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Field-induced ferroelectric state in frustrated magnet $CuFe_{1-x}Al_xO_2$

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Abstract
By magnetization and neutron diffraction measurements in an applied magnetic field up to 15 T, we obtained the field (H) versus temperature (T) magnetic phase diagram of a geometrically frustrated triangular lattice antiferromagnet $CuFe_{1-x}Al_xO_2$ with $x = 0.012$, and found that the first-field-induced incommensurate noncollinear magnetic phase of $CuFeO_2$ accompanying spontaneous electric polarization continuously connects, in the H–T phase diagram for $x = 0.012$, with the impurity-induced low-temperature (LT) phase, in which the spontaneous polarization has recently been observed even in zero field. By pyroelectric measurements on the $x = 0.012$ sample in zero magnetic field, we also demonstrated that the thermal evolution of ferroelectric polarization corresponds to that of LT magnetic ordering.

1. Introduction

Interest in researching multiferroics showing magnetoelectric (ME) effects, the co-existence and interplay of magnetism and ferroelectricity, has recently been enhanced, because a new class of multiferroics, such as $TbMnO_3$ [1], that accompany incommensurate noncollinear magnetic ordering, has been recognized experimentally in recent studies on multiferroics. Correspondingly, a new microscopic mechanism [2] for the ME effect based on the spin supercurrent has been theoretically proposed for noncollinear magnets, where electric polarization is induced by spin supercurrent quantum-mechanically generated through the noncollinearity of magnetic orderings.

The magnetic oxide $CuFeO_2$ with delafossite crystal structure has been studied extensively as one of the geometrically frustrated triangular lattice antiferromagnets [3]. Under magnetic fields applied along the hexagonal c-axis, various magnetic phases with collinear commensurate and noncollinear incommensurate magnetic orderings show up at low

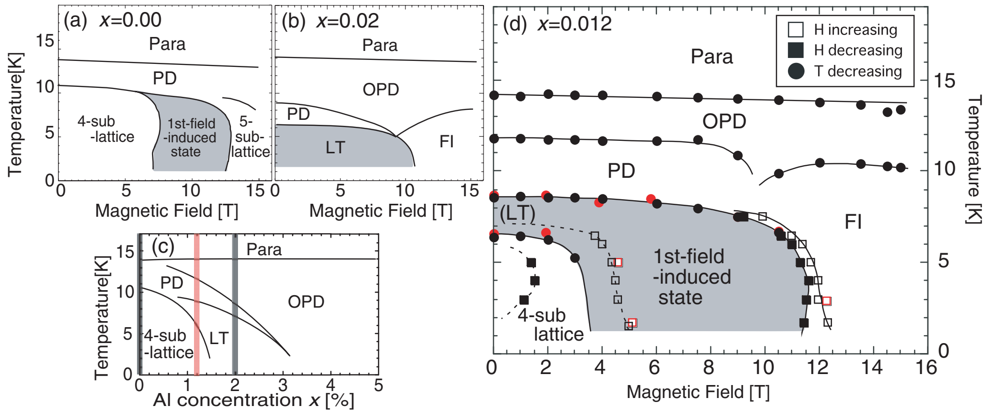

Figure 1. Schematic drawings of H–T magnetic phase diagram of (a) the $x = 0.0$ sample [3] and (b) the $x = 0.02$ sample [5]. (c) Schematic drawings of x–T magnetic phase diagram under zero magnetic field [8]. (d) H–T magnetic phase diagram of the $x = 0.012$ sample. Anomalies found in neutron diffraction measurements and magnetization are depicted by red and black symbols, respectively. Open and closed symbols denote the anomalies that appear with increasing and decreasing H or T, respectively.

temperature, as shown in figure 1(a). Quite recently, spontaneous electric polarization has been found in the first-field-induced phase (7 T $< H <$ 13 T) [4]. Since spontaneous electric polarization appears in neither collinear commensurate four-sublattice nor collinear commensurate five-sublattice phases, but in the first-field-induced phase with noncollinear incommensurate magnetic ordering, a geometrically frustrated magnet $CuFeO_2$ provides a good opportunity to test the spin-supercurrent scenario [2]. The details of the magnetic structure of the first-field-induced state, however, remain unidentified, because accessible magnetic reflection in the (*hk0*) zone under a vertical magnetic field along the c-axis up to 15 T is not a fundamental reflection but only a second-harmonic reflection in our previous neutron diffraction study [3]. Therefore, magnetic structural determination of the first-field-induced state is strongly desired to verify the spin-supercurrent scenario [2] for the ME effect.

