Magnetic-field-induced polarization and depolarization in $HoMn_2O_5$ and $ErMn_2O_5$

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The effects of the magnetic field (H) on dielectric properties have been investigated for RMn_2O_5 (R=Ho and Er), which undergo a transition to a ferroelectric state around 35 K. With further decreasing temperature (T), $HoMn_2O_5$ shows the second dielectric transition to the lowest-T phase (X), where spontaneous polarization is almost zero. The application of H stabilizes the ferroelectric phase in $HoMn_2O_5$, while the X phase in $ErMn_2O_5$ as the ground state. Accordingly, the electric polarization can be induced or extinguished by H, accompanying the hysteresis. Phase diagrams of these compounds have been established in the plane of T vs H.

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I. INTRODUCTION

The correlation between magnetic and dielectric properties in solids has been investigated over a century since Pierre Curie's conjecture in 1894.[1] By numerous research efforts, it has been clarified that several materials show the magnetoelectric (ME) effect (polarization induced by a magnetic field or magnetization by an electric field).[2,3] However, the ME effects in most of these materials are too small to be useful in practical applications. Quite recently, Kimura *et al.* have demonstrated a new approach to the magnetic field (H) control of the spontaneous polarization (P).[4] The approach is based on the phase control of the multiferroic states, in which the ferroelectric order coexists and couples with some magnetic order, being distinct from the conventional liner ME effect. In a perovskite manganese oxide $TbMnO_3$, for example, the ferroelectric P emerges at the incommensurate to commensurate antiferromagnetic transition (27 K). Below 10 K, the Tb $4f$ moments order via coupling with the Mn d-electron spins. Here, H can induce a metamagnetic transition related to the flop of the Tb moments, perhaps altering the commensurate Mn spin structure, and trigger a 90° flop of the spontaneous P. The key ingredients needed for such magnetic-field effects are (1) a commensurate d-electron spin structure that couples magnetoelastically with the lattice modulation producing the spontaneous P, and (2) an f-d exchange interaction that amplifies the action of the external H to alter the d-electron spin state. In this context, a similar mechanism for the H control may also apply to other rare-earth transition-metal oxides that show magnetic-order-induced or reduced ferroelectricity.[5] Apart from the $RMnO_3$ perovskites (R=Gd, Tb, or Dy),[6] one such promising candidate system is RMn_2O_5 (R=a rare earth ion, Y, or Bi), which have been known to exhibit magnetism-dependent ferroelectricity.[7–9] Recently, the gigantic response of the dielectric constant (ε) and ferroelectric P to an external H has been demonstrated for $(Tb,Dy,Ho)Mn_2O_5$.[10–12] In particular, Hur *et al.*[10] reported that $TbMn_2O_5$ shows the reversible P-flip phenomenon depending on the polarity of the H that does not exist in other materials. Although the mechanism of magnetic ferroelectricity in RMn_2O_5 is not thoroughly revealed as yet, the coupling between the magnetism and the lattice distortion as the source of the ferroelectricity is evidenced by the presence of the superlattice peak with twice the magnetic propagation vector in the ferroelectric phase of $DyMn_2O_5$.[12]

RMn_2O_5 compounds are magnetic ferroelectrics that undergo the ferroelectric transition at T_1=25–39 K below the antiferromagnetic transition temperature T_N=39–45 K.[8] In this system, the second dielectric transition occurs at T_2 ($<T_1$) in further lowing temperature (T), where the magnetization as well as the ε and spontaneous P shows an anomaly, implying the strong coupling between magnetic and dielectric states. According to structural studies,[13,14] the orthorhombic crystal ($Pbam$) at room T is composed of $Mn^{4+}O_6$ octahedral and $Mn^{3+}O_5$ pyramidal units, as shown in Fig. 1.

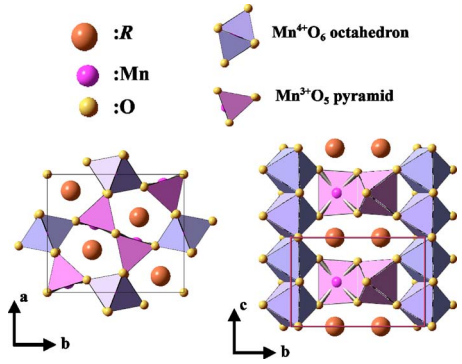

FIG. 1. (Color online) Crystal structure of RMn_2O_5 (R=a rare earth ion, Y, or Bi): View along the c axis (left panel) and along the a axis (right panel).

