering interacts with the lattice polarization.

The coexistence and mutual interaction of magnetic and ferroelectric states, as observed in the multiferroic MnWO_4 , originate from frustrated magnetic orders and strong spin-lattice coupling. Upon decreasing temperature, MnWO_4 exhibits three magnetic transitions, the collinear spin sinusoidal state (AF3), the non-collinear spiral spin state (AF2), and the frustrated collinear up-up-down-down spin structure (AF1). Among these three magnetic phases, the spiral Mn spin structure of the

AF2 phase allows for the ferroelectric (FE) polarization because of the loss of inversion symmetry. Due to competing exchange interactions, the spin system is highly frustrated and susceptible to small perturbations. It is therefore of interest to find a way, by chemical doping or others, to modify the spiral Mn spin structure, that could help us to control the ferroelectric polarization, and this would lead us to the deeper understanding of the multiferroic system. The doping effects of Co^{2+} ($S=3/2$) replacing Mn^{2+} ($S=5/2$) on the multiferroic and magnetic phases of $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ are therefore investigated by magnetic, polarization, heat capacity and neutron scattering (through collaboration) measurements.

We are the first to completely resolve the complex multiferroic and magnetic phase diagram $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ in the doping range $0 \leq x \leq 0.3$. The FE polarization was found reorienting two times with increasing Co concentration, resulting in FE phase I, II and III. The ferroelectric (FE) polarization $\vec{P}$ first flips from b -axis (FE phase I) to a -axis (FE phase II) at the critical Co concentration of $x_{c1} = 0.075$. With further increasing x , the $\vec{P}$ flips a second time from a -axis (FE phase II) back to b -axis (FE phase III) at $x_{c2} = 0.15$. In the FE phase III, the b -axis polarization originates from an incommensurate (ICM) conical structure (AF2/4 phase). The conical structure is weakening with further increasing Co doping level due to stabilization of the commensurate and collinear AF4 phase with simple modulation vector, which is also the ground state in CoWO_4 . The physics of the multiple FE polarization flops is driven by the rotation of the spin helix due to different spin values, tuning of exchange interactions and the change of the average magnetic anisotropy of magnetic moments upon Co doping. It is well known that the polarization is proportional to vector product of normal vector $\vec{k}$ and the propagation vector $\vec{c}$ of the spin spiral structure. With the rotation of the spin helix structure driven by the Co spin anisotropy, the system loses ME energy, and therefore, it changes the orientation of the spin helix to regain the

ME energy. This is associated with a rotation of the FE polarization. Two empirical equations relating magnitude and direction of the FE polarization to the orientation of the spin helix are derived for a qualitative description of the multiferroic states.

The magnetic field-induced reorientations of the spin spiral become more complex, but fortunately we can still separate the field effects in three ranges of Co doping as FE phase I, II and III. In the lower limit of the FE phase I ($0.02 \leq x \leq 0.035$), the H_b fields induce the collinear up-up-down-down spin structure (AF1). For the upper limit of the FE phase I ($0.042 \leq x \leq 0.05$), instead of inducing a new phase, H_b fields rotate the spiral plane to the $a - c$ plane, resulting in a -axis polarization. The origin of the reorientation of the spin helical structure is that magnetic fields first force the spin spiral to become a conical structure with all the spins surrounding the external field direction, and therefore, causes the spiral plane to rotate to be perpendicular to the direction of the applied fields. Whether or not the new spiral component of the conical structure gives rise to FE polarization depends on vector product of normal vector $\vec{k}$ and the propagation vector $\vec{c}$ of the spin spiral structure. This rule can be used to explain our data from the upper limit of the FE phase I up to FE phase III. In the lower limit of FE phase II ($0.075 \leq x \leq 0.1$), the P_a increases with H_b field and decrease with H_c because the H_b fields rotate the spiral plane to the $a - c$ plane whereas H_c fields rotate in the opposite way. Two particular interesting doping levels are $x = 0.12$ and 0.15 . The $x = 0.12$ sample shows a flop of the polarization from a -axis to b -axis with increasing H_c . At $x = 0.15$, we have observed a spontaneous reversal (sign change) of the b -axis polarization in an external field of H_c upon decreasing temperature. The reason is still a open question, but it would be interesting to investigate the domain properties once the collaboration with the Switzerland group is well-established. In the FE phase III, the magnetic fields transform the conical structure (AF2/4 phase) into a simple antiferromagnetic ordering (AF4 phase) by

collapsing the cone to a line orientated the spin easy axis.

