Charge disproportionation associated with spin ordering in delafossite CuFeO₂ as seen via resonant x-ray diffraction

N. Terada,[1,2] T. Nakajima,[3] S. Mitsuda,[3] Y. Tanaka,[2] H. Mamiya,[1] and H. Kitazawa[1]

[1]*National Institute for Materials Science, Sengen 1-2-1, Tsukuba, Ibaraki 305-0044, Japan*
[2]*RIKEN SPring-8 Center, Harima Institute, Sayo, Hyogo 679-5148, Japan*
[3]*Department of Physics, Faculty of Science, Tokyo University of Science, Tokyo 162-8601, Japan*

We have performed the resonant x-ray diffraction measurements on the triangular lattice antiferromagnet CuFeO₂ near the Fe K absorption edge. The resonant enhancement of the space-group-forbidden superlattice 010 reflection was observed below the second Néel temperature $T_{N2}=11$ K at which the four-sublattice ground state is stabilized. The significant azimuthal angle dependence of the superlattice reflection was not observed. On the other hand, the energy spectrum can be explained by the charge disproportionation (CD) model, $2Fe^{3+} \leftrightarrow Fe^{(3+\delta)+} + Fe^{(3-\delta)+}$. We discuss the relationship between the unconventional collinear four-sublattice ground state and the CD state in CuFeO₂.

I. INTRODUCTION

Cross correlation between different order parameters in solids, which is typified by magnetoelectric, piezoelectric, and magnetostrictive effect, is fertile ground for the appearance of novel physical phenomena. In magnetic materials, the discovery of magnetostriction more than 150 years ago has presented an important physical concept for understanding their physical phenomena.[1] Novel physical phenomena discovered recently, such as giant/colossal magnetoresistance[2–4] and magnetoferroelectrics,[5,6] are also understood with interplay between spin and the other degree of freedom. The delafossite CuFeO₂ is one of magnetic materials showing several cross-correlation phenomena of the spontaneous spin-lattice coupling,[7–9] magnetic field-induced ferroelectricity,[10] and multistep lattice changes.[11]

CuFeO₂ has triangular lattice layered structure, which belongs to space group $R\bar{3}m$. The magnetic ions Fe^{3+} which make up the triangular lattice layers are characterized by an isotropic $3d$ orbital state of the electronic configuration with orbital singlet, $S=5/2$ and $L=0$. Since the single-ion anisotropy of Fe^{3+} is considered to be small, the Heisenberg spin behaviors are expected in CuFeO₂. In a Heisenberg spin triangular lattice antiferromagnet (TLA) with weak anisotropy, a noncollinear magnetic ground state so-called 120° state is predicted by the theoretical study.[12] In CuFeO₂, however, its ground state is the collinear four-sublattice ↑↑↓↓ (4SL) state with the magnetic moments confined along the hexagonal c axis.[8,13,14] In magnetic fields along the c axis, multistep magnetization changes occur, which is generally seen in frustrated Ising antiferromagnets with a strong uniaxial anisotropy. Despite great efforts for understanding the unconventional spin behaviors, their origin has not been understood thus far. The previous x-ray diffraction studies[7–9] have pointed out that the lattice distortion lifting the macroscopic degeneracy of the frustrated spin system plays an important role for the stabilization of the 4SL ground state in CuFeO₂. However, no study to directly investigate the electronic state below the Néel temperature in CuFeO₂ have been carried out. Therefore, the origin of the uniaxial anisotropy

of the orbital singlet Fe^{3+} in CuFeO₂ has not been clarified so far. In the present work, in order to obtain knowledge for the electronic state of Fe^{3+} below Néel temperature, we have performed the resonant x-ray diffraction (RXD) experiment on CuFeO₂ near the Fe K absorption edge.

A RXD measurement is one of the most powerful techniques for studying charge orderings,[15–17] orbital orderings[18] and magnetic orderings.[19] As for charge ordering/disproportionation, the generalized scattering factor for a single atom/ion can be given by

$$f_{ee'} = \mathbf{e} \cdot \mathbf{e}' f^{T}(\mathbf{Q}) + f'_{ee'}(E) + i f''_{ee'}(E), \tag{1}$$

where $\mathbf{e}$ and $\mathbf{e}'$ are unit vectors of polarization for the incident and diffracted x-ray beams, respectively. The first term is the Thomson scattering factor which is independent of incident energy E and depends on the scattering vector $\mathbf{Q}$. The terms $f'_{ee'}$ and $f''_{ee'}$ are the real and imaginary parts of the dispersion corrections, respectively, which are dependent on E. They vary significantly near the absorption edges for the elements of which the materials are composed. One can, therefore, detect resonant enhancement for a superlattice reflection near the edge, which is caused by the difference in the scattering factor for different crystal sites.

