The Suppression and Recovery of the Ferroelectric Phase in Multiferroic $\text{MnWO}_4$

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We report the discovery of a complete suppression of ferroelectricity in $\text{MnWO}_4$ by 10% iron substitution and its restoration in external magnetic fields. The spontaneous polarization in $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{WO}_4$ arises below 12 K in external fields above 4 T. The magnetic/ferroelectric phase diagram is constructed from the anomalies of the dielectric constant, polarization, magnetization, and heat capacity. The observations are qualitatively described by a mean field model with competing interactions and strong anisotropy. We propose that the magnetic field induces a non-collinear inversion symmetry breaking magnetic structure in $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{WO}_4$.

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I. INTRODUCTION

Multiferroic materials in which ferroelectric (FE) and magnetic orders coexist and mutually interact have recently attracted attention because of many novel physical phenomena observed in these compounds as well as their potential for applications as magnetoelectric sensors or memory chips. Common features and magnetoelectric properties of compounds with quite different chemical compositions and structures indicate a universal physical mechanism behind the multiferroic phenomena of a large materials class. It was shown that a non-collinear (or helical) spin density wave can break the spatial inversion symmetry and, with sufficiently strong spin-lattice coupling, can result in a lattice distortion with a FE polarization. The helical magnetic order was in fact observed in the FE phases of $\text{TbMnO}_3$, $\text{Ni}_3\text{V}_2\text{O}_8$, $\text{MnWO}_4$, and others. Most multiferroics exhibit highly frustrated magnetic orders due to geometric constraints or competing interactions. Local lattice distortions can therefore release the magnetic frustration, lower the magnetic energy, and induce local electrical dipoles that may add up to a macroscopic polarization if permitted by symmetry. In frustrated magnetic systems several magnetic states are close in energy and compete for the ground state. As a result, in multiferroics the FE polarization, which is induced by magnetic order, is easily controlled by small perturbations affecting the microscopic exchange constants or the magnetic order. For example, is was shown that magnetic fields and external pressure have a significant effect on the ferroelectric polarization and the multiferroic properties.

The multiferroic $\text{MnWO}_4$ passes through three magnetic transitions upon decreasing temperature $T$. The sinusoidal AF3 phase ($12.6 \, K < T < 13.5 \, K$) is followed by a non-collinear helical spin phase AF2 ($7.8 \, K < T < 12.6 \, K$), both phases with an incommensurate (IC) modulation vector $q_{\text{AF2}} = (-0.214, 1/2, 0.457)$. The AF1 phase below 7.8 K is collinear ($q_{\text{AF1}} = (1/4, 1/2, 0/2)$) and shows the typical $\uparrow\uparrow\downarrow\downarrow$ (E-type) spin pattern. Ferroelectricity was only observed in the helical AF2 phase, but Heyer et al. reported a finite value of the FE polarization also in the low temperature AF1 commensurate phase. However, our recent polarization measurements of $\text{MnWO}_4$ at ambient and high pressures are consistent with the paraelectric nature of the AF1 phase. Magnetic frustration due to competing exchange interactions and a strong uniaxial anisotropy lead to the sequence of complex magnetic structures. Tuning the magnetic exchange interactions appears to be imperative to arrive at a deeper understanding of the multiferroic properties of $\text{MnWO}_4$ and related compounds. The superexchange interactions depend on the type of magnetic ions, their interatomic distances and bond angles. The remarkable sensitivity of the FE and magnetic phases of multiferroic materials with respect to hydrostatic pressure was demonstrated for $\text{MnWO}_4$, $\text{Ni}_3\text{V}_2\text{O}_8$, and $\text{RMn}_2\text{O}_4$, proving the high susceptibility of multiferroics to small perturbations. Alternatively, magnetic exchange interactions can be controlled by replacing one kind of magnetic ions with other ions, either nonmagnetic or with different magnetic properties. In $\text{MnWO}_4$ the magnetic $\text{Mn}^{2+}$ ion with spin $S=5/2$ can easily be replaced by the $\text{Fe}^{2+}$ ion with a smaller magnetic moment ($S=2$) and different exchange and anisotropy constants. In an attempt to examine the detailed interplay between magnetic interactions and ferroelectricity we have therefore investigated the solid solution $\text{Mn}_{1-x}\text{Fe}_x\text{WO}_4$. We found that $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{WO}_4$ is paraelectric (PE) in zero magnetic field at all temperatures, however, ferroelectricity and multiferroic properties are induced by magnetic fields above 4 T.

