Incommensurate Orbital Modulation in Multiferroic CuFeO$_2$

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CuFeO$_2$ is one of the multiferroic materials and is the first case that the electric polarization is not explained by the magnetostriction model or the spin-current model. We have studied this material using soft x-ray resonant diffraction and found that superlattice reflection 0, 1-2q, 0 appears in the ferroelectric and incommensurate magnetic ordered phase at the Fe $L_{2,3}$ absorption edges and moreover that the rotation of the x-ray polarization such as from $\sigma$ to $\pi$ or from $\pi$ to $\sigma$ is allowed at this reflection. These findings definitely provide direct evidence that the 3d orbital state of Fe ions has a long range order in the ferroelectric state and support the spin-dependent d-p hybridization mechanism.

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The discovery of ferroelectricity induced by a magnetic order in TbMnO$_3$ [1] has attracted much attention for magnetoelectric (ME) multiferroic materials. This new class of ferroelectric materials are essentially different from conventional ones like BiFeO$_3$ [2] where magnetism and ferroelectricity are independent to each other in principle. The ferroelectricity found in the ME multiferroic materials appears as a result of the phase transition inducing such a magnetic order that breaks the crystal symmetry. Geometrical spin frustration has been recently recognized to be one of the keys for the ME multiferroic materials. The frustrated system, owing to the vast degeneracy arising from competing magnetic interactions, often displays complex magnetic orders at low temperatures like non-centrosymmetric noncollinear or long-period-modulated collinear magnetic orders. These exotic magnetic structures sometimes break the crystal symmetry and can be an origin of the ferroelectricity.

CuFeO$_2$ (CFO), which is one of the model materials of a triangular lattice antiferromagnet, has been extensively investigated as a geometrically frustrated spin system [3,4]. Since the recent discovery of ferroelectricity in the first magnetic-field-induced phase [5], CFO has attracted more attention as a distinct class of ME multiferroics. Three possible mechanisms [5] have been proposed for the coupling between magnetic and electric moments for the ME multiferroic materials: (1) magnetostriction, (2) spin current [2], and (3) spin-dependent d-p hybridization. CFO is the first case that the electric polarization is not explained by either the first or the second model but is possibly explained by the third model, spin-dependent hybridization between transition metal ion Fe 3d and ligand ion O 2p [3,9].

Here we show direct evidence for a long range order of the d-p hybridization using soft x-ray resonant Bragg diffraction. Superlattice reflection 0, 1-2q, 0 (2q = 0.828 is twice of the magnetic wave number along the b axis) has been found at Fe $L_{2,3}$ absorption edges. The integrated intensity of this reflection was measured as a function of temperature, x-ray polarization, and x-ray energy. Our experimental findings definitely show that the 3d orbital state of Fe ions has a long range order in the ferroelectric state.

CFO has the delafossite structure space group $R\bar{3}m$ at room temperature. The structure consists of Fe$^{3+}$ hexagonal layers along the c axis, which are separated by intervening two layers of oxygen and one layer of Cu$^{1+}$ as shown in Figure 1 (a). CFO undergoes two successive magnetic transitions at low temperatures in the absence of external magnetic field. At $T_{N1}$ = 14 K the paramagnetic phase turns to be the sinusoidally modulating partially disordered (PD) state with a wave vector $Q = (0, q, \frac{1}{2})_m$, $q \sim \frac{\pi}{a}$ and then at $T_{N2}$ = 11 K, it turns to be the collinear four-sublattice (4SL) ground state $\uparrow\uparrow\downarrow\downarrow$ with a wave vector $Q = (0, \frac{1}{2}, \frac{1}{2})_m$ [10]. Here the suffix $m$ means that these indices are based on the monoclinic space group $C2/m$ which represents the crystal structure below the temperature $T < T_{N1}$ [11]. Hereafter the monoclinic notation is used unless specified.

A spontaneous electric polarization along the direction parallel to the b axis appears in the first field-induced phase by applying a magnetic field along the hexagonal c axis [3] or substituting a few percentage of Fe ions with non-magnetic (Al or Ga) ions [12, 13] in the absence of external magnetic field. Nakajima et al. have clarified that the ferroelectric phase has a proper helical magnetic order with an incommensurate periodicity [14] and that the magnetic chirality, left-handed or right-handed, directly corresponds to the polarity (+ or −) of the spontaneous electric polarization using polarized neutron diffraction [15]. Figure 1 (a) shows the left-handed proper helical magnetic order in the ferroelectric
and incommensurate magnetic (FE-ICM) ordered phase, where the electric polarization vector $\mathbf{P}$ points to the negative direction along the $b$ axis. Note that the space group in the FE-ICM phase is not $C2/m$ anymore because the magnetic order breaks the $C$-face-centred structure. Moreover the mirror symmetry perpendicular to the $b$-axis is to be broken, too. This symmetry breaking is essential for realizing the spontaneous electric polarization. Figure 1 (b) shows the impurity–temperature magnetic phase diagram [16] of CuFe$_2$O$_4$ consisting of four magnetic phases: 4SL, PD, FE-ICM, and oblique PD (OPD) phases and the paramagnetic (PM) phase.

