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# Magnetic-field-induced spin flop transition and magnetoelectric effect in $Ca_2Fe_{2-x}Al_xO_5$

N. Abe,[1] N. D. Khanh,[2] T. Sasaki,[3] and T. Arima[1]
[1]*Department of Advanced Materials Science, University of Tokyo, Kashiwa 277-8561, Japan*
[2]*Department of Physics, Tohoku University, Sendai 980-8578, Japan*
[3]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

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Magnetic-field-induced spin flop transition and magnetoelectric effect in noncentrosymmetric $Ca_2Fe_{2-x}Al_xO_5$ ($0.5 \leqslant x \leqslant 1$) single crystals have been investigated. Temperature dependence of magnetic susceptibility shows that the compounds have antiferromagnetic transition temperatures $T_N$ above room temperature. The spin easy axis varies from the $c$ axis to the $a$ axis with increasing Al content $x$. When a magnetic field is applied along the spin easy axis, a spin flop transition takes place, accompanied by anomalies in the electric polarization and dielectric constant. The anomalies can be ascribed to a noncollinear spin arrangement in the domain walls between two magnetic phases and/or the spin direction dependent modulation of the metal-ligand hybridization. Such a polarization change with a spin flop transition in polar antiferromagnets may provide a route to realize large magnetoelectric coupling at high temperatures.

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The coupling between ferroelectricity and magnetism in a matter has been attracting much attention [1]. Recent extensive studies show that noncollinear magnetic structures like a spin helix are essential to host the ferroelectricity [2–4]. In this type of multiferroics, the space inversion symmetry is broken by the magnetic order. Based on this strategy, many multiferroic materials have been found so far [5–12]. However, because a noncollinear magnetic structure originates from the competition between several magnetic interactions, termed spin frustration, the magnetic transition temperature $T_N$ is generally much lower than the exchange energies. Rare examples of high-temperature multiferroics are CuO [12] and hexaferrites [13–16]. Other candidates of high-temperature magnetoelectrics would be noncentrosymmetric ferrites. In fact, $GaFeO_3$ [17,18] and $BiFeO_3$ [19], where the inversion symmetry is broken even in the paramagnetic phase, show fairly large magnetoelectric coupling.

$Ca_2FeAlO_5$ is a typical noncentrosymmetric ferrite with high $T_N$ well above room temperature (~350 K) [20]. This compound has the same crystal structure as a mineral brownmillerite [21]. The oxygen-deficient perovskite-type structure is constructed by an alternate stacking of $(Fe,Al)O_6$ octahedra and $(Fe,Al)O_4$ tetrahedra layers, as shown in Fig. 1(a). A previous structure analysis showed that $Ca_2FeAlO_5$ belongs to a noncentrosymmetric space group $Ibm2$, while $Ca_2Fe_2O_5$ has a centrosymmetric crystal structure of space group $Pcmn$ [22]. Colville and Geller investigated the evolution of the crystal structure in the $Ca_2Fe_{2-x}Al_xO_5$ system and concluded that the orientations of $(Fe,Al)O_4$ tetrahedra are uniformly aligned to make the crystal noncentrosymmetric for $x \geqslant 0.5$ [20–23]. When the Al content $x$ is smaller than 0.5, $FeO_4$ sheets stack by alternating the polar direction and form a centrosymmetric crystal. Another advantage of this system is a fairly small magnetic anisotropy, which enables a low-magnetic-field control of magnetic structure. Mössbauer spectroscopy in $Ca_2FeAlO_5$ reveals that the magnetic moments of $Fe^{3+}$ are aligned along the $a$ axis below $T_N$ [24]. The spin easy axis of the $Ca_2Fe_{2-x}Al_xO_5$ system changes from the $a$ axis to the $c$ axis with increasing of the ratio of $Fe^{3+}$ [20]; one can expect a magnetoelectric effect in $Ca_2Fe_{2-x}Al_xO_5$ ($x \geqslant 0.5$) compounds. Here we report a magnetoelectric effect with the magnetic-field-induced spin flop transition in the noncentrosymmetric antiferromagnets $Ca_2Fe_{2-x}Al_xO_5$.

