Re-entrant ferroelectricity and the multiferroic phase diagram of Mn$_{1-x}$Fe$_x$WO$_4$

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**Abstract.** We report the discovery of re-entrant ferroelectricity in the phase diagram of multiferroic Fe-substituted MnWO$_4$. At zero magnetic field ($H$) the spin-spiral ferroelectric (FE) state is completely suppressed at Fe substitutions ($x$) exceeding 0.04. For $x < 0.04$ a zero-field ferroelectric phase exists in a narrow temperature ($T$) range. This phase shows a re-entrant behavior at lower $T$ above a critical magnetic field. The re-entrant FE transition is explored by polarization, dielectric constant, and magnetization measurements. The complete multiferroic $x$–$T$–$H$ phase diagram of Mn$_{1-x}$Fe$_x$WO$_4$ is derived.

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1. Introduction

Multiferroic magnetoelectric compounds have experienced a revival of interest in recent years because of novel physical effects emerging from the coexistence and mutual interaction of ferroelectric and magnetic orders and their potential for applications as magnetoelectric sensors or memory chips [1]–[3]. Different physical mechanisms and interactions may lead to multiferroic properties. One prominent example is the improper ferroelectricity induced by helical magnetic orders. The ferroelectric (FE) polarization can arise from the redistribution of electron densities in their corresponding orbitals mediated by the Dzyaloshinskii–Moriya antisymmetric interaction [4], from ionic displacements due to strong spin–lattice interactions [2], or from both electronic and ionic contributions [5]. Symmetry arguments support the microscopic picture of ferroelectricity induced by an inversion symmetry breaking helical spin modulation [6]. Helical magnetic orders have indeed been observed in the FE phases of TbMnO$_3$ [7], Ni$_3$V$_2$O$_8$ [8], MnWO$_4$ [9] and others [10]. The magnetically ordered state in most multiferroics is highly frustrated due to geometric constraints or competing exchange interactions. This frustration gives rise to an extraordinary sensitivity of the multiferroic and FE states with respect to small perturbations in the form of external magnetic or electric fields [9], [11]–[13], pressure [14]–[17], or chemical substitutions [18, 19].

Three magnetic phases have been reported in multiferroic MnWO$_4$ [20]. Magnetic order sets in at 13.5 K with a sinusoidal (collinear) spin structure and an incommensurate (ICM) modulation, $\vec{q}_{ICM} = (-0.214, 1/2, 0.457)$ . In this AF3 phase, the Mn spins lie in the $a$–$c$ plane at an angle of $\sim 35^\circ$ to the $a$-axis. Below 12.6 K, in the AF2 phase, the spins tilt out of plane and develop a helical (transverse screw type) order with about the same ICM modulation vector, $\vec{q}_{ICM}$. Below 7.8 K (AF1 phase) the spins rotate back into the $a$–$c$ plane forming a commensurate (CM) $\uparrow \downarrow \uparrow \downarrow$ structure with $\vec{q}_{CM} = (\pm 1/4, 1/2, 1/2)$ . Ferroelectricity was observed exclusively in the helical AF2 phase. The magnetic phase diagram of MnWO$_4$ can qualitatively be described by a Heisenberg model with competing exchange interactions and uniaxial anisotropy [18]. Upon substituting Fe for Mn the magnetic phase boundaries change significantly and new magnetic phases appear for Fe contents larger than 0.125 [21]. The FE phase was completely suppressed by the substitution of only 10% Fe demonstrating the dramatic changes in the magnetic orders if exchange or anisotropy constants are tuned [18]. However, little is known about the stability and properties of multiferroic and ferroelectric phases in...
Figure 1. Single crystals of Mn$_{1-x}$Fe$_x$WO$_4$ grown by the floating zone optical furnace.

Single crystals of Mn$_{1-x}$Fe$_x$WO$_4$ between $x = 0$ and 0.1. We have therefore grown and investigated single crystals of Mn$_{1-x}$Fe$_x$WO$_4$ with $x = 0.02$, 0.035 and 0.05. The temperature range in which the zero-field FE phase is stable quickly decreases with increasing $x$. At $H > 0$ a low-$T$ re-entrant FE phase is discovered and the coexistence of the AF2 and AF1 phases in a broad region of the $H$–$T$ phase diagram is observed.

