Sign Reversal of the Dielectric Polarization of MnWO$_4$ in Very High Magnetic Fields

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Abstract. Dielectric polarization $P$ of a geometrically frustrated spin system MnWO$_4$ has been examined for $B \parallel x$ and $E \parallel b^*$ in pulsed magnetic fields up to 52 T. We have observed two new phases IV (38 $\leq$ $B$ $\leq$ 48 T) and V (B $\geq$ 48 T). Moreover, we found that the IV-phase also exhibits ferroelectricity, in addition to the AF2-phase already known. Interestingly, the sign of $P$ of the IV-phase is found to be always opposite to that of AF2 irrespective of the direction of a poling electric field. The results implies that the ferroelectric domain is preserved between the AF2 and IV phases.

Recently, ferroelectricity induced by magnetic orderings, which is often referred to as multiferroics, has attracted much interest [1, 2]. Among various mechanisms proposed so far, the inverse Dzyaloshinskii-Moriya mechanism is the most promising candidate for ferroelectricity of magnetic origin [3, 4]. In this mechanism, a magnetically induced local electric dipole moment $p_{ij}$ is expressed as $p_{ij} \propto -e_{ij} \times (S_i \times S_j)$, where $e_{ij}$ is a vector connecting two spins $S_i$ and $S_j$. For a finite $p_{ij}$ to appear, $S_i$ and $S_j$ need to be canted with each other, and $S_i \times S_j$ should have a component perpendicular to $e_{ij}$. Cycloidal spin structures meet these conditions to give a finite macroscopic dielectric polarization $P$.

Monoclinic compound MnWO$_4$ is known to be one of the typical multiferroic materials [5, 6, 7, 8]. Magnetism of MnWO$_4$ arises from Mn$^{2+}$(3$d^5$, $S = 5/2$, $L = 0$) which constitutes a zigzag chain along the $c$-axis. Antiferromagnetic interactions among the first and the second nearest-neighbor Mn sites in this compound result in a strong geometrical spin frustration. On cooling from a paramagnetic state in zero magnetic field, MnWO$_4$ undergoes three successive phase transitions at $T_{N3} = 13.5$ K, $T_{N2} = 12.5$ K and $T_{N1} = 7.4$ K into three antiferromagnetic phases AF3, AF2 and AF1, respectively [7, 9]. The magnetic easy-axis, named $x$-axis, is in the ac-plane and tilted away from the a-axis by 35 degrees. For convenience, a rectangular coordinate system $(xyz)$ is often adopted in this compound. Here the $y$-axis is equal to $b$- or $b^*$-axis, and the $z$-axis is perpendicular to the $x$- and $y$-axis. Magnetic structures of AF1, AF2 and AF3 are a commensurate collinear spin state with $Q_1 = (\pm 1/4, 1/2, 1/2)$ (up-up-down-down type), an incommensurate noncollinear one with $Q_2 = (-0.214, 1/2, 0.457)$ (cycloidal within the $xy$-plane) and a sinusoidal incommensurate collinear one with $Q_3 = (-0.214, 1/2, 0.457)$, respectively. [10] The magnetic phase diagram for $B \parallel x$ in fields up to 17 T was obtained by the magnon dispersion measurements [11]. Increasing magnetic field at 5 K, successive phase transitions into AF2 and a high-field phase named HF occur at 2.1 T and 12.4 T, respectively [8]. The magnetic structure
of the HF phase is still unknown.

Among the four ordered phases known so far, only AF2 is ferroelectric [8]. In AF2, \( P \) is known to point to the \( b^* \) axis. Since the spin state of AF2 is cycloidal within the \( xy \)-plane at zero magnetic field, \( \langle S_i \times S_j \rangle \), where the brackets mean an average over the spins, points to the \( z \)-axis. On the other hand, \( \langle e_{ij} \rangle \) always points to the \( c \)-axis, because the direction of the zigzag chain of Mn-ions is along the \( c \)-axis. Within the inverse Dzyaloshinskii-Moriya scenario, the average of the polarization \( p_{ij} \) is roughly expressed as \( p_{ij} \propto -\langle e_{ij} \rangle \times \langle S_i \times S_j \rangle \) in the case of an incommensurate structure. As a result, \( P \) parallel to \( b^* \) would appear in agreement with the experimental results. Since the magnetization in the HF phase is far less than the saturation moment expected for Mn\(^{2+}\), further phase transitions might occur at still higher fields [9]. In the present study, we have measured the dielectric polarization of MnWO\(_4\) for \( B \parallel x \) and \( E \parallel a^*, b^* \) and \( c^* \) in pulsed high magnetic fields up to 52 T.

A single crystalline sample was prepared by a floating zone method and cut into three thin plates with the largest surfaces perpendicular to the \( a^* \), \( b^* \) and \( c^* \) directions, respectively. The electrodes were made on those largest surfaces by sputtering copper. Strong magnetic fields up to 52 T were generated by a nondestructive long-pulsed magnet in the International MegaGauss Science Laboratory, Institute for Solid State Physics, University of Tokyo. The shape of \( B(t) \) was approximately a half period (15 ms) of sine wave. Dielectric polarization was measured by a pyroelectric technique, with the poling field \( E_p \) of 200 kV/m [12].

The results of \( P(B) \) for three directions \( a^*, b^* \) and \( c^* \) obtained at 4.2 K in pulsed fields \( B(\parallel x) \) up to 52 T are shown in Fig. 1. We confirmed that the \( a^* \)- and \( c^* \)-components of \( P \) are virtually absent in the present field range, except for a tiny signal seen for \( E \parallel c^* \) possibly due to a misalignment of the crystal. Looking at the response of \( P \parallel b^* \), two new phases (IV and V) can be recognized in a high field region above the HF-phase. \( P \) apparently shows a finite value in phase IV \( (38 \text{ T} < B < 48 \text{ T}) \), while it disappears again in V \( (B > 48 \text{ T}) \).