The octahedra form chains along the c axis with sharing their edges. On the other hand, pairs of pyramids link these chains within the ab plane. The emergence of ferroelectricity is believed to arise from the pyramidal Mn^{3+} sites in RMn_2O_5.[15] The commensurate magnetic structure with the propagation vector $\mathbf{q}=(1/2,0,1/4)$ in the ferroelectric phase between T_1 and T_2 changes into an incommensurate one with $\mathbf{q}=(q_x,0,q_z)$ below T_2 ($q_x\sim0.480, q_z\sim0.292$).[15,16] It has recently been reported that $DyMn_2O_5$ has a commensurate lattice modulation (0, 0, 1/2), which is perhaps accompanied by the spin modulation with the propagation vector (1/2, 0, 1/4) in the ferroelectric region, and the electric P induced by an external H.[12,17] In this paper, we have investigated the dielectric properties under H in other RMn_2O_5 family, $HoMn_2O_5$ and $ErMn_2O_5$, to establish the whole phase diagram in the plane of T vs H in RMn_2O_5.

II. EXPERIMENT

Single crystals of $HoMn_2O_5$ and $ErMn_2O_5$ were grown by a $PbO\text{-}PbF_2\text{-}B_2O_3$ flux method.[18] The crystals were oriented with the use of Laue x-ray diffraction patterns, and cut into thin plates with the widest faces perpendicular to the b axis. Typical dimensions of the shaped specimens are $1.75\times1.95\times0.42$ mm^3 for $HoMn_2O_5$ and $0.75\times1.35\times0.29$ mm^3 for $ErMn_2O_5$. Ag electrodes were evaporated onto the end faces. Electric polarization-field (P-E) hysteresis curves were measured with the E scan at 100 Hz. We could not observe the clear P-E hysteresis loop below 25 K in $HoMn_2O_5$ and below 20 K in $ErMn_2O_5$ because of the increasing coercive force exceeding the dielectric breakdown for $E>0.9$ and 2.2 MV/m, respectively. ε was measured at 1 kHz with the use of a LCR meter while warming the sample at a rate of 2 K/min. Concerning the derivation of the spontaneous P from the pyroelectric current, special caution should be paid to the present system. This is because the lowest-T phase of several RMn_2O_5 compounds has the minimal or null spontaneous P, and accordingly the conventional procedure of the electric-field cooling and subsequent *zero*-electric-field warming procedure for the pyroelectric current measurement is invalidated. In the present study, the samples were cooled down to the lowest T at a rate of 5 K/min, while applying an electric field. After the electric-field cooling, the measurements of the pyroelectric (displacive) current were carried out with applying a relatively small electric field (200 kV/m) in the warming run at a rate of 5 K/min or in the H-scanning run at a rate of 10 mT/sec. The T dependence of the pyroelectric current was measured by applying the electric fields with the positive and negative signs, respectively, to deduce the accurate value of the T-dependent P.

III. RESULTS AND DISCUSSION

In Fig. 2, we display the T dependence of ε and P in various magnetic fields for $HoMn_2O_5$ and $ErMn_2O_5$. The ε and P were measured along the b axis, since the spontaneous P, if any, was always observed only along the b axis. All the ε-T and P-T curves have one or two anomalies corresponding to the phase transition(s). These transition temperatures for the respective compounds are summarized in Fig. 3 as the phase diagrams in the plane of T vs H. (An account for the phase diagrams is given later.) In zero H, there are two distinct transitions at $T_1=36.0$ K and $T_2=19.0$ K in $HoMn_2O_5$. Between T_1 and T_2, the large spontaneous P was observed in this compound. Moreover, we could observe the P-E hysteresis curve in the region between 35.5 and 25 K in $HoMn_2O_5$, as shown in the inset of Fig. 2(b). These results confirm the ferroelectric phase in the T region between T_1 and T_2 in $HoMn_2O_5$. Below T_2, the ε increases steeply and the P be-