2. Synthesis and experimental

Single crystals of Mn$_{1-x}$Fe$_x$WO$_4$ ($x = 0.02$, 0.035, 0.05) were grown in a floating zone optical furnace. Powder x-ray spectra acquired of the starting polycrystalline feed rod showed a single-phase structure of the WMnO$_4$ type. The elemental composition of the single crystals was characterized by wavelength dispersive microprobe analysis and found to be close to the nominal $x$-values. Two examples of crystals with $x = 0.035$ and 0.05 are shown in figure 1. Magnetic, dielectric and polarization measurements have been conducted in magnetic fields up to 7 T using a superconducting quantum interference device (SQUID) magnetometer and a physical property measurement system with external electronics (the AH2500A capacitance bridge for dielectric constant and the K6517A electrometer for polarization measurements via the pyroelectric current method). The crystals were oriented by single-crystal Laue diffractometry, the dielectric and FE properties were measured along the $b$-axis and the magnetic field was oriented along the easy axis in the $a$–$c$ plane.

3. Results and discussion

3.1. Zero-field phase diagram

At zero magnetic field the FE (spin-spiral) AF2 phase is quickly suppressed with increasing Fe substitution. The phase diagram is shown in figure 2. Even at substitution levels as small as $x = 0.05$ no FE phase could be detected. The extrapolated critical concentration, above which
the ferroelectric AF2 phase no longer exists, is $x_c \approx 0.04$. The phase diagram of figure 2 clearly shows that it is mainly the CM $\uparrow\uparrow\downarrow\downarrow$ (AF1) phase that grows at the expense of the spiral phase. The stabilization of the CM phase could be qualitatively explained by a substitution-induced modification of the average exchange coupling and anisotropy parameters [18].

### 3.2. Ferroelectric polarization in magnetic fields

In external magnetic fields, oriented along the spin easy axis, the ferroelectric phase expands its stability range. This is clearly seen in the FE polarization data for Mn$_{0.98}$Fe$_{0.02}$WO$_4$ ($x = 0.02$) shown in figure 3(a). At low fields, $H < 3$ tesla, the phase sequence upon cooling passes from paramagnetic to AF3 (sinusoidal ICM) at $T_N \approx 14$ K and from AF3 to AF2 (helical/FE) at $T_{C1} \approx 12.3$ K. At lower $T$ the paraelectric $\uparrow\uparrow\downarrow\downarrow$ (AF1) phase becomes stable with $T_{C2}$ decreasing from 9.7 to 7.8 K if $H$ increases from 0 to 3 tesla. In magnetic fields above 3 tesla, however, a low-temperature ferroelectric phase emerges below 5 K indicating an interesting re-entrant FE phase behavior, as shown in figure 3(a). The low-$T$ polarization increases with $H$ and saturates above 4 tesla. Up to 3.15 tesla the intermediate AF1 phase is truly paraelectric ($P = 0$) but a finite polarization quickly increases with $H$ between 3.15 and 4 tesla. At higher magnetic fields, $H > 4$ tesla, $P(T)$ increases continuously with decreasing $T$ and its field dependence becomes small. In a narrow field range, between 3.2 and 3.8 tesla, the paraelectric ($\uparrow\uparrow\downarrow\downarrow$) and ferroelectric (spin-spiral) phases coexist at low temperatures. This explains the valley-like $T$-dependence of $P(T)$ around 5 K and the smaller (as compared to the 4 tesla data) values of $P$ at the lowest temperature. The phase coexistence is consistent with the first order nature of the field-induced transition from the AF1 phase to the ferroelectric AF2 phase. This is supported by a sizable temperature and field hysteresis of $P(T, H)$ that is observed in crossing
Figure 3. Ferroelectric polarization $P(T)$ of (a) $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{WO}_4$ and (b) $\text{Mn}_{0.95}\text{Fe}_{0.05}\text{WO}_4$ at different magnetic fields (labels next to the curves denote the field in tesla). The insets show the field dependence $P(H)$ at different temperatures.

3.3. Field–temperature phase diagram for $x = 0.02$ and 0.05

The phase diagram for $x = 0.02$ (figure 4(a)) reveals several interesting features: (i) the $\uparrow\uparrow\downarrow\downarrow$ AF1 phase is quickly suppressed by the field and exhibits a pronounced maximum near 6 K. This maximum explains the re-entrant behavior of the ferroelectric phase that is observed as a function of temperature in a narrow field range (figure 3(a)). (ii) The specifics of the phase diagram indicates that the re-entrant high-field FE phase is the same phase as the AF2 phase that is stable between 9.7 and 12.3 K at zero magnetic field, i.e. the magnetic structure is supposed
Figure 4. Magnetic and ferroelectric phase diagrams of (a) Mn$_{0.98}$Fe$_{0.02}$WO$_4$ and (b) Mn$_{0.95}$Fe$_{0.05}$WO$_4$. The dashed area marks the FE spin-spiral phase. The cross-dashed area denotes the hysteresis region between the AF1 and AF2 phases.

to be the incommensurate spin-spiral phase. However, the latter conclusion has to be verified by detailed neutron scattering experiments under high magnetic fields. (iii) The sizable hysteresis at the transition from the paraelectric AF1 to the FE AF2 phase shows that this transition is of first order nature which may explain the coexistence of the two CM and ICM phases in a narrow field–temperature range.