II. METHODOLOGY

Polycrystalline $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{WO}_4$ was synthesized by solid state reaction at 930°C of the precursor compounds $\text{Mn}_2\text{O}_3$, $\text{WO}_3$, and $\text{Fe}_2\text{O}_3$, mixed in the appropriate ratios. Single crystals have been grown from the polycrystalline feed rod in a Floating Zone Furnace. X-ray analysis showed the monoclinic structure with lattice constants...
a=4.799(2) Å, b=5.736(2) Å, and c=4.980(2) Å, in good agreement with previous reports on natural and synthetic wolframites.17,18 The crystals have been characterized and oriented by single crystal Laue diffractometry. The homogeneity of the crystals and their Fe content were verified by wavelength dispersive spectroscopy analysis. Magnetic measurements were conducted in a superconducting quantum interference device (SQUID) in magnetic fields up to 5 T. For the dielectric constant and polarization measurements a home-made dielectric probe was adapted to the Physical Property Measurement System (PPMS) for temperature and magnetic field (H < 7 T) control. The crystals were shaped as thin parallel plates, the dielectric constant was calculated from the capacitance measured by the high-precision AH2500A capacitance bridge, and the polarization was determined by integrating the pyroelectric current measured by a K6517A electrometer. During the pyroelectric measurements a small poling electric field was applied in order to align domains in the ferroelectric state. The PPMS was also used for heat capacity measurements at temperatures above 1.8 K in different magnetic fields.

III. EXPERIMENTAL RESULTS

The low-field magnetization data are consistent with previous reports and they reveal two successive phase transitions at $T_N=15.4$ K and at $T_L=12$ K, respectively, in excellent agreement with the phase diagram of $Mn_{1-x}Fe_xWO_4$ for $x=0.1$ previously derived from neutron scattering experiments.17 According to the neutron data magnetic order sets in at $T_N$ with an IC modulation vector $q_1 = (-0.235, 1/2, 0.49)$, similar to the AF3 phase of pure $MnWO_4$. At $T_L$ the magnetic modulation locks into a commensurate order described by $q_1 = (±1/4, 1/2, 1/2)$ (AF1 phase of $MnWO_4$). The spins are oriented along the easy axis in the ac-plane at an angle of 35° with the a-axis.

A. Dielectric constant and polarization

In order to search for the signature of ferroelectricity we have performed measurements of the dielectric constant $\varepsilon(T)$ and the pyroelectric current along all three crystallographic orientations. In zero magnetic field, we did not find any indication of a FE transition, in contrast to the ferroelectricity observed in $MnWO_4$. Minute changes of slope of $\varepsilon(T, H = 0)$ near $T_N$ and $T_L$ are barely visible in the inset of Fig. 1. The replacement of 10 % $Mn$ by $Fe$ apparently leads to the complete loss of ferroelectricity and, presumably, the loss of the helical magnetic structure in the compound. This conclusion is supported by the results of neutron scattering experiments that did not show an intermediate phase between $T_N$ and $T_L$ in zero magnetic field.