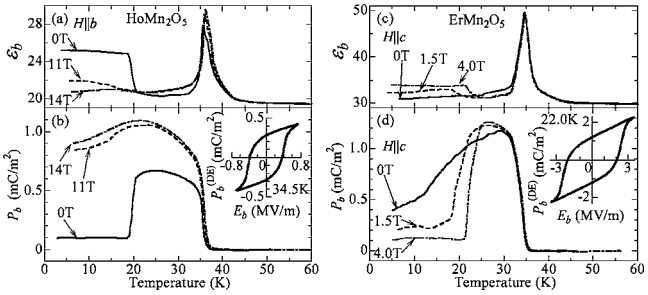

FIG. 2. Temperature dependence of dielectric constant (ε_b) and electric polarization (P_b) parallel to the b axis under various magnetic fields in $HoMn_2O_5$ ((a), (b)) and in $ErMn_2O_5$ ((c), (d)). The magnetic field (H) was applied along the b axis for $HoMn_2O_5$ and along the c axis for $ErMn_2O_5$. The insets show the P_b versus electric-field (E_b) hysteresis curve at 34.5 K under zero H in $HoMn_2O_5$, and that at 22.0 K in $ErMn_2O_5$. The E_b was applied along the b axis.

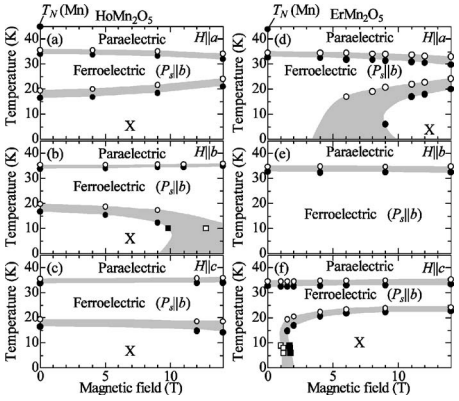

FIG. 3. The phase diagrams in the plane of temperature (T) versus magnetic field (H). The left panels (a)–(c) show the phase diagrams for $HoMn_2O_5$ and the right ones (d)–(f) those for $ErMn_2O_5$. Applied H is along the a axis ((a), (d)), b axis ((b), (e)) and c axis ((c), (f)), respectively. The transition temperatures were determined by the measurements of the dielectric constant. Open and closed circles indicate the transition temperatures obtained in warming and cooling runs, respectively. Open and closed squares in (b) and (f) indicate the transition points obtained in H-increasing and H-decreasing runs, respectively. The antiferromagnetic transition temperatures for the Mn spins (T_N) are also shown in the phase diagrams (a) and (d). In the ferroelectric phase, the spontaneous polarization (P_S) appears along the b axis. X indicates the lowest-T phase, where P_S is almost zero. The shaded areas respect the hysteretic regions.

comes nearly zero, suggesting the transition to a reentrant paraelectric or antiferroelectric state.[19] In this paper, we label the no- or minimal-P phase below T_2 as X. In order to clarify the electronic phase diagram, we measured the dielectric properties in magnetic fields applied parallel to the b axis (magnetic easy axis) in $HoMn_2O_5$.[11,20] As seen in Figs. 2(a) and 2(b), the ε remains small, and the P keeps a large magnitude below T_1 for $H>11$ T. This indicates that above 11 T the lowest-T phase X is extinguished and replaced by the ferroelectric one.

In zero H, $ErMn_2O_5$ undergoes the ferroelectric transition at $T_1=34.6$ K, as shown in Figs. 2(c) and 2(d). The P increases steeply at T_1. With further lowering T, the P-T curve shows a broad peak and decreases gradually below 30 K. The T gradient of the ε changes at 25.7 K, while the spontaneous P does not change significantly. We observed the P-E hysteresis in the T region of 20–34 K, as shown in the inset of Fig. 2(d). Most of RMn_2O_5 compounds undergo the phase transition from the ferroelectric to the X phase at T_2 under a zero magnetic field. In $ErMn_2O_5$, however, the phase transition to the X phase is not observed below T_1. The anomalous behavior in the electric polarization in $ErMn_2O_5$ may be attributed to the effect of the Er f moments. A neutron study has indicated that the magnetic structure in $ErMn_2O_5$ is amplitude modulated at 4.2 and 25 K, where the ordered f moments of 8.1 and 1.6 μ_B direct along the c axis, respectively.[21] In this compound, the dielectric behavior may be affected by the modulated spin structure of the Er f moments with the large magnitude below the relatively high ordering temperature of f moments. In $ErMn_2O_5$, we investigated the dielectric properties in H applied along the c axis that is the magnetic easy axis.[20,22] Above 1.5 T, the ε shows a steep rise and the P rapidly changes into the nearly zero-P state around 20 K. These behaviors are analogous to the zero-H case of $HoMn_2O_5$ (Figs. 2(a) and 2(b)), suggesting that $ErMn_2O_5$ undergoes the transition from the ferroelectric to the X phase above 1.5 T. Note that in both cases of $HoMn_2O_5$ and $ErMn_2O_5$, the P is nearly zero below T_2 when the ε increases steeply at T_2. The similar phenomena have also been observed in the phase transitions of $TbMn_2O_5$[11] and $DyMn_2O_5$[12] under the applied H or zero H.