The Cu doped MnWO_4 behaves similar to the lower limit of the FE phase I in the $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ phase diagram. At low Cu doping range, it shows AF1 and AF2 phase coexistence at low temperature. The AF1 phase is suppressed upon 20% of Cu doping so that the AF2 phase is extended to the lowest temperature, similar to low Co doping MnWO_4 compound. At the same time, the T_C of the AF2 phase and T_N of the sinusoidal AF3 phase shift toward higher temperature, distinguishing the Cu doping effect from the Co doping and Zn doping cases [41]. Since the CuWO_4 crystallizes in triclinic structure, it would be interesting to see if there is a structural transition from monoclinic to triclinic structure in higher Cu doping range, but it requires the Cu doping concentration higher than 30%. Furthermore, the application of b -axis magnetic field induces the AF1 phase and increases the AF1:AF2 ratio as derived from the polarization and specific heat measurements. At Cu doping $x = 0.05$, the H_b field is able to suppress the AF2 phase and stabilizes the pure AF1 phase; however, at higher doping $x = 0.3$, the H_b field effect is barely observable. The magnetic fields along the magnetic easy axis stabilize the AF2 phase as observed in the parent compound MnWO_4 .

For the rare earth borates, the ME effect is associated with a field-induced polar structure distortion from a non-polar structure (space group $R32$). The magnetic measurements of $R\text{Al}_3(\text{BO}_3)_4$ show paramagnetic features with weak coupling of the R moments at low temperature, relatively simple compared to $R\text{Fe}_3(\text{BO}_3)_4$. The magnetic anisotropy of different $R\text{Al}_3(\text{BO}_3)_4$ crystal mainly depends on the splitting of the f -orbital moments in the crystal field and the occupation of the f -levels. Despite of the weak coupling of the f moments, the easy plane magnets ($R = \text{Er}$, Tm and Yb) and nearly isotropic magnet ($R = \text{Ho}$) exhibit large ME effects, exceeding values reported from the $R\text{Fe}_3(\text{BO}_3)_4$ compound system in the same field conditions.

$\text{HoAl}_3(\text{BO}_3)_4$ sets the record of highest ME effect in high fields before the single-crystalline $\text{CaBaCo}_4\text{O}_7$ compound was reported [6]. It is therefore concluded that the d -moments in $R\text{Fe}_3(\text{BO}_3)_4$ are detrimental to the ME effect. The magnetic anisotropy (χ_x/χ_z ratio) decreases in a sequence of Er, Tm and Ho, and, at the same time, the ME effect increases in the same sequence, except the smallest magnetic moment of the Yb sample. It could mean that the $R = \text{Yb}$ compound solely does not fit this trend or imply that the relationship between magnetic anisotropy and ME effect is actually more complex. The magnetic data of solid solution $R_{1-x}R'_x\text{Al}_3(\text{BO}_3)_4$ (R, R' are different rare earth elements) compounds show that the magnetic anisotropy can be modified as expected based on the choice of the R and R' element. However, the corresponding ME polarization does not scale with the ratio of two different elements. The microscopic polar distortion of the crystal is yet to be resolved so future work on X-ray or neutron scattering would lead to a more comprehensive understanding for the ME effects in this compound.

The LiFeP_2O_7 crystallizes in a polar structure, and the Fe-moments experience a canted antiferromagnetic (AFM) ordering through super-super exchange integrations in low temperature. The canted AFM is allowed by crystal symmetry and causes a ferromagnetic component along the crystallographic b -axis. Because of its polar structure, the b -axis polarization continuously increases from room temperature down to T_N . At T_N , a significant internal ME effect is found in form of a sharp λ -shape-like peak anomaly in the pyroelectric current measurement. The associated AFM phase transition is further confirmed as a second-order phase transition by specific heat measurement. The c -axis length also shows a contraction anomaly with the onset of the magnetic order. All the results imply that the polar LiFeP_2O_7 exhibits a strong interaction between magnetic order parameter and electric polarization (internal ME effect). The external ME measurements below T_N display a superposition of

quadratic ME effect and a linear ME effect due to the existence of the spontaneous magnetization, whereas it shows only quadratic ME effect above the magnetic ordering temperature. The coupling of the polarization to the magnetic order parameter and to external magnetic fields is described by a Landau theory based on symmetry considerations.