Recently, we studied the effect of nonmagnetic Al^{3+} impurity on the magnetic properties of $CuFe_{1-x}Al_xO_2$. As is clearly seen in figure 1(b), quite a small amount of nonmagnetic Al^{3+} impurity, $x = 0.02$, entirely modified the field (H) versus temperature (T) magnetic phase diagram [5], where the four-sublattice ground state disappears and, instead, the low-temperature (LT) phase is impurity-induced. Taking account of the experimental fact that spontaneous electric polarization has also been found in the LT phase of the $x = 0.02$ sample even in zero field [6], it can be inferred that the first-field-induced ferroelectric state of $CuFeO_2$ continuously connects with the impurity-induced LT state under zero magnetic field. Actually, a recent systematic study of the high-field magnetization process of $CuFe_{1-x}Al_xO_2$ ($0 < x < 0.05$) up to 42 T [7] seems to support this prediction.

In the present study, to demonstrate directly that the first-field-induced magnetic state itself is the impurity-induced LT magnetic state, we choose the sample with $x = 0.012$ where both the four-sublattice state, from which the first-field-induced magnetic state is field-induced, and the LT state appear under zero magnetic field, as is seen in our x–T magnetic phase diagram shown in figure 1(c) [8]. By neutron diffraction as well as magnetization measurements using a single crystal of $CuFe_{1-x}Al_xO_2$ with $x = 0.012$, we obtained a H–T magnetic phase diagram for the $x = 0.012$ sample. By comparison with the established H–T magnetic phase diagrams