In external magnetic fields, $H_e$, oriented along the magnetic easy axis, however, new anomalies in the dielectric properties, measured along the monoclinic b-axis, could be observed. In the following we discuss dielectric and polarization data measured along the b-axis in external fields $H_e$. With increasing magnetic field a distinct peak of $\varepsilon(T)$ develops near the lock-in transition temperature, $T_L$. The peak appears for fields exceeding about 4 T and increases with $H_e$ (inset of Fig. 1). The pyroelectric current also exhibits a sharp peak indicating the onset of FE order at $T_L$. The results for the polarization $P(T)$ at different magnetic fields are shown in Fig. 1. At 4.5 T, close to $T_L$, $P(T)$ is small but it increases significantly at about 6 K indicating a major change within the ferroelectric phase from a low-polarization (LP) to a high-polarization (HP) state. Similar transitions within the ferroelectric phase have been observed in other multiferroic compounds and are sometimes attributed to spin re-orientations associated with a change of the FE polarization. The $P(T)$ data also reveal a large temperature hysteresis as shown for $H_e=5.5$ T in Fig. 1. With increasing magnetic field $P(T)$ increases quickly and at 7 T the FE polarization increases continuously from $T_L$ towards lower $T$. From the $\varepsilon(T)$- and $P(T)$-data shown in Fig. 1 we conclude that $Mn_{0.9}Fe_{0.1}WO_4$ is paraelectric at zero magnetic field but ferroelectricity is induced by fields above 4 T.

In order to further study the field-induced FE phase we have conducted field-dependent isothermal polarization measurements. The results (Fig. 2) unambiguously prove the ferroelectricity arising above a critical magnetic field. The transition into the FE phase exhibits a field hysteresis of more than 0.5 T (inset of Fig. 2) confirming the first-order nature of this phase transition. $P(H)$ shows a characteristic kink which is consistent with the sudden increase of $P(T)$ from the LP to the HP state, as discussed above. The origin of this distinct feature is not clear and has yet to be investigated. From these data a field-temperature phase diagram for $Mn_{0.9}Fe_{0.1}WO_4$ is constructed and shown in Fig. 3 (the hysteresis across the ferroelectric transition is shown as the dashed area). The field dependence of the Neél temperature ($T_N$) and the lock-in temperature ($T_L$) are derived from magnetic and heat capacity measurements (discussed below). Both temperatures decrease slightly with $H_e$ as expected for an AFM state. At low fields, $T_N$ and $T_L$ define the transitions $PM/PE → AF3/PE → AF1/PE$. The field-induced FE phase is labeled as AF2/FE.

B. Magnetic properties

The ferroelectricity in most multiferroic compounds is strongly coupled to the magnetic order. Therefore, any change of the dielectric state should also be detected as anomalies of the magnetic properties. The magnetization measurements of $Mn_{0.9}Fe_{0.1}WO_4$ shown in Fig. 4 indeed reflect the major phase transitions observed in dielectric and polarization measurements. At the Neél
temperature $M(T)$ exhibits the characteristic maximum with the onset of IC AFM order. $M(T)$ shows a
subtle change with a temperature hysteresis of about 2 K at $T_L$. This hysteresis indicates the first order nature of
the lock-in transition. In high magnetic fields and at
low temperature $M(T)$ reveals another distinct anomaly
with a wide hysteresis similar to the polarization data
shown in Fig. 1. The change of the magnetic order at
the high-field FE transition is also detected in the $M(H)$
measurements (inset of Fig. 4). The sharp increase of
$M(H)$ above 4 T and the observed hysteresis suggests
that the magnetic order undergoes a major modification.
Note that the maximum field of the magnetometer (5 T)
is not enough to complete the transition into the high-
field phase, however, the critical fields and temperatures
derived from the decreasing field cycle (triangles in Fig.
3) agree well with the similar data from the $P(H)$ mea-
measurements (squares in Fig. 3). We conclude that the
magnetic field along the easy axis induces a new mag-
netic order that breaks the spatial inversion symmetry
and is compatible with the FE order. Any other direc-
tion of the magnetic field was found to be less or not at
all efficient in stabilizing the FE phase. We have also ex-
tended the pyroelectric measurements along the a- and
e-axes at zero and high magnetic fields but we did not
find any signature of FE order along these orientations.