Appendix A

Publications and Conference Participation

A.1 Publications

- "Magnetic order and spin-flop transitions in the cobalt-doped multiferroic $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$," Feng Ye, Songxue Chi, Jaime A. Fernandez-Baca, Huibo Cao, K.-C. Liang, Yaqi Wang, Bernd Lorenz, and C. W. Chu, Phys. Rev. B, 86, 094429 (2012)
- "Weak ferromagnetism and internal magnetoelectric effect in LiFeP_2O_7 ," K.-C. Liang, W. Zhang, B. Lorenz, Y. Y. Sun, P. S. Halasyamani, and C. W. Chu, Phys. Rev. B, 86, 094414 (2012)
- "Control of improper ferroelectricity by chemical substitution and magnetic fields in multiferroic $\text{Mn}_{1-x}\text{Cu}_x\text{WO}_4$," K.-C. Liang, B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, (2012) (Submitted)

- " Magnetoelectricity in the system $RAl_3(BO_3)_4$ ($R = Tb, Ho, Er, Tm$)," K.-C. Liang, R. P. Chaudhury, B. Lorenz, Y. Y. Sun, L. N. Bezmaternykh, V. L. Temerov, and C. W. Chu, Journal of Physics: Conference Series 400, 032046, (2012)
- "The complex multiferroic phase diagram of $Mn_{1-x}Co_xWO_4$," K.-C. Liang, Y.-Q. Wang, Y. Y. Sun, B. Lorenz, F. Ye, J. A. Fernandez-Baca, H. A. Mook, and C. W. Chu, New J. Phys. 14 073028, (2012)
- " Field-induced continuous rotation of the polarization in multiferroic $Mn_{0.95}Co_{0.05}WO_4$," K.-C. Liang, R. P. Chaudhury, Y. Q. Wang, Y. Y. Sun, B. Lorenz, and C. W. Chu, J. Appl. Phys. 111, 07D903, (2012)
- " Giant magnetoelectric effect in $HoAl_3(BO_3)_4$," K.-C. Liang, R. P. Chaudhury, B. Lorenz, Y. Y. Sun, L. N. Bezmaternykh, V. L. Temerov, and C. W. Chu, Phys. Rev. B, 83, 1804179(R), (2011)
- " Multiferroic Phase Control in $MnWO_4$ Doped with Fe, Co, and Zn: A Comparative Study," K.-C. Liang, R. P. Chaudhury, B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, Integrated Ferroelectrics, 131:47-55, (2011)

A.2 Conference and Workshop Participation

A.2.1 Presentations

- K.-C. Liang, W. Zhang, B. Lorenz, Y. Y. Sun, P. S. Halasyamani, and C. W. Chu, APS March Meeting (Baltimore, MD), March 2013, "The internal and external magnetoelectric effect in LiFeP_2O_7 "
- K.-C. Liang, Y.-Q. Wang, Y. Y. Sun, B. Lorenz, F. Ye, J. A. Fernandez-Baca, H. A. Mook, and C. W. Chu, 12th MMM-INTERMAG conference (Chicago, IL), January 2013, "The complex multiferroic phase diagram of single-crystalline $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ "
- K.-C. Liang, Y.-Q. Wang, Y. Y. Sun, B. Lorenz, F. Ye, J. A. Fernandez-Baca, H. A. Mook, and C. W. Chu, TcSUH 43th Semiannual Student Symposium, May 2012, "The complex phase diagram of spiral magnet $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ "
- K.-C. Liang, R. P. Chaudhury, B. Lorenz, Y. Y. Sun, L. N. Bezmaternykh, V. L. Temerov, and C. W. Chu, APS March Meeting (Boston, MA), March 2012, "The magnetoelectirc effect in the $R\text{Al}_3(\text{BO}_3)_4$ ($R=\text{Tb}$, Ho , Er , and Tm)"
- K.-C. Liang, Y.-Q. Wang, Y. Y. Sun, B. Lorenz, F. Ye, J. A. Fernandez-Baca, H. A. Mook, and C. W. Chu, 56th MMM conference (Scottsdale, AZ), November 2011, "Chemical doping and magnetic fields effects on the multiferroic phases of single-crystalline $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ "
- K.-C. Liang, R. P. Chaudhury, B. Lorenz, Y. Y. Sun, L. N. Bezmaternykh, V. L. Temerov, and C. W. Chu, TcSUH 41st Semiannual Student Symposium, May