We have conducted an identical investigation for a single crystal of Mn$_{0.965}$Fe$_{0.035}$WO$_4$ ($x = 0.035$). The results of the polarization measurements are very similar to the $x = 0.02$ data with shifts of the critical fields and temperatures where the sample exhibits the re-entrant FE phase behavior. The phase diagram is similar to figure 4(a) with a slight enlargement of the ↑↑↓↓ AF1 phase. At $H = 0$ the FE transition temperature shows only a small change, $T_{c1} = 12.1$ K, but the critical temperature of the AF1 phase increases from 7.8 K ($x = 0$) to 10.6 K ($x = 0.035$, figure 2). In magnetic fields the maximum of the AF1 phase boundary shifts to 7 K and it extends to about 4.3 tesla in the field–temperature phase diagram.

Above the critical value of $x_c \simeq 0.04$ the ferroelectric AF2 phase is completely missing at $H = 0$. However, for $x = 0.1$ the magnetic field was shown to induce the FE phase for high enough field values [18]. In order to investigate the transition across the tricritical point at $x_c$ in detail we have conducted polarization measurements for Mn$_{0.95}$Fe$_{0.05}$WO$_4$ ($x = 0.05$). The $P(T)$ data shown in figure 3(b) clearly confirm the $H$-induced FE state if the magnetic field exceeds 4 tesla. The re-entrant phase property is also observed although not as pronounced as in the $x = 0.02$ data of figure 3(a). The peak-like $P(T)$ at 5 tesla near 11 K clearly indicates the existence of ferroelectricity in a narrow $T$ range and the rise of $P(T)$ near 5 K proves the re-entrant behavior of this FE phase. However, it should be noted that a small polarization exists between 5 and 10 K which is due to the coexistence of both phases, the paraelectric ↑↑↓↓ phase and the FE spin-spiral phase. With increasing field the weight shifts toward the FE phase and above 6.5 tesla the pure FE phase is stabilized below 11.5 K. The phase diagram derived from polarization and magnetic data is shown in figure 4(b). It is interesting to note
that the maximum of the AF1–AF2 phase boundary becomes sharper and is shifted to larger temperatures, \( T = 9 \text{ K} \). At the higher Fe substitution level, \( x = 0.1 \), this maximum moves too close to the AF1–AF3 phase boundary and the re-entrant ferroelectric behavior could not be resolved in our previous work on Mn\(_{0.9}\)Fe\(_{0.1}\)WO\(_4\) [18]. The conclusion of a field-induced transition from the CM AF1 phase to the ICM AF2 phase is supported by the results of recent neutron scattering experiments [22] where a clear change of the magnetic modulation vector with increasing field was observed. However, these experiments did not distinguish between the collinear (sinusoidal) and non-collinear (helical) spin orders and, therefore, could not separate the ferroelectric AF2 and paraelectric AF3 phases as in the present pyroelectric current measurements.

From the temperature and field dependent polarization measurements it becomes obvious that the ground state value of the FE polarization, \( P_0 = P(T = 0) \), of the spin-spiral phase is only uncovered in high magnetic fields. At zero-field \( P(T) \) is cut off at lower \( T \) by the transition into the commensurate \( \uparrow \uparrow \downarrow \downarrow \) phase. Even in non-substituted MnWO\(_4\) the maximum polarization at \( H = 0 \), \( P_{\text{max}} = 57 \mu \text{C m}^{-2} \) is further enhanced in magnetic fields and approaches the ground state value of \( P_0 \approx 70 \mu \text{C m}^{-2} \) at 3 tesla [23]. The relative increase of the maximum \( P \) is even larger in the Fe-substituted compounds where \( P_0 \) in high magnetic fields is enhanced with respect to \( P_{\text{max}} \) at zero field by a factor of 2 and 10 for \( x = 0.02 \) and 0.035, respectively. The absolute value of the high-field \( P_0 \), however, decreases with increasing \( x \) and is expected to vanish at a higher Fe substitution (note that even for \( x = 0.1 \), \( P_0 \) is still as large as 22 \( \mu \text{C m}^{-2} \) [18]). Whether the field-induced ferroelectric phase is completely suppressed at a critical substitution level is a matter for further investigations. According to the magnetic phase diagram derived from neutron scattering experiments [21] the \( \uparrow \uparrow \downarrow \downarrow \) phase extends to \( x \approx 0.22 \) with a maximum stability range near \( x = 0.12 \). According to simple arguments derived from a mean field model [18] one might suspect that the magnetic field can introduce the FE spin-spiral phase for even larger \( x \) values up to 0.22 which has to be confirmed by future experiments. It should be noted that all phase boundaries shown in figures 2 and 4 are accompanied by distinct anomalies of the dielectric constant and that the phase diagrams derived from these anomalies are consistent with the data derived from the polarization and magnetic measurements.