As can be seen in Fig. 1, we observed unusual hysteresis in the field variation of \( P \). In the measurement with the peak field of 45 T that is within phase IV, the data of rising and falling field sweeps almost fall on top of each other, except for a small hysteresis upon the phase transitions that are all of first-order at 4.2 K. Remarkably, \( P \) in phase IV has a negative value, in spite of positive \( E_p \) applied. When the peak field is increased to 52 T, well inside phase V, a dramatic change occurs in the data for the falling field scan. On entering phase IV from above, positive \( P \) appears. When AF2 is entered on further decreasing \( B \), however, \( P \) becomes negative, i.e., antiparallel to \( E_p \). Accordingly, the sign of \( P(B) \) is totally reversed in phases AF2 and IV.

In order to clarify the mechanism for the sign change in phase IV, we instantaneously reversed \( E_p \) just at the top of \( B(t) \) within phase V. Although not shown, we observed that negative (positive) \( P \) appears on entering phase IV (AF2) from above in the falling field sweep. These observations indicate that the sign of \( P \) of phase IV, when entering from phase V, is solely determined by the polarity of \( E_p \). This is what one would expect for a transition from a paraelectric to a ferroelectric state. Therefore, what remains unsolved regarding the unusual hysteretic behavior of \( P(B) \) in Fig. 1 is why the polarities of \( P \) for the phases AF2 and IV are always opposite to each other.

Regarding this issue, we demonstrate by a series of measurements shown in Fig. 2 that the appearance of \( P \) in AF2 on entering from either sides AF1 and HF is not as simple as an ordinary ferroelectric transition from a paraelectric state. Here we performed a series of measurements as indicated by the arrows in Fig. 2. Before the measurements, the sample was cooled to 4.2 K from a paramagnetic and paraelectric state under a positive \( E_p \) in zero magnetic field. The first two data (peak fields of 9 T and 45 T) were measured with a positive \( E_p \). The results are the same with the first plot in Fig. 1. Then we reversed \( E_p \) between the second and the third shots. Interestingly, for the subsequent three measurements a positive \( P \) has still been observed.
in AF2 in spite of a negative $E_p$ applied. This means that some trace of a ferroelectric domain remains in AF1 as well as in HF-phase. In the sixth shot, however, a negative $P$ appears in AF2 in accordance with the polarity of $E_p$. This suggests that the the memory of the ferroelectric domain is lost after the system experiences phase-IV. We confirmed these by repeating the procedure several times.

Figure 3 shows $P(B)$ for $B \parallel x$ and $E \parallel b^*$ up to 52 T obtained at various temperatures. As temperature increases, the critical field of the HF-IV transition rapidly decreases while the onset field of the HF-phase increases slightly. Accordingly, the HF region vanishes around 8 K and a direct phase transition from AF2 to IV occurs at higher $T$. Upon the AF2-IV transition, the polarity of $P$ is reversed almost continuously; the inversion of $P$ has been confirmed as a direct transition from AF2 to IV-phase. This fact implies that a ferroelectric domain is preserved upon the AF2-IV transition.

The magnetic phase diagram for $B \parallel x$ obtained by the present measurements is shown in Fig. 4, where the phase boundaries determined from other experiments are also plotted \cite{7}. We found that a new phase (IV) with a finite dielectric polarization exists in a high field and high temperature region outside the HF-phase. The V-phase might be identical to a paramagnetic (PM) phase above $T_{N3}$, since no boundary has been observed between these two regions. The observed value of the magnetic moment at 52 T in V-phase is, however, less than a saturated moment value (5 $\mu_B$/f.u.) of a bare Mn$^{2+}$ ion. This fact leaves a possibility that a new phase boundary exists between the V and the PM phases.

Finally, we consider the reason why the polarity of $P$ of AF2 and IV phase is always opposite to each other. We confine ourself to the case of the direct transition between the AF2 and IV phases as observed at 9.1 K. Since the ferroelectric domain is preserved upon the AF2-IV transition, it is unlikely that a drastic change occurs in the spin structures. Consider the situation of a high magnetic field limit for $B \parallel x$. There $S_i$ would take a cone structure with respect to the $z$-axis before completely saturates along the $x$-axis. Then $\langle S_i \times S_j \rangle$ will be oriented toward the $z$-axis, because $S_i \times S_j$ will also lie on a cone around the $z$-axis. In this situation, $\langle p_{ij} \rangle$ will point toward the $b^*$-direction. If $\langle S_i \times S_j \rangle$ rotates continuously within the $xz$-plane from $z$- to $x$-axis by increasing $B \parallel z$-axis, $\langle p_{ij} \rangle$ always stays along the $b^*$-direction. When $\langle S_i \times S_j \rangle$
traverses across the c-axis, the polarity of $\langle p_{ij} \rangle$ reverses without a change in the spin chirality. This model partially explains our experimental results.

To summarize, dielectric polarization $P$ of a zigzag chain antiferromagnet MnWO$_4$ has been measured by a pyroelectric technique in pulsed high magnetic fields up to 52 T applied along the magnetic easy axis (x-axis). Two phase (named IV and V) are newly observed in high magnetic field regions. We found that $P(\parallel b^*)$ of the IV-phase has a finite value and its polarity is always opposite to that of the AF2-phase, irrespective of the polarity of a poling field. This result would impose a constraint on the spin structure of the IV-phase.

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