C. Heat capacity

The thermodynamic signature of transitions between
different phases or orders is usually detected in distinct
anomalies of the heat capacity, $C_p(T)$. Multiferroic ma-
terials with a sequence of subsequent transitions may show
more or less pronounced sudden changes of $C_p$, some can
be subtle and difficult to detect. Fig. 5 shows the heat
capacity data, $C_p/T$, for $Mn_{0.9}Fe_{0.1}WO_4$ in different ex-
ternal magnetic fields $H_e$. For $H_e=0$ a sharp increase of
$C_p(T)$ at $T_N$ indicates the onset of the IC sinusoidal
order. At the lock-in transition $C_p$ exhibits a sharp peak
which is difficult to resolve in detail because of the strong
first order nature of this transition. No significant field
dependence of $C_p/T$ is noted up to 3 T. The only change
in this low-field range is a small shift of the step-like in-
crease at $T_N$ and the peak at $T_L$ towards lower $T$. At
higher magnetic fields, however, $C_p/T$ shows a well re-
solved enhancement below the critical temperature of the
ferroelectric order (indicated by dashed arrows in Fig. 5).
This anomaly quickly shifts to higher $T$ with increasing
$H_e$ and it merges with the lock-in temperature, $T_L$, at
the highest field (7 T in Fig. 5). The enhanced heat
capacity is a clear thermodynamic signature of the fer-
roelectric order in the AF2/FE phase and it proves the bulk
nature of the FE high-field phase.

IV. MODEL CALCULATIONS

Ferroelectricity induced by a magnetic field is a rare
phenomenon and it shows the sensitivity of the frustrated
magnetic system towards small perturbations. A simple
model describing the different magnetic structures (com-
mensurate $q = 1/4$ at $T = 0$, IC helical and sinusoidal
orders at $T > 0$) has to include the competing exchange
interactions, the magnetic anisotropy, and the external
field ($\vec{H}$). It should be noted that the spin order in the
low-temperature commensurate phase of $MnWO_4$ can
be represented by a stack of spin chains in the ac plane
with equal spin values within each chain but a fourfold
modulation ($q = 1/4$) of moments perpendicular to the
chains. The order of spin chains is then described by the
characteristic $\uparrow\uparrow\downarrow\downarrow$ (E-type) modulation. Within a sim-
plicated description we can describe the major features of
the magnetic order by a mean field model of spin chains
stacked along one dimension with effective exchange cou-
pling and anisotropy parameters.

The Heisenberg model with competing nearest ($J_1$)
and next nearest neighbor interactions ($J_2$) and spin
anisotropy ($K$) interpolates between the helical ground
state (isotropic model) and the E-type ($\uparrow\uparrow\downarrow\downarrow$) modula-
tion for strong uniaxial anisotropy (Ising limit). A simi-
lar model has been employed to describe qualitatively the
magnetic phase sequence in $\text{Ni}_2\text{V}_2\text{O}_8$. For simplicity we
consider the $S=1$ model with the easy axis of magnetiza-
tion along the z-direction

$$
H = J_1 \sum S_n \vec{S}_{n+1} + J_2 \sum S_n \vec{S}_{n+2} - K \sum (S_n^z)^2 - \vec{H} \sum \vec{S}_n
$$