To clarify the phase diagrams of $HoMn_2O_5$ and $ErMn_2O_5$, the H dependence of magnetization M, ε, and P (i.e., ME effect) have been investigated in more detail. Figure 4 exemplifies the result for $HoMn_2O_5$. No clear transition was discerned in the results of ε and P, when the measurement was performed after the sample was cooled down to the lowest T at zero H. Therefore, at first, we applied the H of 14 T along the b axis of $HoMn_2O_5$ at 70 K, and subsequently cooled the sample down to 10 K while applying the electric field. Then we measured the ε and pyroelectric current in decreasing and increasing H. Such a trajectory is shown in the inset of Fig. 4(c). The large anomalies of ε and P corresponding to the transition from the ferroelectric to X (almost-null P) phase appear around 10 T only in the H-decreasing process, as seen in Figs. 4(b) and 4(c). Although the full recovery of the P is not observed up to 14 T, the small kink of P and the steep rise of ε at 12.5 T in the H-increasing process suggest the strong first-order nature of the transition between the ferroelectric and X phases. In this compound, the H of 14 T

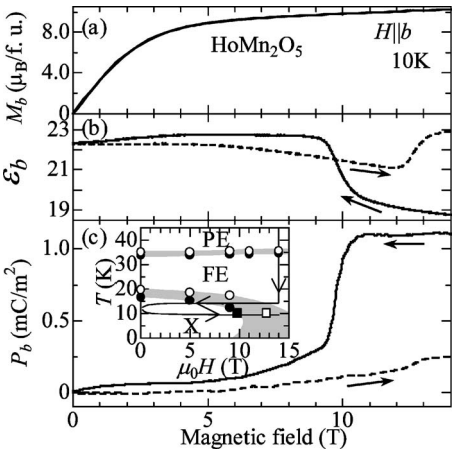

FIG. 4. The magnetic-field dependence of (a) magnetization M_b, (b) dielectric constant ε_b, and (c) polarization P_b at 10 K in $HoMn_2O_5$. All the quantities were measured along the b axis. The external magnetic field (H) is applied along the b axis. In the measurements of the magnetocapacitance (ε vs H) and magnetoelectric (P vs H) effects, H of 14 T was at first applied on the sample at 70 K, and then the sample was cooled down to 10 K. After this procedure, the measurements were performed in decreasing and increasing H. The track is shown in the inset of the panel (c). In this inset, PE, FE, and X stand for paraelectric, ferroelectric, and lowest-temperature almost zero-P phases.

appears insufficient to complete the X to ferroelectric phase transition at 10 K in the H-increasing run. These imply the existence of even a larger field-hysteresis region at low temperatures in the phase diagram for $HoMn_2O_5$ (Fig. 3(b)).

Figure 5 presents the magnetic-field dependence of M, ε, and P up to 14 T at 6 K in $ErMn_2O_5$.[23] In this compound, the ME effect was measured in the E-cooling at zero H and

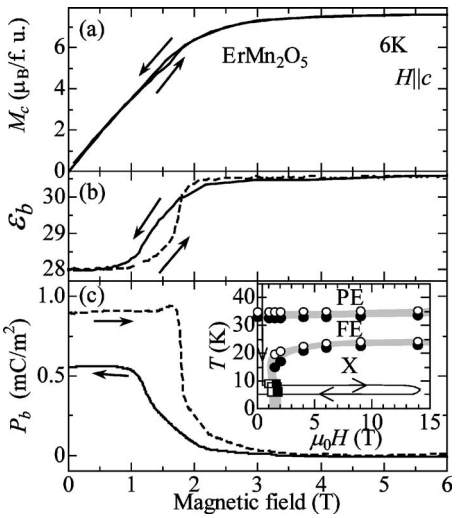

FIG. 5. The magnetic-field dependence of (a) magnetization M_c, (b) dielectric constant ε_b, and (c) polarization P_b at 6 K in $ErMn_2O_5$. The external magnetic field (H) is applied along the c axis. The magnetocapacitance (ε vs H) and magnetoelectric (P vs H) effects were measured in keeping the track shown in the inset of the panel (c). In this inset, PE, FE, and X stand for paraelectric, ferroelectric, and lowest-temperature almost zero-P phases.