3.4. Magnetization studies

In MnWO\(_4\), and the corresponding Fe-substituted compounds the FE polarization is supposedly associated with the inversion symmetry breaking helical magnetic order. Magnetization (\( M \)) measurements are therefore of interest to correlate the magnetic and ferroelectric phase transitions. The temperature dependence of \( M \) for Mn\(_{0.99}\)Fe\(_{0.02}\)WO\(_4\) and Mn\(_{0.95}\)Fe\(_{0.05}\)WO\(_4\) at different magnetic fields is shown in figures 5 and 6, respectively. Upon decreasing temperature the onset of the incommensurate collinear (sinusoidal) magnetic order is clearly revealed as a drop of the \( b \)-axis magnetization at \( T_N \). However, the transition from the AF3 into the FE AF2 phase is not accompanied by a significant anomaly in \( M(T) \). This is consistent with the magnetic data for MnWO\(_4\) [23]. The sequence of phase transitions AF3 \( \rightarrow \) AF2 \( \rightarrow \) AF1 can be described by a mean-field anisotropic Heisenberg model with competing exchange interactions [18]. According to the solution of this model the AF3 \( \rightarrow \) AF2 transition is second order and the magnetization changes smoothly, the major effect being the \( b \)-axis component of \( M \) arising continuously in the spin-spiral phase. Since the modulation vector of the magnetic order is the same in both phases there appears to be no significant anomaly of \( M(T) \) at this transition. At
the lock-in transition into the \(\uparrow\uparrow\downarrow\downarrow\) AF1 phase, however, a clear drop of \(M(T)\) is detected at \(T_L\) with a small temperature hysteresis (figures 5 and 6). The first-order nature of this transition at \(T_L\) with an abrupt change of the magnetic modulation vector was also verified in the model calculations [18].

With increasing magnetic field, above 2.5 and 4 tesla in \(\text{Mn}_{0.98}\text{Fe}_{0.02}\text{WO}_4\) (figure 5) and \(\text{Mn}_{0.95}\text{Fe}_{0.05}\text{WO}_4\) (figure 6), respectively, another sharp increase of the magnetization indicates the re-entrant phase transition from the \(\uparrow\uparrow\downarrow\downarrow\) AF1 phase into the ferroelectric (spin-spiral) AF2 phase. The increase of \(M(T)\) across this transition is consistent with the unlocking of the magnetic modulation vector which becomes incommensurate again in the high-field phase. The large temperature hysteresis proves the strongly first order nature of this transition. At constant temperature the field-dependent magnetization shows a sharp metamagnetic transition from the low-field AF1 phase to the high-field (FE) AF2 phase, as shown in the inset of figure 5 (only data for increasing field are shown). All magnetic anomalies derived from the magnetization measurements fit perfectly into the phase diagram for both compounds as shown in figure 4. The distinct anomalies of the magnetization at the low-\(T\) ferroelectric transition confirms the intrinsic coupling between the magnetic and dielectric orders. The results indicate that the magnetic field destabilizes the collinear and commensurate \(\uparrow\uparrow\downarrow\downarrow\) phase and causes the Mn/Fe spins to tilt out of the \(a–c\) plane forming the incommensurate spin-spiral magnetic structure. This could be further investigated by neutron scattering experiments.

*Figure 5.* Magnetization \(M(T)\) of \(\text{Mn}_{0.98}\text{Fe}_{0.02}\text{WO}_4\) between 2.5 and 4 tesla. The inset shows the field dependent \(M(H)\) at constant temperatures.

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4. Summary

The magnetic and ferroelectric phase diagram of Mn$_{1-x}$Fe$_x$WO$_4$ was investigated by dielectric, pyroelectric current and magnetic measurements. At zero magnetic field, the ferroelectric spin-spiral phase is quickly suppressed by only 4% of Fe substitution. However, the ferroelectricity in compounds with $x > 0.04$ is restored in high magnetic fields. In a narrow range of magnetic field, a re-entrant FE phase behavior is observed. The complete magnetic field–temperature phase diagram is constructed for different values of $x$. The results of all measurements indicate that the paraelectric, collinear $↑↑\downarrow\downarrow$ magnetic order is stabilized by the Fe substitution but it is transformed into the non-collinear spin-spiral phase in external magnetic fields oriented along the easy axis of magnetization.

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