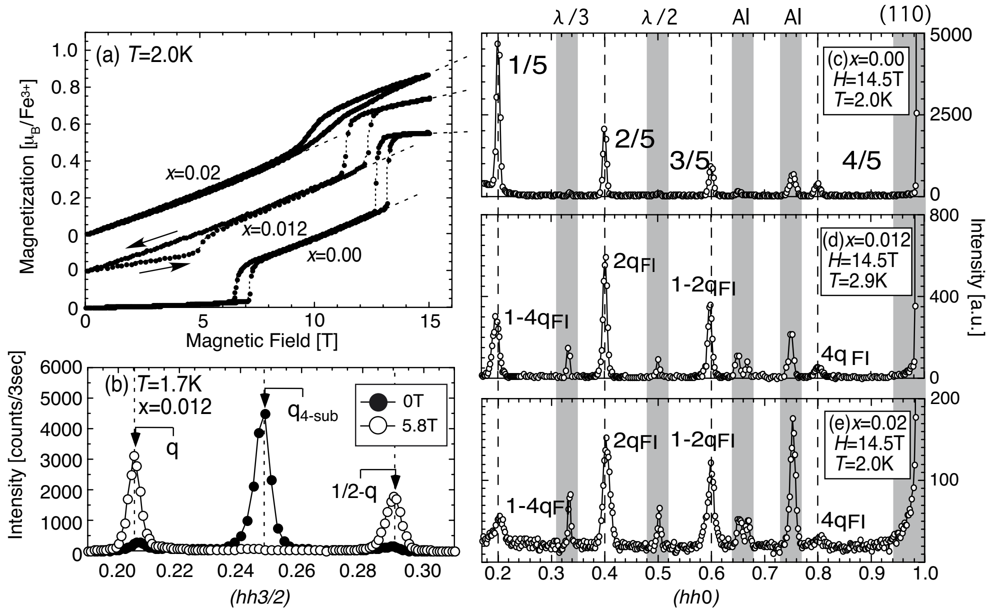

Figure 2. (a) Magnetization curves measured by extraction method at $T = 2.0$ K for $x = 0.00$, 0.012 and 0.02. The data for $x = 0.00$ and 0.02 are taken from [5]. Note that, for the $x = 0.012$ sample, the four-sublattice state does not show up on decreasing the field and the first-field-induced state survives down to zero magnetic field. (b) Typical magnetic diffraction profiles for the $x = 0.012$ sample at 1.7 K along $(hh3/2)$ reciprocal lattice scans in $H = 0$ T and in $H = 5.8$ T. (c)–(e) Typical diffraction profiles at the lowest temperature of $\sim$2 K in $H = 14.5$ T along the $(hh0)$ reciprocal lattice scans for $x = 0.00$, 0.012 and 0.02, where these intensities are normalized by the (110) nuclear Bragg intensity. The data for $x = 0.00$ and 0.02 are taken from [3] and [5], respectively. Contamination peaks are masked by the shaded area.

of the $x = 0.0$ [3] and $x = 0.02$ [5], we conclude that the field-induced ferroelectric state of $CuFeO_2$ continuously connects with the impurity-induced LT state under zero magnetic field, adding pyroelectric measurements on the $x = 0.012$ sample under zero magnetic field.

2. Experimental results and discussions

2.1. Magnetic phase diagram of the $x = 0.012$ sample

A single crystal of $CuFe_{1-x}Al_xO_2$ with $x = 0.012$ was prepared by the floating zone technique. For the magnetization measurements, we mainly used the MagLab^{VSM} vibrating sample magnetometer of Oxford Instruments up to 12 T. For additional high-field measurements up to 15 T, we also used the extraction method. For the neutron diffraction experiments under magnetic field applied along the *c*-axis, we also used the two-axis diffractometer E4 at the Berlin Neutron Scattering Center (BENSC) of the Hahn–Meitner Institut. Using the HM-1 and VM-1 cryomagnets, we provided access to the hexagonal (*hhl*) reciprocal lattice zone with a horizontal magnetic field up to 6 T and a hexagonal (*hk0*) reciprocal lattice zone with a vertical magnetic field of up to 15 T, respectively.

As shown in figure 2(a), with increasing magnetic field at $T = 2$ K, a discontinuous change in the magnetization of the $x = 0.012$ sample is clearly observed at around $H \sim 5$ T, indicating a lowering of the transition field from a four-sublattice to a first-field-induced state with increasing x. Actually, as shown in figure 2(b), in a magnetic field of 5.8 T, four-sublattice magnetic reflection (1/4, 1/4, 3/2) seen in zero magnetic field disappears and, instead, magnetic reflections assigned as $(q, q, 3/2)$ and $(1/2-q, 1/2-q, 3/2)$ with $q \sim 0.205$ newly appear. The appearance of these magnetic Bragg reflections is characteristic to the impurity-induced LT state, where the magnetic diffraction pattern is represented by not the hexagonal bases but the orthorhombic bases [8], suggesting strongly that the first-field-induced magnetic state itself is impurity-induced LT magnetic state.

Here, we would like to emphasize that, using the $x = 0.012$ sample with lower transition field of $H_c \sim 5.0$ T, in present study, we successfully provided access to fundamental magnetic Bragg reflections of the first-field-induced state, in contrast with that accessible magnetic Bragg reflections in our previous study [3] which was only second-harmonic reflections such as $(2q, 2q, 0)$, $(1-2q, 1-2q, 0)$ and $(1/2+2q, 1/2+2q, 0)$. It should be noted that the wavenumber $1/2+2q$ can be recognized as second harmonics of the fundamental wavenumber of $1/2+q$.