subsequent H-sweeping procedure while keeping the E, as shown in the inset of Fig. 5(c). The hysteresis of M and the large modification of ε were observed between 1.2 and 1.8 T at 6 K (Figs. 5(a) and 5(b)). The P is reduced significantly around 1.8 T in the H-increasing run, and induced around 1.2 T in the H-decreasing one. The H-dependent P corresponds to the dielectric transition between the ferroelectric and X phases. The anomaly of the dielectric property accompanies that of M, confirming again the strong coupling between magnetic and dielectric states. Incidentally, the magnitudes of the P at the same magnetic field at 6 K in Figs. 2(d) and 5(c) are considerably different. The magnitude of the spontaneous P is obviously dependent on the measurement parameters such as the T-sweeping rate, perhaps reflecting the strong first-order nature of the phase transition.

To overview the behaviors of the H-induced polarization and depolarization in $HoMn_2O_5$ and $ErMn_2O_5$, the phase diagrams in the plane of T vs H are shown in Fig. 3. We present not only the phase diagrams for the H along the b axis in $HoMn_2O_5$ and along the c axis in $ErMn_2O_5$, but also those for the H along other crystallographic axes in Fig. 3. In zero H, Mn spins in the ferroelectric phase form the commensurate magnetic structure with the propagation vector of (1/2, 0, 1/4).[16] The ferroelectric phase in $HoMn_2O_5$ and $ErMn_2O_5$ tends to shrink, when H is applied along the a axis. In contrast, the ferroelectric state is stabilized by the H along the b axis. Typically in the case of $ErMn_2O_5$, the H along the a and c axes induces the X phase, while the lowest-T ferroelectric one survives under the H up to 14 T applied along the b axis. A similar anisotropic magnetic-field effect was also observed in YMn_2O_5 without f moment.[24,25] These common features in R=Ho, Er, and Y compounds suggest that the change of dielectric properties with the H is ascribed to the field modification of the Mn spin structure through the exchange striction. Below the ordering T of the R-site f moments, on the other hand, the dielectric features in the H are affected significantly not only by the Mn spins but also by the rare-earth moments in RMn_2O_5. We previously reported one such case of $DyMn_2O_5$.[12] In this material, the ferroelectric phase transition coupled with the Dy-site f moment is also driven by the H. The phenomena in $DyMn_2O_5$ were explained in terms of the enhanced magnetic-field action on the Mn spin structure by the f-d spin exchange interaction. $DyMn_2O_5$ undergoes other extraordinary dielectric transitions related to the flop of the f moments at low temperatures, and has a complex phase diagram. Similarly to $DyMn_2O_5$, $ErMn_2O_5$ also shows the phenomena related to the f moments. As shown in Figs. 3(f) and 5(c), the P is easily reduced by the small H applied parallel to the c axis below the magnetic transition T, suggesting that the magnetically ordered f moments produce molecular field and magnify the action of the external field. Above the f-moment ordering T (perhaps between 10 and 25 K[16,20,21]), by contrast, the ferroelectric-to-X phase transition is caused only by a relatively high H, or the critical T of the dielectric transition is hardly changed by H.

IV. CONCLUSION

In summary, we have shown that the spontaneous electric polarization can be controlled by the magnetic field in $HoMn_2O_5$ and $ErMn_2O_5$. In these compounds, the ferroelectric phase shrinks as the magnetic field is applied along the a axis, while rather stabilized by the field along the b axis. The results suggest that the magnetic-field action on the Mn spins alone can modify, in principle, the dielectric properties through the exchange striction effect. On the other hand, the f moment on the rare-earth site appends molecular fields to the Mn spin system via the f-d spin exchange interaction. Consequently, the magnetoelectric phase diagrams in these systems show an augmented response to external fields at low temperatures around or below the f-moment ordering temperature, showing a large variety of magnetoelectric phenomena depending on the f-d coupling nature.

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