Electric Polarization Induced by a Proper Helical Magnetic Ordering in a Delafossite Multiferroic CuFe$_{1−x}$Al$_x$O$_2$

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Multiferroic CuFe$_{1−x}$Al$_x$O$_2$ ($x = 0.02$) exhibits a ferroelectric field accompanying a proper helical magnetic ordering below $T = 7$K under zero magnetic field. By polarized neutron diffraction and pyroelectric measurements, we have revealed a one-to-one correspondence between the spin helicity and the direction of the spontaneous electric polarization. This result indicates that the spin helicity of the proper helical magnetic ordering is essential for the ferroelectricity in CuFe$_{1−x}$Al$_x$O$_2$. The induction of the electric polarization by the proper helical magnetic ordering is, however, cannot be explained by the Katsura-Nagaosa-Balatsky model, which successfully explains the ferroelectricity in the recently explored ferroelectric helimagnets, such as TbMnO$_3$. We thus conclude that CuFe$_{1−x}$Al$_x$O$_2$ is a new class of magnetic ferroelectrics.

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Novel types of couplings between dielectric property and magnetism, which produce colossal magnetoelectric (ME) effects, have been extensively investigated since a gigantic ME effect was discovered in RManO$_3$ (R is a rare earth material) [1]. Among several types of couplings between spins and electric polarizations, a ferroelectricity induced by noncollinear spin arrangements has been most widely investigated experimentally and theoretically [2, 3, 4, 5, 6, 7, 8]. Katsura, Nagaosa and Baratsky (KNB) proposed that the local electric dipole moment $p$, which arises between neighboring two spins $S_i$ and $S_{i+1}$, can be described in the form of $p \propto e_{i,i+1} \times (S_i \times S_{i+1})$, where $e_{i,i+1}$ is a unit vector connecting two spins [2]. This formula successfully explains the ferroelectric property in cycloidal or conical magnetic orderings of some transition metal oxides, such as RManO$_3$ ($R=$Tb, Tb$_{1−x}$Dy$_x$), Ni$_2$V$_2$O$_8$, MnWO$_4$ and CoCr$_2$O$_4$. Moreover, a recent polarized neutron diffraction study on TbMnO$_3$ demonstrated that the spin helicity, clockwise or counterclockwise, correlates with the direction of the electric polarization, as predicted in the formula [2]. It is, however, recently reported that ferroelectricity in a helical magnetic ordering of a delafossite multiferroic CuFe$_{1−x}$Al$_x$O$_2$ cannot be explained by the above formula [10]. Therefore, CuFe$_{1−x}$Al$_x$O$_2$ provides an opportunity to explore another type of spin-polarization coupling.

CuFeO$_2$, which is one of model materials of a triangular lattice antiferromagnet, has been extensively investigated as a geometrically frustrated spin system for last fifteen years [11, 12, 13]. The ground state of CuFeO$_2$ is a collinear commensurate 4-sublattice ($\uparrow\uparrow\downarrow\downarrow$) state with the magnetic moments along the $c$ axis, which is normal to the triangular lattice layers, in spite of the Heisenberg spin character expected from the electronic configuration of Fe$^{3+}$ ($S = \frac{5}{2}$, $L = 0$). When a magnetic field is applied along the $c$ axis at low temperature, CuFeO$_2$ exhibits a multi-step magnetization process consisting of several magnetization plateaus and slopes, which is accompanied by stepwise changes of lattice constants [14, 15]. Since Kimura and co-workers discovered a spontaneous electric polarization in the first field-induced phase of CuFeO$_2$, which emerges along the direction perpendicular to the $c$ axis [11], CuFeO$_2$ has also been investigated as a candidate of novel multiferroic materials. Recent studies on the slightly diluted system CuFe$_{1−x}$Al$_x$O$_2$ showed that only a few percent dilution of Fe$^{3+}$ sites with nonmagnetic Al$^{3+}$ ions considerably reduces the transition field from the 4-sublattice phase to the field-induced ferroelectric phase. Moreover, the ferroelectric phase shows

![FIG. 1: (Color online) Schematic illustrations of the experimental configurations and the relationship between the direction of the poling electric field $E$ and the proper helical magnetic structure in the FEIC phase for (a) the $E_{||[110]}$ sample and (b) the $E_{||[110]}$ sample.](image-url)
up even under zero field in the concentration region of $0.014 < x < 0.030$ [17, 18, 19]. Quite recently, the magnetic structure in the ferroelectric phase was elucidated to be an antiferromagnetically-stacked proper helical structure with an incommensurate propagation wave vector $(q, q, 0)$ where $q \sim 0.21$ [10]. In this letter, we refer to this ferroelectric phase as ferroelectric incommensurate (FEIC) phase. This magnetic structure, however, cannot lead to a finite uniform electric polarization through the formula $p \propto e_{i,i+1} \times (S_i \times S_{i+1})$, because the direction of $e_{i,i+1}$ is parallel to the direction of $S_i \times S_{i+1}$ in average. Nevertheless, the spin helicity, a right-handed (RH) or left-handed (LH) proper helical arrangement of spins, is expected to correlate with the direction of the electric polarization, because space inversion operation flips the spin helicity, as well as the direction of electric polarization. In present work, we thus performed polarized neutron diffraction and pyroelectric measurements using CuFe$_{1-x}$Al$_x$O$_2$ samples with $x = 0.02$, which exhibits the ferroelectric ordering below $T = 7K$, in order to elucidate the relationship between the spin helicity and the electric polarization.