Single crystals of $Ca_2Fe_{2-x}Al_xO_5$ with $x = 0.5$, 0.6, 0.7, 0.8, 0.9, and 1.0 were grown by a floating zone method in Ar atmosphere. The obtained crystals were characterized by powder x-ray diffraction and oriented by Laue photographs. Magnetization measurements were performed by a superconducting quantum interference device magnetometer (Quantum Design MPMS-XL). Differential electric polarization was obtained by integrating displacement current measured by using an electrometer (KEITHLEY 6517A) [25]. Dielectric constant at a frequency 10 kHz was measured by using an LCR meter (Agilent E4980A). These measurements were performed at the Center for Low Temperature Science, and High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University, Japan. Some magnetization measurements were performed at the Institute of Solid State Physics, University of Tokyo, Japan.

Figure 1(b) shows temperature dependence of the magnetic susceptibility $\chi$ of $Ca_2Fe_{2-x}Al_xO_5$ crystals for $0.6 \leqslant x \leqslant 1$. In $Ca_2FeAlO_5$ ($x = 1$), the $a$-axis magnetic susceptibility $\chi_a$ is monotonically decreased below $T_N = 350$ K, while the susceptibilities in a magnetic field along the $b$ and the $c$ axis are increased. This behavior of magnetic susceptibility clearly shows an antiferromagnetic arrangement of $Fe^{3+}$ spin moments along the $a$ axis. These results are consistent with the previous Mössbauer measurements [24]. For $0.7 \leqslant x \leqslant 0.9$, $\chi_a$ and $\chi_c$ exhibit a crossing in temperature evolution, indicating a switch in the spin easy axis from the $a$ axis to the $c$ axis with decreasing temperature. The $x = 0.6$ and $x = 0.5$ (not shown) samples show simple temperature dependence with $\chi_c$ smaller than $\chi_a$ and $\chi_b$, proving the easy axis along the $c$ axis. Because the spin easy axis in $Ca_2Fe_{2-x}Al_xO_5$ system is switched between the $a$ axis and the $c$ axis with a change in $x$, a magnetic-field-induced spin flop is expected to happen in a fairly low magnetic field.

Left panels in Fig. 2 show magnetic-field $H$ dependence of magnetization, electric polarization, and dielectric constant of $Ca_2FeAlO_5$ ($x = 1$) when $H$ is parallel to the $a$ axis

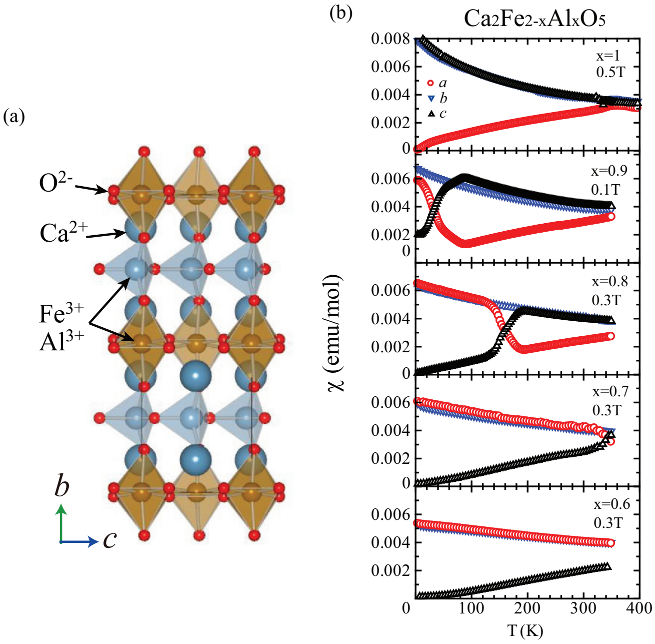

FIG. 1. (Color online) (a) Crystal structure of $Ca_2FeAlO_5$ ($x = 1$). $(Fe,Al)O_6$ octahedra and $(Fe,Al)O_4$ tetrahedra alternately stack along the $b$ axis. The crystal structure is drawn by VESTA [31]. (b) Temperature dependence of magnetic susceptibility in $Ca_2Fe_{2-x}Al_xO_5$ ($0.6 \leqslant x \leqslant 1$). $\chi_a$, $\chi_b$, and $\chi_c$ are shown by (red) circles, (blue) reverse triangles, and (black) triangles, respectively.