There have been presented mainly three possible mechanisms to explain the ferroelectricity in the ME multiferroic materials. Among them, the magnetostriction model induces the electric polarization only for a commensurate magnetic order but not for an incommensurate magnetic order. The spin-current model [3] conflicts with the above experimental findings because it does not predict that the electric polarization vector is parallel to the magnetic wave vector. Most plausible mechanism for CFO is the spin-dependent $d$-$p$ hybridization model [8]. According the model, the spin-orbit coupling in Fe ions gives rise to a spatial variation of metal-ligand (Fe-O) hybridization associated with the proper helical magnetic structure. It predicts (1) that a charge transfer between Fe and O ions spatially varies together with a variation of the hybridization, (2) that an electric polarization is induced parallel to the magnetic wave vector (along the $b$ axis), (3) that the polarity of the electric polarization corresponds to the magnetic chirality, and (4) that the electric polarization has spatial modulations of wave numbers of $2q$ and $4q$. Here $q$ is the wave number of the proper helical magnetic structure. Actually, Nakajima et al. have found superlattice reflections having $2q$ modulation in the FE-ICM phase of CuFe$_{1-y}$Ga$_y$O$_2$ ($y = 0.0155$) using the non-resonant x-ray diffraction [8]. They have pointed out that the Fourier-transform spectrum of the spatial modulation based on the model is consistent with the experimental results including the intensity ratio of the superlattice reflections. On the other hand, the conventional magnetostriction mechanism does not fit the experimental results. This result supports the spin-dependent $d$-$p$ hybridization model in the FE-ICM phase of CFO but does not provide any direct evidence of a spatial variation of the metal-ligand hybridization.

We have performed soft x-ray resonant diffraction to elucidate the mechanism of the ferroelectricity in CFO at Fe $L_{2,3}$ absorption edges. Conventional x-ray diffraction is commonly used to determine structures of a variety of materials ranging from inorganic compounds to biomolecules. On the other hand, resonant x-ray diffraction (RXD) provides a powerful tool to investigate a variety of ordered states, such as magnetic, charge or orbital orders. Most important feature of RXD is the strong dependence on the polarization state of photons. This property was first demonstrated by Templeton and Templeton in 1982 [17]. RXD occurs as the second perturbation in the interaction between photons and atomic electrons, where photons exchange the energy with the electron system by electric or magnetic multipole transitions. Passing through the intermediate states (unoccupied states), the x-ray scattering is quite sensitive to the local electric environment of the resonant element. The scattering cross-section, then, is described by the atomic tensors [18] or the anisotropy of x-ray susceptibility [19].

Single crystals of CuFe$_{1-y}$Ga$_y$O$_2$ with $y = 0.022$ were grown by the floating-zone technique. They were cut into disks with 2 mm in thickness and polished to remove the surface roughness. The surface is perpendicular to the

![Fig. 1. (Color online) Appearance of ferroelectricity in CuFe$_2$O$_4$. (a) Atomic configuration and magnetic structure of CuFe$_2$O$_4$. Below temperature $T < T_{N1}$, the crystal structure is the monoclinic space group $C2/m$. The unit cell is drawn with a setting of unique axis $b$ and cell choice 1 of the monoclinic space group $C2/m$. Black lines show the unit cell. The left-handed proper helical magnetic structure in ferroelectric phase is illustrated by green arrows at iron ions. When the magnetic chirality is left-handed, the electric polarization vector points the negative direction along the $b$ axis. (b) Magnetic phase diagram of CuFe$_{1-y}$Ga$_y$O$_2$ drawn as functions of temperature and the content of Ga ions. Data are taken from Ref. [14]. The sample used for the soft x-ray diffraction has 2.2 % Ga, indicated by a dash line.](image-url)
monoclinic b axis. We have performed RXD experiments for L_{2,3} absorption edges of Fe using a soft x-ray diffractometer built at beam line 17SU [20] in SPring-8. The sample was mounted in a liquid 4He flow-type cryostat. The incident x-ray energy was tuned by the grating apparatus. The polarization of the incident photons was switched by the electromagnet of the undulator [21] and that of the diffracted photons was analyzed by a W/B4C multilayer. The bilayer thickness of the multilayer is adjusted to the wavelength for Fe L_3 edge at Bragg angle 2θ = 90 degrees. Note that the degree of linear polarization of the x-ray beam is determined by the components perpendicular (σ) and parallel (π) to the scattering plane, which is spanned by the incident and diffracted propagation vectors k_i and k_d. Our insertion device for the incident beam can control the polarization of the incident beam, but not perfectly. Thus, the actual linear polarization in the experiments has 98.8% for π incident beam and 83% for σ incident beam, respectively. Data shown in Figure 2 are corrected with these factors.

