Electric field dependence of magnetic correlation in magneto-electric multiferroic CuFe$_{1-x}$Al$_x$O$_2$

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Abstract. Magneto-electric (ME) multiferroic CuFeO$_2$ and slightly diluted CuFe$_{1-x}$Al$_x$O$_2$ are rare examples of ME-multiferroics whose ferroelectricity originates from the 'proper-screw' type magnetic ordering. Recent polarized neutron diffraction studies have revealed that there is a one-to-one correspondence between the spin helicity and the polarity of induced ferroelectric polarization. In the present study, we have performed unpolarized neutron diffraction measurements under applied poling electric field up to $\sim$ 2.2 MV/m using CuFe$_{1-x}$Al$_x$O$_2$ ($x = 0.02$) sample, which undergoes ferroelectric transition at $T_c \sim$ 7 K in zero magnetic field. The present results revealed that the shape of the magnetic diffraction profile in the ferroelectric phase significantly depends on applied poling electric field, while the integrated intensity of the magnetic reflection does not. This implies that the poling electric field affects the magnetic correlation through the local ME-coupling in this system.

1. Introduction

A triangular lattice antiferromagnet CuFeO$_2$ (CFO) has been intensively investigated as a new class of magneto-electric (ME) multiferroics, since the discovery of the ferroelectricity in a magnetic-field- or impurity-induced phase[1, 2, 3]. Unlike recently explored ME-multiferroics with cycloidal magnetic structures, such as TbMnO$_3$[4], CFO and slightly diluted CuFe$_{1-x}$Al$_x$O$_2$ (CFAO) exhibit a proper-screw type magnetic structure with a magnetic propagation wave vector of $(q, q, q)$ where $q \sim 0.21$, in the ferroelectric phase[5]. Recent polarized neutron diffraction studies have revealed that the spin-helicity, left-handed (LH) or right-handed (RH) helical arrangement of spins, determines the polarity of the local ferroelectric polarization emerging along the helical axis (the hexagonal [110] axis)[6, 7].

In the present study, we have investigated the electric field dependence of the magnetic ordering in CFAO($x = 0.02$), which exhibits ferroelectric phase below $\sim$ 7 K in zero magnetic field. In this paper, we refer to this ferroelectric phase as ferroelectric incommensurate-magnetic (FE-ICM) phase. Although the previous studies have already revealed the one-to-one correspondence between the spin-helicity and polarity of the local ferroelectric polarization in this system[6, 7], further details on electric field dependences of the magnetic domain structure and/or the magnetic correlation have not yet been investigated. We thus performed unpolarized neutron diffraction measurements with applied electric fields up to $\sim$ 2.2 MV/m.
Figure 1. (a) Crystal structure of CuFeO$_2$. (b) Poling electric field ($E_p$) dependences of the integrated intensities of $(\frac{1}{2} - q, \frac{1}{2} - q, \frac{3}{2})$, $(\frac{1}{2} - q, -1 + 2q, \frac{1}{2})$ and $(-1 + 2q, \frac{1}{2} - q, \frac{3}{2})$ magnetic reflections, which correspond to the volume fractions of the three magnetic domains. Inset shows the directions of the $c^*$-projections of the three equivalent magnetic modulation wave vectors. [(c-1),(c-2)] Comparisons between the diffraction profiles measured under applied and zero electric fields, (c-1) in the PD phase ($T = 7.1$ K) and (c-2) the FE-ICM phase ($T = 2.5$ K).

2. Experimental details

Single crystals of CFAO ($x = 0.02$) of nominal compositions were prepared by the floating zone method[8]. To survey anisotropy in the electric field dependence of the magnetic ordering, we prepared two disc-shaped samples ($\sim 3 \times 3 \times 1$ mm$^3$); one has the widest surface normal to the [110] axis ($E_p$$\parallel$[110] sample), the other has the widest surface normal to the [110] axis ($E_p$$\parallel$[110] sample). Silver paste was applied to the large surfaces to form the electrodes.

Neutron diffraction measurements on CFAO ($x = 0.02$) were carried out using a four-circle neutron diffractometer FONDER(T2-2) and triple-axis neutron spectrometers HQR(T1-1) and HER(C1-1) installed at JRR-3, Tokai, Japan. The samples were mounted in a closed-cycle He-gas refrigerator and a pumped $^4$He cryostat in the four-circle and triple-axis neutron diffraction measurements, respectively. Before each neutron diffraction measurement, we performed cooling with an applied poling electric field ($E_p$) from 15 K to 2.5 $\sim$ 3.0 K.

3. Results and discussions

In CFO systems, the magnetic ordering with the wave vector of $(q, q, \frac{3}{2})$ results in three magnetic domains, whose wave vectors of $(q, q, \frac{3}{2})$, $(q, -2q, \frac{3}{2})$ and $(-2q, q, \frac{3}{2})$ are crystallographically equivalent to each other, because of the threefold rotational symmetry along the hexagonal $c$ axis. (see Fig. 1(a).) To elucidate the electric field dependence of the volume fractions of the three magnetic domains, we have performed neutron diffraction measurements on using the four-circle neutron diffractometer FONDER and the $E_p$$\parallel$[110] sample.