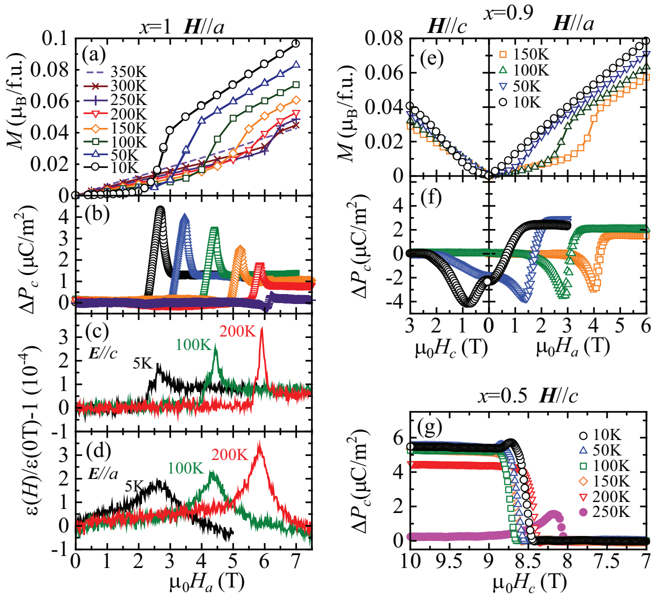

FIG. 2. (Color online) Magnetic-field dependence of physical properties in $Ca_2Fe_{2-x}Al_xO_5$ single crystals at several temperatures. (a) Magnetization, (b) differential polarization along the $c$ axis $\Delta P_c$, and magnetocapacitance for electric fields of 10 kHz applied along (c) the $c$ axis and (d) the $a$ axis, in $Ca_2FeAlO_5$. The magnetic field is applied along the $a$ axis. (e) Magnetization and (f) $\Delta P_c$ in $Ca_2Fe_{1.1}Al_{0.9}O_5$. Left and right sides indicate the magnetic fields along the $c$ axis and the $a$ axis, respectively. Here we define $\Delta P_c = 0$ in the $\mathbf{s}||a$ state. (g) $\Delta P_c$ in $Ca_2Fe_{1.5}Al_{0.5}O_5$ in a magnetic field applied along the $c$ axis.

(spin easy axis). Below $T_N$, the magnetic field induces a clear metamagnetic transition, as shown in Fig. 2(a). The high-field $M/H$ values well agree with the $\chi_b$ and $\chi_c$ values at the corresponding temperatures shown in Fig. 1(b), indicating that the metamagnetic transition is caused by a flop of $Fe^{3+}$ moments. The temperature dependence of the critical magnetic field for $x = 1$ and $x = 0.5$ (shown below), as well as the zero-field phase diagram, are summarized in Fig. 3. It is noteworthy that the electric polarization $P_c$ along the $c$ axis shows a peak in the phase coexistence state, as shown in Fig. 2(b). In addition, the $P_c$ value in the spin flopped phase for $x = 1$ is shifted from the $H = 0$ state. The observed shift in $\Delta P_c$ is monotonically decreased with increasing temperature, indicating that the polarization shift should be related to the temperature dependence of the ordered $Fe^{3+}$ spin moments. Figures 2(c) and 2(d) show magnetic-field dependence of the dielectric constants of $Ca_2FeAlO_5$ along the $c$ and $a$ axes, respectively. Not only $\varepsilon_c$ but also $\varepsilon_a$ show an anomaly at the spin-flop transition, despite that the electric polarization along the $a$ axis remains zero across the transition (not shown). This behavior may be ascribed to some enhancement of the electric polarizability of ions along the $a$ axis around domain walls.

Figure 2(g) shows magnetic-field dependence of $P_c$ in $Ca_2Fe_{1.5}Al_{0.5}O_5$ ($x = 0.5$) when the magnetic field is applied along the $c$ axis (spin easy axis). The electric polarization shows a steplike change across the magnetic-field-induced spin-flop transition, as in the case of $Ca_2FeAlO_5$. The change in $P_c$ across the spin flop transition is slightly larger than $Ca_2FeAlO_5$, which may be related to the composition of $Fe^{3+}$.