II. EXPERIMENTAL DETAIL

A single crystal of CuFeO₂, which was prepared by the floating zone technique,[20] was cut into a disk with a thickness of 2 mm and subsequently polished in air to remove the surface roughness. The RXD experiments were carried out with a standard four-circle diffractometer in BL29XU at SPring-8. The cut crystal was mounted in a liquid ⁴He refrigerator that can cool a sample down to 3 K. The incident x-ray beam had almost perfect horizontal polarization and its energy was tuned to near the Fe-K absorption edge ($E \approx 7.112$ keV) The diffracted x-rays were analyzed using the 006 reflection of a pyrolytic graphite crystal. The azimuthal reference vector was chosen as the (001) direction. The x-ray absorption spectrum was measured at room temperature using the powder sample.
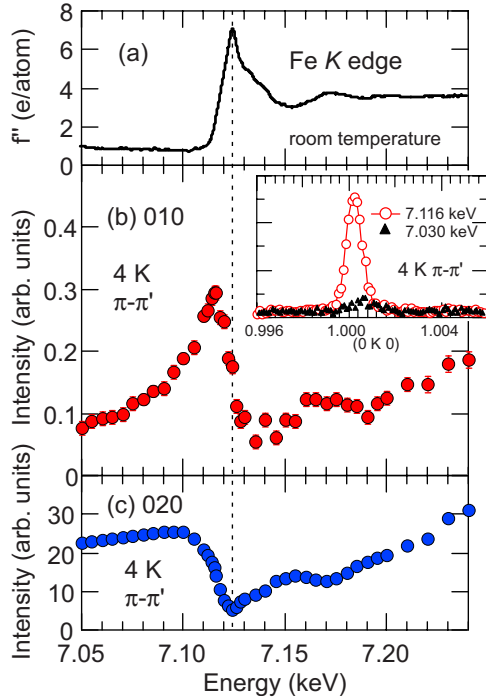
FIG. 1. (Color online) (a) X-ray absorption spectrum at room temperature. Energy dependence of the integrated intensity of (b) superlattice 010 and (c) fundamental 020 reflections. The inset in (b) shows the reciprocal lattice (0*K*0) scan profiles for E =7.116 keV and E=7.030 keV. The diffraction data were obtained at 4 K and with $\pi-\pi'$ polarization. No absorption corrections are carried out on these data.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the x-ray absorption spectrum (XAS) at room temperature and the x-ray intensity for the superlattice 010 and the fundamental 020 reflections at 4 K. The indices are represented by the monoclinic notation defined in a previous paper.[9] The space group below the Néel temperature was determined to be monoclinic $C2/m$ by the previous neutron powder diffraction measurements.[8] As clearly seen in the figures, the superlattice 010 reflection, which is not allowed by the space group, is enhanced near the Fe K absorption edge, while a simple absorption spectrum is observed in the fundamental 020 reflection near the edge. As shown in the inset of Fig. 1(b), the superlattice 010 reflection is observed for both on-resonant and off-resonant energies. The intensity in the off-resonant case, small but detectable, is consistent with the previous nonresonant x-ray diffraction measurements.[7–9] To investigate whether the 010 reflection is coupled with the 4SL magnetic ordering or not, the temperature dependence of the reflection was examined. As shown in Fig. 2, the 010 reflection appears below T_{N2} for both on-resonant and off-resonant energies. Hence, it is concluded that the resonant enhancement of the 010 reflection is coupled with the 4SL magnetic ordering.

