High-Field Study of Multiferroic Properties in Orthorhombic Eu$_{1-x}$Y$_x$MnO$_3$

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Abstract. Magnetic and dielectric properties of Eu$_{1-x}$Y$_x$MnO$_3$ ($0 \leq x \leq 0.4$) were studied in pulsed-magnetic fields up to 55 T. In paraelectrical EuMnO$_3$, application of magnetic fields along the $b$-axis causes a first order transition to the ferroelectric phase with the electric polarization parallel to the $a$-axis. Similar first order transitions are also observed in Eu$_{0.6}$Y$_{0.4}$MnO$_3$, in which the ferroelectric phase is already stable in zero field. A possible microscopic origin of the novel multiferroic phase in high field is discussed.

1. Introduction
Manganites with the perovskite-type structure have attracted considerable attention as a playground to study unconventional phenomena caused by cross-correlation among multiple degrees of freedom in solids. As one of these phenomena, a gigantic magneto-electric effect was found in the orthorhombic RMnO$_3$ ($R$ is a rare-earth ion) [1]. In this compound, spontaneous electric polarization ($P$) appears simultaneously with the cycloidal magnetic ordering. Recent theoretical studies revealed the relationship between the spatially modulated spin structures and the electric polarization in a clear form [2, 3], and thus accelerate discovery of novel multiferroic materials in spiral magnets [4, 5, 6, 7]. The origin of the field-induced flop of $P$ in the RMnO$_3$, however, remains unclear because the presence of two kinds of magnetic ions (R and Mn) complicates the system. In this study, we investigated magnetic and dielectric properties of Eu$_{1-x}$Y$_x$MnO$_3$ in high magnetic fields. Since Eu$^{3+}$ and Y$^{3+}$ have no 4$f$-moment in the ground state, this system is suitable to study the essential role of magnetic fields ($H$) in the frustrated Mn-spin network in this class of manganites [8, 9, 10]. Application of high magnetic fields enables us to realize magneto-electric phase transitions without help of magnetic moments in the R ions.

2. Experimental
Single crystals of Eu$_{1-x}$Y$_x$MnO$_3$ ($x = 0$, 0.1 and 0.4) were grown by the floating-zone method. Pulsed magnetic fields up to 55 T were generated using non-destructive magnets in the
International MegaGauss Science Laboratory of ISSP, The University of Tokyo. Magnetization \((M)\) along the field direction was measured by the induction method using coaxial pick-up coils. The \(H\)-induced change in \(P\) was detected with monitoring the pyroelectric current through a voltage drop in the shunt resistance connected in series. By integrating the current with respect to time, we obtained the \(P\) as a function of \(H\). In this study, electric fields \((E)\) were continuously applied during all the measurements of the \(P-H\) curves.

3. Results and discussion

On decreasing temperature \((T)\), EuMnO\(_3\) shows successive magnetic phase transitions from the collinear sinusoidal state below 51 K to the layered-antiferromagnetic state with canting moment along the interplane direction at \(T < 46\) K [9, 10]. There is no spontaneous \(P\) in all the states at zero field. Application of high magnetic fields along the \(b\)-axis, which is parallel/antiparallel to the antiferromagnetic spin components, causes a steep increase in \(P\) along the \(a\)-axis (Fig. 1). In this high-field state, we observed the \(P\) component along neither the \(b\) nor the \(c\) axis. The induced \(P_a\) reaches 440 \(\mu\)C/cm\(^2\) at 35 K, and appears to decrease with both increasing and decreasing \(T\). Although the presence of the field-induced change in \(P\) was reported earlier [11], the reported magnitude of \(P\) was significantly small (\(\sim 10\) \(\mu\)C/cm\(^2\)).

To clarify the reason for this discrepancy, we studied the \(P_a-H_b\) curves in various values of \(E\) (Fig. 2). To extend the applicable range of \(E\), we used the thinner sample than that used in the experiments shown in Fig. 1. According to the change in \(E\), the \(P_a-H_b\) curve changes its magnitude with remaining the similar profile. The direction of \(P\) changes with alternating the sign of \(E\), which is characteristic of ferroelectric materials.

The peak values of \(P\) (\(P_p\)) were plotted as a function of \(E\) in Fig. 3. In the small \(E\) region, the \(P_p\) steeply increases at 35 K (open squares) in comparison with that at 4.2 K (closed squares). Therefore, the observed reduction in \(P\) at low \(T\) can be caused by the difference in the degree of domain orientation, and may not be caused by the reduction in the spontaneous polarization within a single domain. We consider this difference in the domain orientation could be the origin of the discrepancy in the magnitude of \(P\) from the literature [11]. These changes in \(P\) are accompanied with the metamagnetic transitions [see Fig. 4(b)]. Magnetization measurements in the presence of \(E\) indicate that the change in \(M\) at the metamagnetic transition \((\delta M)\) remains unchanged at least for \(|E| \leq 3.5\) MV/m (circles in Fig. 3).