The spin easy axis for $x = 0.9$ changes from the $a$ axis to the $c$ axis at low temperatures, as evidenced by Fig. 1(b). At low temperatures, in general, the phase coexistence range

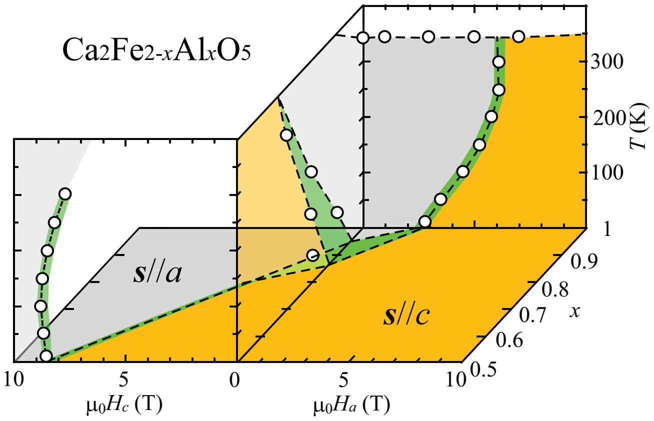

FIG. 3. (Color online) Magnetic phase diagram in $Ca_2Fe_{2-x}Al_xO_5$ ($0.5 \leqslant x \leqslant 1$). Vertical, horizontal, and depth axes are temperature, magnetic field, and Al concentration $x$, respectively. Left and right sides of the horizontal axis indicate the magnetic fields along the $c$ and $a$ axes, respectively. Antiferromagnetic phases with $Fe^{3+}$moments along the $a$ and $c$ axes are denoted as $\mathbf{s}||a$ and $\mathbf{s}||c$, respectively. The $\mathbf{s}||c$ (orange) and $\mathbf{s}||a$ (gray) phases coexist in shaded (green) regions. Circles show critical values determined by measurements of magnetic susceptibility, dielectric constant, and electric polarization.

is expected to spread, because the phase of the second-lowest energy can be metastable even by a small energy barrier between two phases. In such a phase-coexistence state, the domain-wall-driven magnetoelectric effects may become prominent. Figure 2(e) shows magnetic-field dependence of magnetization. A metamagnetic transition takes place in a magnetic field applied along the $a$ axis and the $c$ axis at temperatures above 50 K and below 50 K, respectively. The magnetic field dependence of electric polarization shown in Fig. 2(f) is slightly complicated. The magnetic field dependence of $\Delta P_c$ is gradually changed with increasing temperature. Above 100 K, the electric polarization changes only in $\boldsymbol{H}||a$. As in the case of $x = 1$, a dip structure of $\Delta P_c$ at the phase coexisting state and a finite difference of $P_c$ in between $\boldsymbol{s}||a$ and $\boldsymbol{s}||c$ states are observed. These results indicate that the magnetic-field-induced polarization change originates from the rotation of the spin easy axis of $\mathrm{Fe}^{3+}$ in the $ac$ plane.

There are two possible sources of the observed nonlinear magnetoelectric effect in $\mathrm{Ca_2Fe_{2-x}Al_xO_5}$: One is the spin-dependent metal-ligand hybridization [26–28] and the other is the inverse Dzyaloshinskii-Moriya interaction [2,3,29,30], which may work only when the neighboring spin moments are noncollinear to each other. The $P_c$ value was observed to be different between the $\boldsymbol{s}||c$ state and the $\boldsymbol{s}||a$ state. The difference is ascribed to the spin-direction-dependent metal-ligand hybridization [26–28]. The electric dipole moment along the $c$ axis, $p_c$, at each tetrahedral $\mathrm{FeO_4}$ site is modulated by the $\mathrm{Fe}^{3+}$ moment $\boldsymbol{s}$ as

$$\Delta p_c \propto \sum_{i=1}^{4} C_i \boldsymbol{e}_i \cdot \boldsymbol{e}_c (\boldsymbol{e}_i \cdot \boldsymbol{s})^2. \tag{1}$$

Here $\boldsymbol{e}_i$ is the unit vector pointing from $\mathrm{Fe}^{3+}$ to the $i$th ligand, $\boldsymbol{e}_c$ is the unit vector along the $c$ axis, and $C_i$ is a constant. By using the structure parameter of $\mathrm{Ca_2FeAlO_5}$ [21] and neglecting the bond dependence of the coefficients $C_i$, the averaged $\Delta p_c$ value is predicted to change with rotating $\boldsymbol{s}$ around the $b$ axis (hard axis) from along the $c$ axis to along the $a$ axis, as shown in Fig. 4(a). We also confirmed that the contributions of octahedral sites are negligibly small.