As shown in figure 2(a), on further increasing magnetic field at $T = 2$ K, another discontinuous change in magnetization accompanied with hysteresis is clearly observed at around 12 T for the $x = 0.012$ sample. Although this second-field induced state in the $x = 0.012$ sample looks like a five-sublattice state [3] seen in the $x = 0.0$ sample, the magnetization curve dose not show a complete plateau of $\sim 1\ \mu_B$ originating from a collinear commensurate five-sublattice magnetic structure but has a finite slope seen in field-induced (FI) phase [5] of the $x = 0.02$ sample. Actually, a neutron diffraction pattern along the $(hh0)$ scan of the $x = 0.012$ sample shown in figure 2(d) is entirely different from that of the $x = 0.0$ sample shown in figure 2(c), and is rather close to that of the $x = 0.02$ sample shown in figure 2(e). This suggests that the five-sublattice state is easily destroyed and changed into a field-induced (FI) state [5] by a quite small amount of nonmagnetic Al^{3+} impurity. This instability of the five-sublattice state is in contrast to other magnetic phases at low temperatures.

To explore how the first-field-induced ferroelectric state connects with the impurity-induced LT state in the H–T magnetic phase diagram as well as how thermally induced-magnetic phases such as the partially disordered (PD) phase and the oblique partially disordered (OPD) phase locate in the high-temperature region of the H–T magnetic phase diagram, we systematically performed measurements of the temperature dependence of the magnetization, $M(T)$, as shown in figures 3(a) and (b), in addition to measurements of $M(H)$ at various temperatures. Here, the transition temperatures are defined by anomalies in the temperature derivative of $M(T)$, as shown in figures 3(c) and (d).

The anomalies found in the present neutron diffraction measurements, as well as the magnetization measurements, are depicted in the H–T phase diagram shown in figure 1(d). By comparison with the established H–T magnetic phase diagram for $x = 0.0$ [3] and $x = 0.02$ [5], we conclude that the field-induced ferroelectric state of $CuFeO_2$ *continuously* connects with the impurity-induced LT state under zero magnetic field. Namely, the first-field-induced magnetic state itself is the impurity-induced LT magnetic state.

Here, we should mention the orthogonal-double-sinusoidal (ODS) magnetic structure [9] that has been recently proposed for the impurity-induced LT magnetic state, because the spin-supercurrent scenario can be applied to the ODS magnetic structure to explain the electric polarization induced in the LT phase. Applying the spin-supercurrent scenario [2] to the ODS magnetic structure, no spontaneous electric polarization is predicted, in contradiction to the experimental fact that spontaneous polarization is found in the LT phase of the $x = 0.02$ sample [6]. This is because the ODS magnetic structure might be misidentified for the LT phase [6].