Next, we show the composition dependence of this transition. Figures 4 show the \(H_b\)-dependence of (a) \(P_a\) and (b) \(M_b\) in Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) with \(x = 0, 0.1\) and 0.4 at 4.2 K. With decreasing \(T\), the sample of \(x = 0.1\) first shows the collinear sinusoidal spin ordering below 48 K, and then the canted antiferromagnetic one below 36 K. The overall profiles of the \(P_a-H_b\) and \(M_b-H_b\) curves are similar in between the samples of \(x = 0\) and 0.1. In the crystal of \(x = 0.1\), however, the first order transition is clearly observed even at 38 K (not shown), which is in the collinear phase at zero field. The \(x = 0.4\) sample is in the cycloidal spin state with the rotational axis parallel to the \(c\)-axis at 4.2 K [12]. Using the spin-current model [2], this cycloidal spin ordering results in the \(P||a\), which is consistent with the observed spontaneous \(P\) at zero field [8]. On applying the \(H||b\), the \(P_b\) first increases and then decreases with showing a broad maximum at around 16 T. Although the origin of this hump structure is not clear yet, this profile reminds us of the theoretical prediction of the \(P-H\) curve in a helicoidal magnet under the in-plane field (Fig. 4 of Ref. 3). Further increase in the \(H||b\) causes an abrupt change in the slope of the \(P_x-H_b\) curve at 21 T. In this field, the \(M_b-H_b\) curve shows metamagnetic behavior [Fig. 4(b)] indicating the presence of the first order transition from the low-field \(P_a-I\) to the high-field \(P_a-II\) phase. Judging from the similarity in the \(P_a-H_b\) curves in high fields [Fig. 4(a)], we consider that the field-induced \(P_a\) phase in \(x = 0\) and 0.1 shares the same origin with the \(P_a-II\) phase in \(x = 0.4\). The \(P_a-II\) phase appears in the similar region of the \(H-T\) plane for all the \(x\) regardless of the underlying magnetic phases.
Figure 1. $P$ along the $a$-axis in EuMnO$_3$ as a function of $H||b$ at various $T$. $E = 0.29$ MV/m was continuously applied during the measurements. The $P$-$H$ curve at each $T$ was offset for clarity.

Figure 2. The relationship between $P_a$ and $H_b$ in EuMnO$_3$ at 4 K. The $P$-$H$ curves were measured under various values of $E$ between $-3.5$ and $+3.5$ MV/m.

Figure 3. The closed- (open-) squares represent the peak values of $P$ at 4.2 K (35 K) as a function of $E$. Closed circles represent the change in $M$ at the simultaneous metamagnetic transition.

Figure 4. (a) $P_a$ and (b) $M_b$ in Eu$_{1-x}$Y$_x$MnO$_3$ with $x = 0, 0.1$ and $0.4$ as a function of $H_b$ at $T = 4.2$ K. The $P$-$H$ curve in the $x = 0.4$ sample was offset so that the $P$ approaches zero in the high-field limit. The $M$-$H$ curves were also offset for clarity.

Now we discuss possible origins of the $P_a$-II phase. In Eu$_{1-x}$Y$_x$MnO$_3$ with $x \sim 0.4$, application of $H||a$ causes a flop of the $P$ from the $a$- to the $c$-direction [8]. This change is understood as the flop of the spin rotational axis from the $c$- to the $a$-axis, which results in the flop of $P$ as observed through the inverse effect of the Dzyaloshinskii-Moriya interaction [10]. Assuming the similar situation, application of the $H||b$ may change the spin rotational axis to the $b$-axis. In this case, we have to assume also the change in the propagation vector to the $c$-axis to realize the observed $P||a$. Such a change in the propagation vector, however, is unnatural if we
take into account the exchange interaction in the actual crystal [13]. In addition, the relationship between the \( P \) and \( M \) is different in between the \( P_a\-I \) and \( P_a\-II \) phase [14]. These results suggest that the microscopic origin of the \( P_a\-II \) phase cannot be ascribed to the spin-current model that successfully explains the multiferroic features in the \( P_a\-I \) phase. Taking into account the actual space group of this class of manganites (\( Pbnm \)), some kinds of commensurate magnetic ordering with the vector propagation parallel to the \( b\)-axis break the \( b\)-glide, and change the crystallographic symmetry to that having \( P\)|\( a \) [15]. In this case, electric polarization is induced by the exchange striction, and hence significant spin-lattice coupling should be expected. In the early report, Kadomtseva \textit{et al.} observed large magnetostriction at the first order transition to the \( P\)|\( a \)-II phase [11]. This result indicates the presence of prominent role of the spin-lattice coupling at this transition, and hence suggests the possibility of multiferroic phase derived by the exchange striction. At present, it is not clear how the \( P \) should change as a function of \( M \) in the multiferroic state caused by this mechanism. However, we can expect that application of large \( H \) reduces \( P \) toward zero in the fully spin-polarized state, as observed in the \( P_a\-II \) phase, as long as the \( P \) is derived from magnetic ordering.

4. Conclusion

In conclusion, we measured the magnetization and electric polarization in the single crystals of Eu\(_{1-x}\)Y\(_x\)MnO\(_3\) with \( x = 0, 0.1 \) and 0.4 as a function of magnetic fields up to 55 T. Application of magnetic fields parallel to the \( b\)-axis causes first-order transitions to the ferroelectric phase with the polarization parallel to the \( a\)-axis. The observed \( P\)|\( a \) phase in high magnetic fields should be distinguished from the known \( P\)|\( a \) phase that is caused by cycloidal spin structures, and possibly has a different origin from that in the low-field region.

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5. References

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