On the other hand, the peak structure of $\Delta P_c$ across the spin flop shown in Figs. 2(b) and 2(f) cannot be explained by this scenario. The most possible origin of the peak is a noncollinear spin arrangement at the domain walls between the coexisting $\boldsymbol{s}||a$ and $\boldsymbol{s}||c$ phases. In general, magnetic-field-induced spin-flop transition is of first-order type. Therefore two phases with different spin directions coexist in the vicinity of the phase boundary. The arrangement of the spin moments should become noncollinear at the boundaries between the two phases with different spin orientations, which are termed domain walls here. In $\mathrm{Ca_2Fe_{2-x}Al_xO_5}$, a fairly strong Dzyaloshinskii-Moriya interaction is expected to act between each $\mathrm{Fe}^{3+}$ pair bonding along the $a$ axis, because the mirror symmetry normal to the $c$ axis is absent. As a result, the spin moment tends to rotate in the $ac$ plane and the cycloidal-type noncollinear spin arrangement in the $ac$ plane may appear to form a Néel type magnetic domain wall [Fig. 4(b)], resulting in the additional electric polarization through the inverse Dzyaloshinskii-Moriya interaction [2,3,29,30], although it is not possible to directly observe the spin structure in an antiferromagnetic domain wall. The apparent qualitative difference in the $\Delta P_c(H)$ behavior between $x = 0.9$ and 1.0 suggests that the relative signs of the two contributions should be opposite for the two compositions.

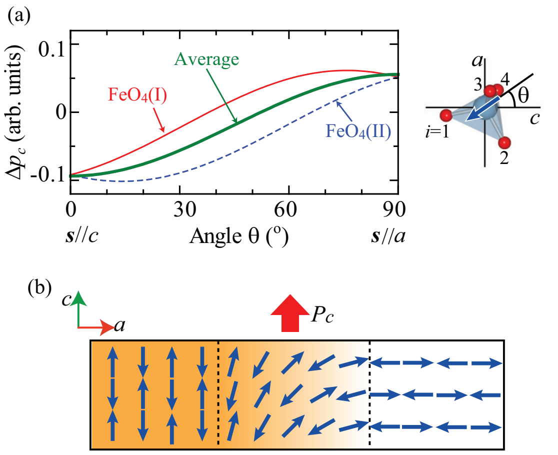

FIG. 4. (Color online) (a) The electric dipole moments along the $c$ axis at tetrahedral sites calculated by the spin-direction-dependent metal-ligand hybridization model. The horizontal axis is an angle $\theta$ between the $c$ axis and $\mathrm{Fe}^{3+}$ spin moment. The $\theta$ values for the $\boldsymbol{s}||c$ and $\boldsymbol{s}||a$ states are 0° and 90°, respectively. (b) Cycloidal-type noncollinear spin arrangement in a Néel type magnetic domain wall in the phase-coexisting state.

Another possible origin of the electric polarization change in the spin flop transition is piezoelectric effect with magnetostriction. Because the crystal structure of $\mathrm{Ca_2Fe_{2-x}Al_xO_5}$ lacks the inversion symmetry, the piezoelectric effect is allowed. If the spin flop is accompanied by magnetostriction, the electric polarization may be changed by the striction through the piezoelectric effect. We performed magnetostriction measurements of $x = 1$ and 0.9 samples and found that the magnetostriction $\Delta L/L$ at the spin flop transition is less than $10^{-6}$ (not shown) and a peak structure is absent at the spin flop transition. Therefore to explain the observed difference in polarization between $\boldsymbol{s}||a$ and $\boldsymbol{s}||c$ phases, one must assume an extremely large piezoelectric effect of $10^{-10}$ C/N, which is as large as in $\mathrm{BaTiO_3}$. This indicates that the electric polarization change in the $\mathrm{Ca_2Fe_{2-x}Al_xO_5}$ system is likely to be caused by the magnetoelectric origin as noted above.

In summary, we investigated the magnetic field induced spin-flop transition and magnetoelectric effect in the noncentrosymmetric antiferromagnetic $\mathrm{Ca_2Fe_{2-x}Al_xO_5}$ system. The collinear antiferromagnetic structures are flopped by the application of a magnetic field along the spin easy axis. The spin-flop transition accompanies anomalies in the electric polarization along the $c$ axis and dielectric constant along the $a$ and the $c$ axes. These anomalies can be explained by the spin-direction dependence of metal-ligand hybridization in tetrahedral sites and the noncollinear spin alignments at the domain walls between the coexisting $\boldsymbol{s}||a$ and $\boldsymbol{s}||c$ phases. These results may open a route to the magnetoelectric effect in a simple collinear antiferromagnet.

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