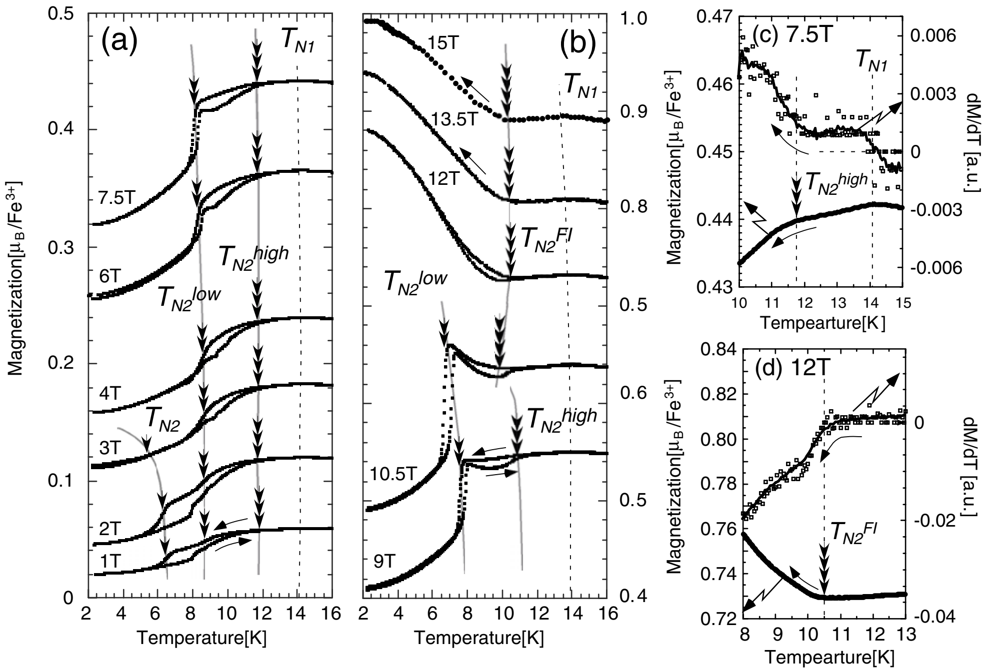

Figure 3. (a) and (b) Temperature dependence of magnetization, $M(T)$, at several magnetic fields applied along the hexagonal c-axis. Note that $M(T)$ in $H = 13.5$ and 15 T are available only for a decreasing temperature process. The single, double, triple and quadruple arrows denote the magnetic phase transition temperature T_{N2} (first-field-induced state → four-sublattice), T_{N2}^{low} (PD → first field-induced state), T_{N2}^{high} (OPD → PD), T_{N2}^{FI} (OPD → FI). The dotted lines denote T_{N1} (Para → OPD). (c) and (d) The temperature derivative of $M(T)$ in $H = 7.5$ and 12 T around the phase transition temperatures. All the phase transition temperature is defined by anomalies in the temperature derivative.

2.2. *Pyroelectric and neutron diffraction measurements in zero magnetic field*

In the present neutron diffraction experiments, we did not succeed in determining the magnetic structure of the first-field-induced state to test the spin-supercurrent scenario [2], because only two magnetic reflections of $(q, q, 3/2)$ and $(-q, -q, -9/2)$ were accessible under the horizontal magnetic field of a HM1 cryomagnet. However, in order to discuss the ferroelectricity of $CuFe_{1-x}Al_xO_2$ along the spin-supercurrent scenario, it is necessary to check if the appearance of spontaneous electric polarization corresponds to a degree of magnetic order in an LT magnetic state or a first-field-induced magnetic state with noncollinear incommensurate magnetic structure. Thus, using pyroelectric and additional neutron diffraction measurements on the sample with $x = 0.012$ under zero magnetic field, we measured the temperature dependence of the spontaneous electric polarization and magnetic ordering in the LT phase.

For the pyroelectric measurements, the single-crystal sample was cut into a thin plate (0.4 mm × 1.2 mm) parallel to the hexagonal [110] plane. The polling electric field to align the electric domains was typically 300 kV m^{-1} and was applied along $\langle 110 \rangle$ axis. For the additional neutron diffraction measurements in zero field, we used the triple-axis spectrometer HQR of JRR-3M at the Japan Atomic Energy Research Institute.

The temperature dependence of the magnetic diffraction profiles at typical temperatures is shown in figures 4(a)–(c), and the temperature variation of the integrated intensity of