which includes the most basic parameters and inter-
actions to describe the various spin orders in $\text{Mn}_{1-x}\text{Fe}_x\text{WO}_4$ and other multiferroics. Neutron scat-
tering experiments on $\text{MnWO}_4$ suggest a competition
between ferromagnetic (FM, $J_1 < 0$) and AFM ($J_2 > 0$)
exchange interactions and a strong uniaxial anisotropy
($K > 0$) favoring the spin orientation along the easy axis
in the ac-plane. The model (1) is solved in the mean
field approximation. In this approximation the two-spin
interaction is replaced by a single spin term in an effec-
tive field of the neighboring spins that is proportional to
the corresponding exchange coupling constants and the
thermal average of the spins at nearest or next-nearest
neighbor sites. The thermodynamic average of all spins
is then calculated selfconsistently from a set of $N$ coupled
equations, with $N$ being the total number of spins along
the chain. For simple commensurate spin orders the set
of $N$ equations can be reduced to a smaller number of
equations assuming translational symmetry of the aver-
age spin values according to the specific order. For ex-
ample, for a two-sublattice antiferromagnetic order the self-
consistency equations are reduced to two coupled equa-
tions, one for each sublattice. However, in the case of
arbitrary (commensurate or incommensurate) magnetic
orders no assumption about the periodicity of the magnetic order can be made and a large set of N coupled equations has to be considered. We solve the mean-field equations for finite lattices of up to 100 spins assuming periodic boundary conditions. The solution of the mean-field equations for a given set of parameters \((K, J_1, J_2, T, \text{ or magnetic field})\) without any initial constraints on the magnetic order reproduces the different magnetic structures observed in \(Mn_{1-x}Fe_xWO_4\) and \(MnWO_4\), E-type and sinusoidal (IC) collinear as well as IC helical spin modulations. Wherever more than one type of order was obtained selfconsistently from the equations the solution with the lower free energy was determined as the stable magnetic configuration.

The ground state phase diagram of (1) for zero field is shown in Fig. 6. At \(K = 0\) the ground state is FM for \(J_2/|J_1| < 1/4\) and it assumes the non-collinear (NC) incommensurate spin structure for larger \(J_2\). For large \(K\) the Ising limit is reproduced and the transition from FM to the collinear E-type magnetic order takes place at \(J_2/|J_1| = 1/2\) as in the ANNNI model.\(^2\) The E-type phase is stable for larger \(J_2\) and \(K\) and the NC helical phase covers the left section of the ground state phase diagram. For \(J_2/|J_1| \approx 1/2\) the helical spin component perpendicular to the easy axis rapidly decreases with increasing \(K\) and it disappears at the transition into the collinear sinusoidal structure close to \(K/|J_1| \approx 1.25\) (vertically dashed area in Fig. 6). The horizontally dashed area in Fig. 6 marks the region of special interest. Within this area the NC helical spin order appears at finite temperatures between the E-type ground-state and the sinusoidal phase. This phase sequence is typical for \(MnWO_4\).

With increasing \(K\), however, the helical phase becomes unstable at all \(T\) and, with increasing temperature, the transition proceeds directly from the E-type state to the sinusoidal phase, as observed for \(Mn_{0.9}Fe_{0.1}WO_4\). The lack of ferroelectricity (at zero field) in \(Mn_{0.9}Fe_{0.1}WO_4\) is therefore explained by the increase of the uniaxial anisotropy \(K\). Evidence for the increase of \(K\) with \(Fe\)-substitution was also derived from the results of neutron scattering experiments.\(^18\) The chosen set of parameters, \(J_2 \approx |J_1|\), results in a spin modulation in the IC phase, \(Q_{SIN} = 0.21\), that is comparable with the experimental results.\(^14\)\(^-\)\(^20\)

In order to understand the magnetic field induced ferroelectricity in \(Mn_{0.9}Fe_{0.1}WO_4\) we have to consider the model (1) in fields oriented along the easy axis (\(z\)-axis) and search for NC (helical) spin structures. The solution of (1) in the mean field approximation for parameters \(J_1 = -1, J_2 = 1, K = 1.05\), and \(H = (0, 0, H^z)\) indeed reveals a magnetic field induced transition from the E-type order to a NC helical phase at low temperatures. The \(H^z - T\) phase diagram for this case is shown in Fig. 7a. At zero magnetic field the phase sequence with increasing \(T\) is E-type \(\Rightarrow\) SIN \(\Rightarrow\) PM but above a critical field the helical spin structure is stabilized as an intermediate phase. The helical and the sinusoidal phases are incommensurate with a modulation comparable to the experimental results. It is remarkable that the simple model (1) describes the main physical effects of the Fe-substitution, namely: (i) the loss of the FE (helical) phase with the increase of the anisotropy (Fe-substitution) and (ii) the re-appearance of this phase above a critical magnetic field oriented along the easy axis of magnetization. For lower anisotropy \((K = 0.8)\) the known magnetic phase diagram for \(MnWO_4\) is qualitatively reproduced, as shown in Fig. 7b. Note that the sinusoidal spin order is also suppressed by \(H^z\) in agreement with the experimental results for \(MnWO_4\).