A single crystal of CuFe$_{1-x}$Al$_x$O$_2$ with $x = 0.02$ of nominal composition was prepared by the floating zone technique [20], and cut into two pieces with disk shapes; one of them has the widest surface normal to the [110] axis ($E_{[110]}$ sample), the other has that normal to the [110] axis ($E_{[10]}$ sample). The experimental configurations for these samples are illustrated in Figs. 1(a) and (b). Silver paste was pasted on the widest surface of each sample to make the electrodes. The polarized neutron diffraction measurements were carried out at the triple-axis neutron spectrometer PONTA installed by University of Tokyo at JRR-3 in Japan Atomic Energy Agency. The incident polarized neutron with the energy of 34.05 meV was obtained by a Heusler (111) monochromator. The flipping ratio of the polarized neutron beam was 19.0, and the polarization vector of the incident neutron, $P_N$, was set to be parallel (or antiparallel) to the scattering vector, $\kappa$, by a guide-field of a helmholtz coil and a spin flipper. The collimation was 40’-40’-40’-40’, and a pyrolytic graphite analyzer was employed. The sample was mounted in a pumped $^3$He cryostat with the (hhl) scattering plane. Note that, in the present experiment, we employed a conventional hexagonal basis as was in the previous works, while CuFe$_{1-x}$Al$_x$O$_2$ originally has a trigonal (rhombohedral) crystal structure. The definition of the hexagonal basis is shown in Fig. 2(a). For the measurements of the spontaneous electric polarization $P_s$, pyroelectric current was measured under zero electric field with increasing temperature, using an electrometer (Keithley 6517A). Before each neutron diffraction (or pyroelectric) measurement, we performed a proper cooling with applied electric field from 20K to 2K.

Before discussing the results of the present measurements, we briefly review the scattering cross section for polarized neutrons. Let us assume that scattering system consists of RH- and LH-proper helical magnetic orderings with a propagation wave vector $q$. According to the Blume’s notation [21], the scattering cross section for a pair of magnetic satellite reflections located at $\tau \pm q$, where $\tau$ is a reciprocal lattice vector, is described as follows:

\[
\frac{d\sigma}{d\Omega} |_{\tau \pm q} \propto S(\kappa) \{1 + (\vec{C} \cdot \hat{\kappa})^2\} (V_{RH} + V_{LH}) + 2(p_N \cdot \hat{\kappa})(\vec{C} \cdot \hat{\kappa})(V_{RH} - V_{LH}),
\]

where $S(\kappa)$ is the factor depending on the magnetic structure factor, $V_{RH}$ and $V_{LH}$ are the volumes of the RH- and LH-helical orderings, respectively, $\hat{\kappa}$ is a unit vector of $\kappa$, $|P_N| = 1$, and $\vec{C}$ is a unit vector corresponding to the spin helicity, (referred as ‘vector spin chi-

\[\text{FIG. 2: (Color online) (a) The hexagonal basis represented on the Fe}^{3+} \text{ triangular layer lattice. Open and filled blue circles denote O}^{2-}\text{ ions located above and below the Fe}^{3+} \text{ layer, respectively. (b) The location of the magnetic reflections surveyed in present measurement in (HHL) zone. (c-1)-(f-2) The diffraction profiles of (H, H, \frac{\tau}{2}) \text{ reciprocal lattice scans for the (q, q, \frac{\tau}{2}) and (\frac{\tau}{2} - q, \frac{\tau}{2} - q, \frac{\tau}{2}) magnetic Bragg reflections at } T = 2K \text{ in the FEIC phase.}\]
rality' in Ref. [9]) which is defined so that $S_i, S_{i+1}$ and $C$ in this order form a right-handed coordinate system (see Fig. 3(a)). Note that the above expression of the scattering cross section includes both the 'spin-flip' and 'non spin-flip' scatterings, and thus polarization analysis for scattered neutrons is not necessary. In the present experiment, $C$ is parallel (antiparallel) to the [110] direction for the RH- (LH-) proper helical ordering, and the cross sections of two magnetic Bragg reflections at $(q, q, 0)$ and $(\frac{1}{2} - q, \frac{1}{2} - q, \frac{1}{2})$, which are mainly surveyed in the present measurements, correspond to $(d\sigma/d\Omega)_{\tau + q}$ and $(d\sigma/d\Omega)_{\tau - q}$, respectively (see Fig. 2(b)). In this case, the imbalance between $V_{RH}$ and $V_{LH}$ is expressed as follows:

$$\frac{V_{RH} - V_{LH}}{V_{RH} + V_{LH}} = A(\kappa) \left( \frac{I_{ON} - I_{OFF}}{I_{ON} + I_{OFF}} \right),$$