The results of RXD measured at Fe L_{2,3} absorption edges are summarized in Figure 2. Panel a shows the x-ray absorption spectrum (XAS) of Fe L_{2,3} edges obtained in the total x-ray fluorescence yield mode. The maxima of Fe absorption appear at 710.3 eV and 723.3 eV, corresponding to L_3 and L_2 absorption edges, respectively. Double-peak structures observed both at L_3 and L_2 edges originate from the crystal-field splitting of Fe ions [22]. Peaks observed at lower and higher energies correspond to the transition to the 3d t_{2g} and e_g states, respectively, for both L_3 and L_2 edges. Panel b shows the integrated intensity observed at E = 708.6 eV as a function of temperature. It gradually decreases with increasing temperatures and disappears around 9 K and it gradually increases with decreasing temperatures after the sample is warmed up to 20 K, where the system is in the paramagnetic phase. As shown in Figure 1 b, the sample (\(y = 0.022\)) has the magnetic transition at \(T_{N2} = 8\) K. The intensity appears differently in two ways because the magnetic transition at \(T_{N2}\) is the first order and the monoclinic domains appear differently for each time in cooling process from the PM phase.

Energy spectra of the integrated intensity of superlattice reflection 0, 1 − 2q, 0 measured at temperature \(T = 4.2\) K for polarization-unrotated channels σ′σ and π′π and rotated channels π′σ and σ′π are displayed in Figure 2, panels c to f. Here σ (σ′) and π (π′) show the polarization in the scattering for incident (diffracted) photons. We have clearly found superlattice reflection 0, 1 − 2q, 0 in the FE-ICM phase for the x-ray polarization channels (panels c, d, e and f) at both L_3 and L_2 edges. Note that the maximum of the peak at L_3 edge for each panel corresponds to the resonant transition to the t_{2g↓} orbit according to the lower-energy peak of the XAS. Most important feature found in these energy spectra is that superlattice reflection 0, 1 − 2q, 0 is observed for polarization-rotated channels π′σ and σ′π. The rotation of polarization is forbidden for conventional x-ray diffraction. It is allowed only when the local electronic state of the resonant ion, which is expressed by the second or higher rank of tensors, is aspherical and has a periodic spatial modulation as well. Thus the rotation of the polarization found here clearly proves that the Fe 3d orbital state has a motif of a wave vector 2q along the b axis.

Let us discuss what picture we deduce for the appearance of ferroelectricity from our findings. The proper helical magnetic structure found in the polarized neutron diffraction conflicts with the crystal symmetry and breaks it. Most probable mechanism of this symmetry-breaking is the spin-dependent hybridization between the Fe 3d state and the O 2p state as described in Ref [8]. The spin-orbit interaction in Fe ions lifts the degeneracy of the t_{2g↓} orbits of the Fe high spin state \(^6\)S as a perturbation and this lifting causes the spatial periodic modulation of the Fe 3d state along the b axis, coupling with the magnetic structure. Our findings provide direct evidence of the modulation of the t_{2g↓} orbit in the FE-ICM phase having wave number 2q. Arima [8] has

![Figure 2](https://via.placeholder.com/150)
proposed that a charge transfer between the Fe and the O ions appears according to the hybridization. However, we have no evidence for a charge-transfer modulation so far \[23\]. If it exists, some resonant signature should have been observed at Fe K edge. For example we have found that forbidden reflection 010 in the 4SL phase of pure CuFeO\(_2\) is strongly enhanced at Fe K edge due to the charge disproportionation \[24\]. Thus our findings agree with the spin-dependent \( d-p \) hybridization model but do not support a charge-transfer modulation.

We would rather propose that the position of O ions varies with the hybridization between Fe 3d and O 2p via spin-orbit coupling than a charge-transfer modulation. This spatial modulation breaks the crystal symmetry and invokes the ferroelectricity in this compound. Actually, we have observed that superlattice reflection 0, 1 + 2\( q \), 0 appears in non-resonant energies around Fe K absorption edge \[23\]. On the other hand, we have not found any signature of resonant intensity for reflection 0, 1 − 2\( q \), 0 at O K absorption edge, yet. Polishing the sample may damage the surface structure associated with an oxygen loss. Such a bad surface condition might prevent the observation.

In summary we have performed resonant soft x-ray diffraction on the multiferroic material CuFe\(_{1-x}\)Ga\(_x\)O\(_2\), \( y = 0.022 \) and found that a superlattice reflection 0, 1-2\( q \), 0 at Fe L\(_2,3\) absorption edges appears in the FE-ICM phase and that the x-ray polarization for this reflection rotates. These findings provide direct evidence for the spatial periodic modulation of the Fe 3d orbital state.

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