The phase transitions from the E-type to sinusoidal and helical phases (Fig. 7) are first order transitions whereas a second order transition takes place from the sinusoidal to the paramagnetic phase, in accordance with our experimental results discussed above.

V. SUMMARY AND CONCLUSIONS

We have shown that the ferroelectric and helical magnetic orders in \(MnWO_4\) are easily suppressed by replacing only 10% of the magnetic \(Mn^{2+}\) ion by another magnetic ion, \(Fe^{2+}\). The ferroelectric state is restored in external magnetic fields applied along the easy axis of the spins. We have resolved the field-temperature phase diagram for \(Mn_{0.9}Fe_{0.1}WO_4\) showing three distinct magnetic and/or ferroelectric phases. The experimental observations are explained by a mean field solution of the Heisenberg model with competing interactions, uniaxial anisotropy, and external magnetic field. The destruction of the ferroelectric/helical phase is due to an increase of the uniaxial anisotropy with the iron substitution. The calculated phase diagrams describe the experimental results for \(Mn_{0.9}Fe_{0.1}WO_4\) and \(MnWO_4\) qualitatively well. While the model is too simple to allow for any quantitative comparison with the experiments it includes the major physical interactions to describe qualitatively the different magnetic phases in \(MnWO_4\) and \(Mn_{0.9}Fe_{0.1}WO_4\). Improvements of the model description should include the 3d lattice structure and spin order, the differences in the exchange coupling constants between Mn- and Fe-ions, and the effects of disorder. The results of our simple model calculation should also be relevant to other multiferroic materials such as \(CuFeO_2\) where magnetic field induced ferroelectricity has been observed very recently.\(^23\)\(^-\)\(^24\) Our experimental results and calculations for \(Mn_{0.9}Fe_{0.1}WO_4\) suggest that with increasing magnetic field the collinear E-type spin modulation turns into a helical IC magnetic order breaking the spatial inversion symmetry which allows for the observed ferroelectricity. This transition could be verified by high-field neutron scattering experiments. It is expected that these experiments also reveal additional details of the magnetic orders within the FE phase as observed by us in \(Mn_{0.9}Fe_{0.1}WO_4\). Large single crystals are currently being grown for further investigations.
Acknowledgments