2011, "Giant magnetoelectric effect in the $\text{HoAl}_3(\text{BO}_3)_4$ "

- K.-C. Liang, Y.-Q. Wang, Y. Y. Sun, B. Lorenz, F. Ye, J. A. Fernandez-Baca, H. A. Mook, and C. W. Chu, APS March Meeting (Dallas, TX), March 2011, "Magnetic and multiferroic phases of single-crystalline $\text{Mn}_{1-x}\text{Co}_x\text{WO}_4$ "
- Kao-Chen Liang, Completion of Magnetic Structure Determination from Neutron Diffraction Data Workshop, (Oak Ridge, TN), September 2012

Bibliography

- [1] R. P. Chaudhury, B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, Phys. Rev. B **77**, 104406 (2008).
- [2] T. Kimura, Annual Review of Materials Research **37**, 387 (2007).
- [3] S.-W. Cheong and M. Mostovoy, Nature Materials **6**, 13 (2007).
- [4] M.-H. Whangbo, D. Dai, and H.-J. Koo, Dalton Trans. **2004**, 3019 (2004).
- [5] C. W. Chu, Int. J. Mod. Phys. B **24**, 4102 (2010).
- [6] V. Caignaert, A. Maignan, K. Singh, C. Simon, V. Pralong, B. Raveau, J. Mitchell, H. Zheng, and L. Chapon, Gigantic ferroelectric polarization and magnetoelectric coupling in a ferrimagnetic oxide $\text{CaBaCo}_4\text{O}_7$, Preprint, arXiv:1302.5541.
- [7] I. E. Chupis, Ferroelectromagnets. Fifty years after discovery, Preprint, arXiv:cond-mat/1012.2024., 2010.
- [8] H. Schmid, Ferroelectrics **162**, 317 (1994).
- [9] J. Ziman, *Principles of the Theory of Solids*, Cambridge University Press, London, England, 1964.
- [10] N. W. Ashcroft and D. N. Mermin, *Solid state physics*, Thomson Learning, Toronto, 1 edition, 1976.
- [11] G. Lawes, A. B. Harris, T. Kimura, N. Rogado, R. J. Cava, A. Aharony, O. Entin-Wohlman, T. Yildirim, M. Kenzelmann, C. Broholm, and A. P. Ramirez, Phys. Rev. Lett. **95**, 087205 (2005).
- [12] A. B. Harris, T. Yildirim, A. Aharony, and O. Entin-Wohlman, Phys. Rev. B **73**, 184433 (2006).
- [13] M. Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006).
- [14] D. J. Griffiths, *Introduction to Electrodynamics (3rd Edition)*, Addison Wesley, 1998.