After cooling the sample under an applied poling electric field along the [110] direction, we measured integrated intensities of three equivalent magnetic reflections, specifically $(\frac{1}{2} - q, \frac{1}{2} - q, \frac{3}{2})$, $(\frac{1}{2} - q, -1 + 2q, \frac{1}{2})$ and $(-1 + 2q, \frac{1}{2} - q, \frac{3}{2})$ magnetic reflections, which correspond to the volume fractions of the three magnetic domains. Since the directions of the ferroelectric polarization vectors in the three magnetic domain are different from each other, we anticipated that an applied poling electric field along the [110] direction populates the magnetic domains
Figure 2. [(a-1),(b-1)] Schematic drawing of the magnetic structure in the FE-ICM phase and the directions of the local ferroelectric polarization and the poling electric fields for the (a-1) \( E_p^{\parallel[110]} \) and (b-1) \( E_p^{\parallel[\overline{1}10]} \) samples. [(a-2),(b-2)] Comparisons between the diffraction profiles measured under applied and zero poling electric fields, (a-2) for the \( E_p^{\parallel[110]} \) and (b-2) \( E_p^{\parallel[\overline{1}10]} \) samples, at \( T = 3.0 \) K. Horizontal bars represent the experimental resolution. (c) \( E_p \)-dependence of the half width at half-maximum obtained from \( (q, q, \frac{3}{2}) \) magnetic diffraction profiles of the \( E_p^{\parallel[110]} \) sample at \( T = 3.0 \) K and that of asymmetry in the spin helicity (taken from Ref. [7]).

with the wave vector \( (q, q, \frac{3}{2}) \) so that the macroscopic ferroelectric polarization is maximized. However, no significant \( E_p \)-dependences were detected in the intensities of the three magnetic reflections, as shown in Fig. 1(b). Instead, we found that the shape of the magnetic diffraction profile in the FE-ICM phase significantly depends on \( E_p \), as shown in Fig. 1(c-2), while that in the thermally induced partially disordered (PD) magnetic phase does not, as shown in Fig. 1(c-1). These results indicate that an application of the poling electric field does not affect the volume fractions of the three magnetic domains, but does affect the magnetic correlation in the FE-ICM phase.

In order to investigate the electric field effect on the magnetic correlation in the FE-ICM phase in detail, we have performed neutron diffraction measurements under applied electric field using triple-axis spectrometers HQR and HER. We used the \( E_p^{\parallel[110]} \) and \( E_p^{\parallel[\overline{1}10]} \) samples for these measurements. Figures 2(a-2) and 2(b-2) show the comparisons between the magnetic diffraction profiles of the \( (H, H, \frac{3}{2}) \) reciprocal lattice scans measured after cooling with applied and zero poling electric fields from 15 K to 3.0 K, for the \( E_p^{\parallel[110]} \) and \( E_p^{\parallel[\overline{1}10]} \) samples. We found that a poling electric field applied parallel to the helical axis sharpens the diffraction profile in the FE-ICM phase, but that applied perpendicular to the helical axis does not. We also found that the half width at half-maximum (HWHM) of the diffraction profile in the \( E_p^{\parallel[110]} \) sample monotonically decreases with increasing \( E_p \), as shown in Fig. 2(c); specifically, the HWHM was reduced by about 20% at 1600 kV/m, compared with the value at zero electric field. These results suggest that the magnetic correlation length, which is approximately proportional to an inverse of the HWHM, increases with increasing poling electric field along the [110] axis, along which the ferroelectric polarization emerges in the magnetic domains having the propagation wave vector of \( (q, q, \frac{3}{2}) \).

In the previous polarized neutron studies[6, 7], Nakajima et al. have revealed that the asymmetry of the volume fractions having the RH- and LH-helical magnetic orderings varies with \( E_p \) applied along [110] axis. In Fig. 2(c), we also show the \( E_p \)-dependence of the asymmetry in CFAO(\( x = 0.015 \)) taken from Ref. [7]. Here, we employed the definition of the asymmetry, \( D \),
used in Ref. [7]; specifically, $D = (V_{\text{LH}} - V_{\text{RH}})/(V_{\text{LH}} + V_{\text{RH}})$, where $V_{\text{RH}}$ and $V_{\text{LH}}$ are the volume fractions having LH- and RH-helical magnetic ordering in the $(q, q, \frac{3}{2})$-domains. Comparing the $E_p$-dependences of the HWHM and $D$, we found a correlation between them. Specifically, around $E_p = 0$, the value of $D$ rapidly increases and the HWHM significantly decreases with increasing $E_p$. On the other hand, in the relatively high field region where the LH-helical magnetic ordering almost dominates in the $(q, q, \frac{3}{2})$-domains, both of the HWHM and $D$ tend to be insensitive to $E_p$.

On the basis of these results, we conclude that the $E_p$-dependence of the magnetic correlation length observed in the present measurements reflects that of average size of the ferroelectric domains. This is because an application of the poling electric field should enlarge ferroelectric domains having spontaneous ferroelectric polarization parallel to it, and the sizes of the ferroelectric and magnetic domains must be closely related to each other through the local ME-coupling.

It is worth mentioning here that this $E_p$-dependence of the magnetic correlation length might not be clearly observed in the typical multiferroics such as TbMnO$_3$, but is observed in CFAO. This is because the magnetic correlation in the ferroelectric phase of CFAO ($x = 0.02$) is originally disturbed by site-random Al$^{3+}$-substitutions, and therefore the change in the magnetic correlation length was easily detected by neutron diffraction measurements.

It should be also noted that an unpolarized neutron diffraction profiles of $(q, q, \frac{3}{2})$ reflection is a superposition of the magnetic reflections from the RH- and LH-helical magnetic ordering. In order to elucidate the $E_p$-dependence of the magnetic correlation in each of the RH- and LH-helical orderings separately, a spin-helicity-selective measurement, that is, a polarized neutron diffraction measurement, is required.

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