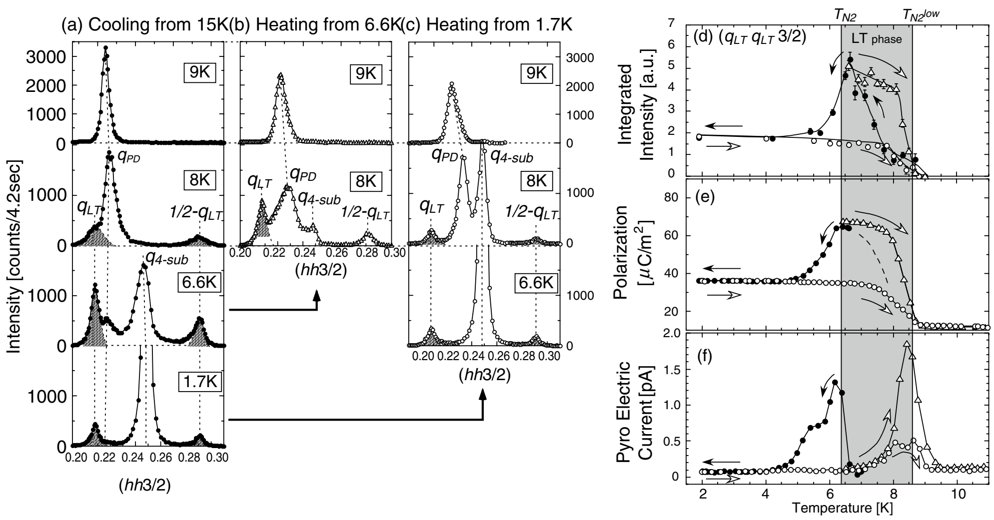

Figure 4. Temperature dependence of the magnetic diffraction profiles along the $(hh3/2)$ reciprocal lattice scan under zero field (a) on cooling down to the lowest temperature of 1.7 K, (b) on heating after cooling down to $T = 6.6$ K, and (c) on heating after cooling down to $T = 1.7$ K. Note that, at a temperature of 6.6 K, the intensity of the q_{LT}-reflection takes its maximum. The q_{LT} and $1/2$-q_{LT} reflections are hatched to enhance the visibility of their thermal evolution in the LT phase. (d) The temperature dependence of the integrated intensity of the $(q_{LT}\ q_{LT}3/2)$ magnetic Bragg reflections corresponding to the temperature sequence taken in (a)–(c). T_{N2} and T_{N2}^{low} are defined by magnetic susceptibility, respectively. ((e) and (f)) The temperature dependence of the pyroelectric polarization and current. It should be noted that a finite polarization above T_{N2}^{Low} exists, as seen in (e). This finite polarization exists up to $\sim T = 20$ K beyond the magnetic phase transition temperature of T_{N1} and is, therefore, irrelevant to magnetic ordering.

q_{LT}-reflection is summarized in figure 4(d). As was reported in previous work on the $x = 0.0126$ sample [8], the q_{LT}-reflection (i.e. LT magnetic ordering) appears only for a decreasing temperature process in the temperature region between T_{N2} and T_{N2}^{low}, and for an increasing temperature process the magnetic phase transition from a four-sublattice state to a PD state occurs directly. In addition to this intrinsic temperature dependence of LT ordering with significant thermal hysteresis, extrinsic macroscopic inhomogeneity, however, brings concomitant monotonic temperature variation of LT magnetic ordering surviving down to the lowest temperature, as is seen in the diffraction profile at $T = 1.7$ K shown in figure 4(a), because the x variation of the transition temperature $T_{N2}(x)$ is very steep around $x \sim 0.013$.

Keeping the above-mentioned temperature dependence of intensity of LT ordering in mind, we now present the results of pyroelectric measurements. As shown in figure 4(e), we successfully observed the spontaneous electric polarization, P, whose temperature dependence corresponds well to that of the integrated intensity of the q_{LT}-reflection with thermal hysteresis mentioned above. Note that, since electric poling is necessary to align the electric domains, the measurements of P must be started at $T = 6.6$ K, at which LT magnetic ordering shows its maximum in the cooling process. Thus, temperature dependence of P down to $T = 6.6$ K is not able to be measured in our experiments, as is denoted by a dashed line in figure 4(e). Furthermore, we measured the temperature variation of P from $T = 6.6$ K with increasing temperature. As seen in figures 4(d) and (e), P rapidly decreases around $T = 8$ K, corresponding to a decrease in the intensity of q_{LT}-reflection measured in the same temperature sequence. We also measured the pyroelectric current and found the peaks corresponding to the temperature variation of P. It should be noted that we also measured P along the $\langle 001 \rangle$ axis and found no significant signal, being consistent with the previous works [4, 6].

3. Conclusion

We have performed magnetization and neutron diffraction experiments in an applied magnetic field up to 15 T, in order to obtain the H–T magnetic phase diagram of a geometrically frustrated triangular lattice antiferromagnet $CuFe_{1-x}Al_xO_2$ with $x = 0.012$, and found that the first-field-induced incommensurate noncollinear magnetic phase of $CuFeO_2$ accompanying spontaneous electric polarization [4] connects continuously, in the H–T phase diagram for $x = 0.012$, with the impurity-induced low-temperature (LT) phase, in which the spontaneous polarization is recently observed even in zero field [6]. We also demonstrated that the thermal evolution of ferroelectric polarization corresponds to that of LT magnetic ordering by pyroelectric measurements on the $x = 0.012$ sample in zero magnetic field.

Acknowledgments

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