- [15] L. Landau, Ukr. J. Phys. **53**, 25 (2008), Special Issue.
- [16] C. Kittel, *Introduction to Solid State Physics*, John Wiley & Sons, Inc., New York, 6th edition, 1986.
- [17] P. Curie, J. de Physique **3**, 393 (1894).
- [18] P. Debye, Z. Physik **36**, 300 (1926).
- [19] I. E. Dzyaloshinskii, Sov. Phys. JETP **10**, 628 (1960), (Zh. Eksp. Teor. Fiz. 33, 881 (1959)).
- [20] D. N. Astrov, Sov. Phys. JETP **13**, 729 (1961), (Zh. Eksp. Teor. Fiz. 40, 1035 (1961)).
- [21] T. H. O'Dell, Phil. Mag. **8**, 411 (1963).
- [22] J. W. F. Brown, R. M. Hornreich, and S. Shtrikman, Phys. Rev. **168**, 574 (1968).
- [23] E. Ascher and A. G. M. Janner, Phys. Lett. A **29**, 295 (1969).
- [24] M. Kenzelmann, A. B. Harris, S. Jonas, C. Broholm, J. Schefer, S. B. Kim, C. L. Zhang, S.-W. Cheong, O. P. Vajk, and J. W. Lynn, Phys. Rev. Lett. **95**, 087206 (2005).
- [25] A. H. Arkenbout, T. T. M. Palstra, T. Siegrist, and T. Kimura, Phys. Rev. B **74**, 184431 (2006).
- [26] K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa, and T. Arima, Phys. Rev. Lett. **97**, 097203 (2006).
- [27] H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. **95**, 057205 (2005).
- [28] V. L. Temerov, A. E. Sokolov, A. L. Sukhachev, A. F. Bovina, I. S. Edelman, and A. V. Malakhovskii, Crystall. Rep. **53**, 1157 (2008).
- [29] W. Zhang and P. S. Halasyamani, Cryst. Growth Des. **12**, 2127 (2012).
- [30] Q. Design, *Physical Property MEasurement System: Heat Capacity Option User's Manual*, 2010, Part Number 1085-150, L1.
- [31] I. Keithley Instruments, *Low Level Measurements Handbook 6th Edition*, 2004.
- [32] R. P. Chaudhury, F. Yen, B. Lorenz, Y. Y. Sun, L. N. Bezmaternykh, V. L. Temerov, and C. W. Chu, Phys. Rev. B **80**, 104424 (2009).
- [33] G. Lautenschläger, H. Weitzel, T. Vogt, R. Hock, A. Bohm, M. Bonnet, and H. Fuess, Phys. Rev. B **48**, 6087 (1993).
- [34] F. Ye, R. S. Fishman, J. A. Fernandez-Baca, A. A. Podlesnyak, G. Ehlers, H. A. Mook, Y.-Q. Wang, B. Lorenz, and C. W. Chu, Phys. Rev. B **83**, 140401(R) (2011).

- [35] H. Kleykamp, J. Less-Common Metals **71**, 127 (1980).
- [36] H. Weitzel, Solid State Commun. **8**, 2071 (1970).
- [37] K. Takagi, T. Oi, and T. Fukazawa, J. Crystal Growth **52**, 580 (1981).
- [38] E. Garcia-Matres, N. Stüßer, M. Hofmann, and M. Reehuis, Eur. Phys. J. B **32**, 35 (2003).
- [39] N. Stüßer, Y. Ding, M. Hofmann, M. Reehuis, B. Ouladdiaf, G. Ehlers, D. Günther, M. Meißner, and M. Steiner, J. Phys.: Condens. Matter **13**, 2753 (2001).
- [40] L. Meddar, M. Josse, P. Deniard, C. La, G. Andre, F. Damay, V. Petricek, S. Jobic, M.-H. Whangbo, M. Maglione, and C. Payen, Chem. Mat. **21**, 5203 (2009).
- [41] R. P. Chaudhury, F. Ye, J. A. Fernandez-Baca, B. Lorenz, Y. Q. Wang, Y. Y. Sun, H. A. Mook, and C. W. Chu, Phys. Rev. B **83**, 014401 (2011).
- [42] Y.-S. Song, J.-H. Chung, J. M. S. Park, and Y.-N. Choi, Phys. Rev. B **79**, 224415 (2009).
- [43] Y.-S. Song, L. Q. Yan, B. Lee, S. H. Chun, K. H. Kim, S. B. Kim, A. Nogami, T. Katsufuji, J. Schefer, and J.-H. Chung, Phys. Rev. B **82**, 214418 (2010).
- [44] I. Urcelay-Olabarria, E. Ressouche, A. A. Mukhin, Y. Y. Ivanov, A. M. Balbashov, G. P. Vorobev, Y. F. Popov, A. M. Kadomtseva, J. L. Garcia-Munoz, and V. Skumryev, Phys. Rev. B **85**, 094436 (2012).
- [45] R. P. Chaudhury, F. Ye, J. A. Fernandez-Baca, Y.-Q. Wang, Y. Y. Sun, B. Lorenz, H. A. Mook, and C. W. Chu, Phys. Rev. B **82**, 184422 (2010).
- [46] J. B. Forsyth and C. Wilkinson, J. Phys.: Condens. Matter **6**, 3073 (1994).
- [47] F. Ye, S. Chi, J. A. Fernandez-Baca, H. Cao, K.-C. Liang, Y. Wang, B. Lorenz, and C. W. Chu, PRB **86**, 094429 (2012).
- [48] H. Sagayama, K. Taniguchi, N. Abe, T. Arima, M. Soda, M. Matsuura, and K. Hirota, Phys. Rev. B **77**, 220407(R) (2008).
- [49] R. P. Chaudhury, F. Yen, C. R. dela Cruz, B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, Physica B **403**, 1428 (2008).
- [50] H. Weitzel and H. Langhof, J. Mag. Mag. Mat. **4**, 265 (1977).
- [51] F. Ye, private communication on the neutron scattering results in the magnetic fields of $\text{Mn}_{0.95}\text{Co}_{0.05}\text{WO}_4$, 2011.
- [52] J.-C. Joubert, W. B. White, and R. Roy, J. Appl. Crystallogr. **1**, 318 (1968).