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1 N. A. Spaldin and M. Fiebig, Science 309, 391 (2005).
2 Y. Tokura, J. Mag. Mag. Mat. 310, 1145 (2007).
3 M. Mostovoy, Phys. Rev. Lett. 96, 067601 (2006).
4 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).
5 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).
6 K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa, and T. Arima, Phys. Rev. Lett. 97, 097203 (2006).
7 C. R. dela Cruz, F. Yen, B. Lorenz, M. M. Gospodinov, C. W. Chu, W. Ratcliff, J. W. Lynn, S. Park, and S.-W. Cheong, Phys. Rev. B 73, 100406(R) (2006).
8 D. Higashiyama, S. Miyasaka, N. Kida, T. Arima, and Y. Tokura, Phys. Rev. B 70, 174405 (2004).
9 N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, Nature (London) 429, 392 (2004).
10 C. R. dela Cruz, B. Lorenz, Y. Y. Sun, C. W. Chu, S. Park, and S.-W. Cheong, Phys. Rev. B 74, 180402(R) (2006).
11 R. P. Chaudhury, F. Yen, C. R. dela Cruz, B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, Phys. Rev. B 75, 012407 (2007).
12 C. R. dela Cruz, B. Lorenz, Y. Y. Sun, Y. Wang, S. Park, S.-W. Cheong, M. M. Gospodinov, and C. W. Chu, Phys. Rev. B 76, 174106 (2007).
13 R. P. Chaudhury, F. Yen, C. R. dela Cruz, B. Lorenz, Y. Q. Wang, Y. Y. Sun, and C. W. Chu, preprint cond-mat/0705.4675, unpublished.
14 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. B 74, 014429 (2006).
15 R. Guillen and J. R. Regnard, Phys. Chem. Minerals 12, 246 (1985).
16 E. Garcia-Matres, N. Stüßer, M. Hofmann, and M. Reehuis, Eur. Phys. J. B 32, 35 (2003).
17 M. Kenzelmann, A. B. Harris, A. Aharony, O. Entin-Wohlman, T. Yildirim, Q. Huang, S. Park, G. Lawes, C. Broholm, N. Rogado, R. J. Cava, K. H. Kim, G. Jorge, and A. P. Ramirez, Phys. Rev. B 74, 014429 (2006).
18 N. Stüßer, Y. Ding, M. Hofmann, M. Reehuis, B. Oulad-dia, G. Ehlers, D. Günther, M. Meißner, and M. Steiner, J. Phys.: Condens. Matter 13, 2753 (2001).
19 T. Nagamiya, Solid State Physics 20, 305 (1967).
20 P. Bak, Rep. Prog. Phys. 45, 587 (1982).
21 T. Kimura, J. C. Lashley, and A. P. Ramirez, Phys. Rev. B 73, 220401(R) (2006).
22 S. Kanetsuki, S. Mitsuda, T. Nakajima, D. Anazawa, H. A. Katori, and K. Prokes, J. Phys.: Condens. Matter 19, 145244 (2007).
FIG. 1: (Color online) Polarization $P(T)$ of $Mn_{0.9}Fe_{0.1}WO_4$ in different fields above 4 T (cooling data included at 5.5 T as dashed line, all other data are shown for increasing $T$). Inset: $\varepsilon(T)$ at fields from 0 to 7 T (curves are vertically offset).

FIG. 2: (Color online) Isothermal field dependence of the FE polarization (data shown for decreasing field only). Inset: 5 K data with increasing an decreasing field.

FIG. 3: (Color online) Magnetic phase diagram of $Mn_{0.9}Fe_{0.1}WO_4$ with H along the easy axis. The FE phase is labeled AF2/FE. Data are from polarization (squares) and magnetization (triangles) measurements. $T_{FE}$ was determined from $P(H)$ and $M(H)$. The shaded area indicates the field hysteresis of the FE transition.

FIG. 4: (Color online) High-field magnetization $M$ of $Mn_{0.9}Fe_{0.1}WO_4$. The loop at low $T$ indicates the transition into the AF2/HP phase. Inset: $M(H_e)$ at different temperatures (data for $T < 5$ K are vertically shifted).

FIG. 5: (Color online) Heat capacity $C_p/T$ of $M$ of $Mn_{0.9}Fe_{0.1}WO_4$ at zero and high magnetic fields (field along the easy axis). The dashed vertical arrows point to the anomaly associated with the ferroelectric transition at 5, 6, and 7 T, respectively (left to right).

FIG. 6: (Color online) Ground state phase diagram of the model (1) in mean field approximation.

FIG. 7: Field-Temperature phase diagrams for model parameters qualitatively describing the phase sequence in (a) $Mn_{0.9}Fe_{0.1}WO_4$ and (b) $MnWO_4$. 
$T = 5 \text{ K}$

$P \text{ (}\mu\text{C/m}^2\text{)}$ vs $H_e \text{ (T)}$

Inset: $T = 5 \text{ K}$

Graphs for $5 \text{ K}$ to $10 \text{ K}$
E-Type helix at $T>0$

$J_2$ / $|J_1|$

$K / |J_1|$
Figure (a) shows a plot of $H_z/J_1$ against $T/J_1$ for helix states with $K/|J_1| = 1.05$. The plot includes data points for E-type, SIN, and PM states. Figure (b) displays a similar plot for $K/|J_1| = 0.8$. The helix states are denoted by a specific pattern on the graph.