There are three possible orderings giving a resonant enhancement of a reflection in RXD: magnetic ordering,[19] orbital ordering[15] and charge ordering/disproportionation.[16–18] The magnetic reflection in the 4SL state of $CuFeO_2$ appears
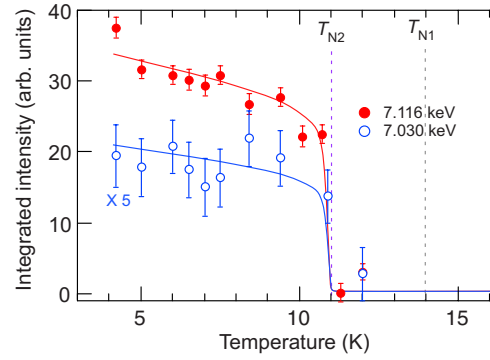

FIG. 2. (Color online) The temperature dependence of the integrated intensity of the 010 reflection for the resonant energy (E =7.116 KeV) and the nonresonant energy (E=7.030 KeV). For improved visibility, the data for E=7.030 KeV are multiplied by five.

not at (010) but at (0 0.5 0.5) in the reciprocal lattice space, which has been confirmed by neutron diffraction measurements.[8,13]

Next, we discuss whether an orbital ordering originates from the enhancement of the 010 reflection or not. In the case of orbital orderings, the intensity of the 010 reflection could depend on both the azimuthal angle and the polarization of x rays. Since the monoclinic b axis is a twofold rotational axis, the 010 reflection could be expected to show the twofold symmetry as a function of azimuthal angle. However, we did not observe significant azimuthal angle dependence of the intensity for the $\pi-\pi'$ and $\pi-\sigma'$ channels, as shown in Fig. 3. Therefore, we conclude that an orbital ordering is not a main source for the resonant enhancement. Nevertheless, it should be noted that the azimuthal dependence for $\pi-\pi'$ channel shows a slightly quasiperiodic behavior. Although an orbital ordering is not the main source, it might be one of the components giving the resonant enhancement. The quasiperiodic behavior has not been understood at the present stage.
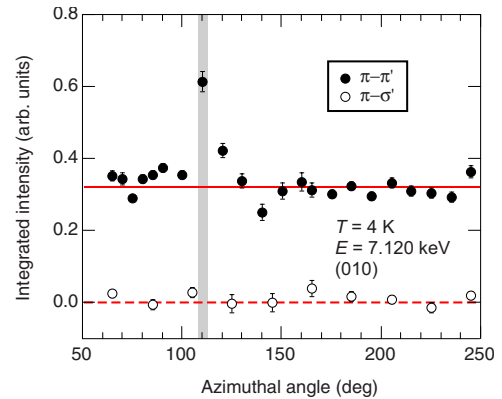

FIG. 3. (Color online) The azimuthal angle dependence of the 010 reflections with $\pi-\pi'$ and $\pi-\sigma'$ polarization for E =7.120 KeV at 4 K. The intensity data are normalized to the fundamental 020 reflection for each azimuthal angle. The solid and dotted lines are guides for the eyes. The data point masked by the shadow is accidentally large, which might be caused by Renninger reflection.
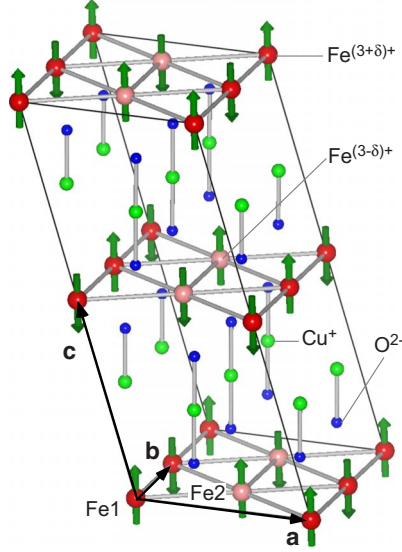
FIG. 4. (Color online) Schematic drawing of the charge dispro-portionation model with the monoclinic unit cell.