- [53] F. Yen, B. Lorenz, Y. Y. Sun, C. W. Chu, L. N. Bezmaternykh, and A. N. Vasiliev, Phys. Rev. B **73**, 054435 (2006).
- [54] Y. Hinatsu, Y. Doi, K. Ito, M. Wakeshima, and A. Alemi, J. Solid State Chem. **172**, 438 (2003).
- [55] A. M. Kadomtseva, Y. F. Popov, G. P. Vorob'ev, A. P. Pyatakov, S. S. Krotov, K. I. Kamilov, V. Y. Ivanov, A. A. Mukhin, A. K. Zvezdin, A. M. Kuz'menko, L. N. Bezmaternykh, I. A. Gudim, and V. L. Temerov, Low Temp. Phys. **36**, 511 (2010).
- [56] R. P. Chaudhury, B. Lorenz, Y. Y. Sun, L. N. Bezmaternykh, V. L. Temerov, and C. W. Chu, J. Appl. Phys. **107**, 09D913 (2010).
- [57] D. Neogy, K. N. Chattopadhyay, P. K. Chakrabarti, H. Sen, and B. M. Wanklyn, J. Mag. Mag. Mater. **154**, 127 (1996).
- [58] T. Kimura, G. Lawes, T. Goto, Y. Tokura, and A. P. Ramirez, Phys. Rev. B **71**, 224425 (2005).
- [59] L. N. Bezmaternykh, private communication on the twinning structure observed $\text{Ho}_{0.5}\text{Tm}_{0.5}\text{Al}_3(\text{BO}_3)_4$.
- [60] R. P. Chaudhury, B. Lorenz, Y. Y. Sun, L. N. Bezmaternykh, V. L. Temerov, and C. W. Chu, Phys. Rev. B **81**, 220402(R) (2010).
- [61] K.-C. Liang, R. P. Chaudhury, B. Lorenz, Y. Y. Sun, L. N. Bezmaternykh, V. L. Temerov, and C. W. Chu, Phys. Rev. B **83**, 180417(R) (2011).
- [62] D. Riou, N. Nguyen, R. Benloucif, and B. Raveau, Mat. Res. Bull. **25**, 1363 (1990).
- [63] G. Rousse, J. Rodriguez-Carvajal, C. Wurm, and C. Masquelier, Solid State Sciences **4**, 973 (2002).
- [64] M.-H. Whangbo, H.-J. Koo, and D. Dai, Journal of Solid State Chemistry **176**, 417 (2003).
- [65] H. Bih, I. Saadoune, H. Ehrenberg, and H. Fuess, Journal of Solid State Chemistry **182**, 821 (2009).
- [66] R. C. Mercader, L. Terminiello, G. J. Long, D. G. Reichel, K. Dickhaus, R. Zysler, R. Sanchez, and M. Tovar, PRB **42**, 25 (1990).
- [67] G. Vītiņš, Z. Kaņepe, A. Vītiņš, J. Ronis, A. Dindūne, and A. Lūsis, J. Solid State Electrochem. **4**, 146 (2000).
- [68] S.-K. Ma, *Modern Theory of Critical Phenomena*, W. A. Benjamin, Inc., 1976.