(2)

where $I_{ON}$ and $I_{OFF}$ are the intensities of a magnetic Bragg reflection measured when the spin flipper is on ($P_N \parallel -\kappa$) and off ($P_N \parallel \kappa$), respectively. The values of the proportional constant $A(\kappa)$ for the $(q, q, \frac{3}{2})$ and $(\frac{1}{2} - q, \frac{1}{2} - q, \frac{1}{2})$ magnetic reflections are approximately 1 and $-1$, respectively.

In Fig. 2 we now show typical diffraction profiles of magnetic reflections in the FEIC phase ($T = 2 K$). After cooling the $E_{[110]}$ sample under zero electric field, as shown in Figs. 2(c-1) and (c-2), there was no difference between $I_{ON}$ and $I_{OFF}$ for both of the $(q, q, \frac{3}{2})$ and the $(\frac{1}{2} - q, \frac{1}{2} - q, \frac{1}{2})$ reflections. This result indicates that the fractions of the RH- and LH-helical magnetic orderings were equal to each other. After cooling the $E_{[110]}$ sample under a poling electric field (120 kV/m) parallel to the [110] direction, $I_{ON}$ was greater than $I_{OFF}$ for the $(q, q, \frac{3}{2})$ reflection, and this relationship between $I_{ON}$ and $I_{OFF}$ was reversed for the $(\frac{1}{2} - q, \frac{1}{2} - q, \frac{1}{2})$ reflection, as shown in Figs. 2(d-1) and (d-2). By a reversal of the direction of the poling electric field applied on cooling, this relationship between $I_{ON}$ and $I_{OFF}$ for each magnetic satellite was reversed, as shown in Figs. 2(e-1) and (e-2). No imbalance between $I_{ON}$ and $I_{OFF}$, however, was observed for the $E_{[110]}$ sample after cooling under the poling electric field (128 kV/m) parallel to the [110] direction, as shown in Figs. 2(f-1) and (f-2). These results show that the poling electric field along the [110] axis induces an imbalance between the fractions of the RH- and LH-helical orderings, but the poling electric field along [110] axis does not. Taking account of the fact that the poling electric field along the [110] axis also induces the macroscopic electric polarization along the [110] axis (see Fig. 3(b)), we conclude that a proper helical magnetic ordering generates an electric polarization along the helical axis, and moreover, there is the one-to-one correspondence between the spin helicity and the direction of electric polarization, as illustrated in Fig. 3(a).

Although the poling electric field along the [110] axis also induces the macroscopic electric polarization along the [110] axis, as shown in Fig. 3(b), this can be ascribed to the existence of three magnetic domains reflecting the trigonal three-fold symmetry of the crystal structure (see Fig. 3(a)). When the electric polarization emerges along the [110] axis, the imbalance between the fractions of the RH- and LH-helical ordering must be induced in the domains out of the scattering plane, as illustrated in Fig. 3(c).
In summary, we performed polarized neutron diffraction and pyroelectric measurements on the delafossite multiferroic CuFe$_{1-x}$Al$_x$O$_2$ with $x = 0.02$, and demonstrated that the proper helical magnetic ordering of CuFe$_{1-x}$Al$_x$O$_2$ generates a spontaneous electric polarization parallel to the helical axis. This indicates that the local spin-polarization coupling in CuFe$_{1-x}$Al$_x$O$_2$ cannot be explained by the KNB-model ($\mathbf{p} \propto \mathbf{e}_{i,i+1} \times (\mathbf{S}_i \times \mathbf{S}_{i+1})$). Nevertheless, the results of the present study revealed a one-to-one correspondence between the spin helicity and the direction of the electric polarization, indicating that the spin helicity of the proper helical magnetic ordering is essential for the ferroelectricity in CuFe$_{1-x}$Al$_x$O$_2$. Quite recently, Arima proposed that a proper helical magnetic order can generate ferroelectricity through the variation in the metal-ligand hybridization with spin-orbit coupling [22]. The present results suggest that this mechanism is applicable to CuFe$_{1-x}$Al$_x$O$_2$. We thus conclude that CuFe$_{1-x}$Al$_x$O$_2$ is a new class of magnetic ferroelectrics, which will pave another way to design multiferroic materials.

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