The final possible ordering is charge disproportionation (CD). Taking into consideration the index 010, we can put forward a unique CD model in which the two Fe sites, Fe1 and Fe2, have a different valence of $Fe^{(3+\delta)+}$ and $Fe^{(3-\delta)+}$, respectively, which is illustrated in Fig. 4. Note that the magnetic structure drawn in Fig. 4 was determined in the previous neutron diffraction measurements.[8,13] The energy dependence of the structure factor of the 010 reflection can be written as

$$F_{010}(E) \propto (f'_{Fe1}(E) - f'_{Fe2}(E)) + i[f''_{Fe1}(E) - f''_{Fe2}(E)] + C,$$
(2)

where C is independent of energy. $f'_{Fe1}(f''_{Fe1})$ and $f'_{Fe2}(f''_{Fe2})$ are the real (imaginary) parts of the dispersion correction for the Fe1 and Fe2 sites. We first experimentally obtained f'' through the XAS data at room temperature [Fig. 1(a)]. Subsequently, we assume that f''_{Fe1} and f''_{Fe2} result from shifting f'' by an energy $+\Delta$ and $-\Delta$, respectively, i.e., $f''_{Fe1}(E) = f''(E - \Delta)$ and $f''_{Fe2}(E) = f''(E + \Delta)$. The factors f'_{Fe1} and f'_{Fe2} are transformed by the Kramers-Kronig transformation of the $f''_{Fe1}(E)$ and $f''_{Fe2}(E)$, respectively. Based on Eq. (2), we can calculate the energy spectra for Δ varying continuously. Comparing the calculated spectra with the experimental data after absorption correction, we find that the intensity spectrum calculated for $\Delta = 1.3 \pm 0.5$ eV best fits the experimental data as shown in Fig. 5(a). We also show the typical examples for $\Delta = 2.5, 1.5, 0.5$ eV, which are shown in Figs. 5(b)–5(d), respectively.

In the typical iron systems of FeO and Fe_2O_3, the chemical shift between Fe^{2+} and Fe^{3+} was reported as 5 eV.[21] Assuming that the chemical shift Δ is proportional to the valence shift δ between $Fe^{3+\delta}$ and $Fe^{3-\delta}$, we obtain the relationship between δ and Δ, $\delta = 2\Delta/5$. Since $\Delta = 1.3 \pm 0.5$ below T_{N2} in CuFeO$_2$ as mentioned above, the valence shift can be estimated to be $\delta = 0.26 \pm 0.10$ with this relation.
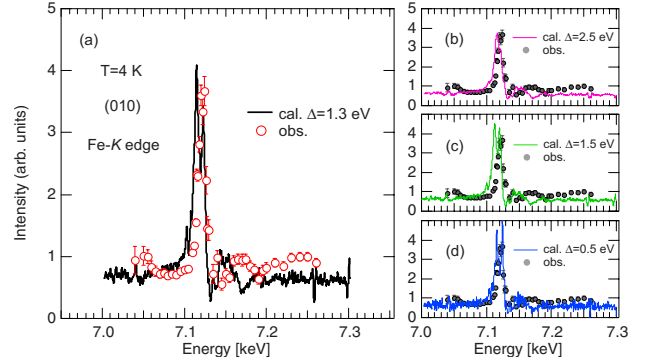

FIG. 5. (Color online) Comparison between the energy dependence of the 010 reflection at 4 K (open circle) and the calculated curve using Eq. (2) for (a) $\Delta = 1.3$ eV, (b) $\Delta = 2.5$ eV, (c) $\Delta = 1.5$ eV, and (d) $\Delta = 0.5$ eV.

From the experimental facts and the consideration mentioned above, we concluded that the resonant enhancement of the superlattice 010 reflection is due to the CD resulting from the alternative ordering of $Fe^{(3+\delta)+}$ and $Fe^{(3-\delta)+}$ in the ab planes, as illustrated in Fig. 4.[22]

We will now discuss the relationship between the unconventional magnetic ground state and the CD in CuFeO$_2$. As mentioned above, the collinear 4SL state becomes the magnetic ground state in CuFeO$_2$, though a noncollinear 120° state is theoretically expected in a typical Heisenberg spin TLA.[12] There are two necessarily important factors to realize the unconventional collinear ground state. One is the lowering of the symmetry in the exchange interaction and the other is the uniaxial anisotropy. The former is due to the lattice distortion. In the previous x-ray diffraction measurements, the lattice distortion associated with the 4SL ordering has been observed.[7–9] The latter is to confine spins to the hexagonal c axis. The ionic state above T_{N2} is Fe^{3+} with a half-filled d^5 configuration, in which the orbital momentum $L = 0$ and significant single ion anisotropy cannot be expected. When the CD state is realized, $2Fe^{3+} \leftrightarrow Fe^{(3+\delta)+} + Fe^{(3-\delta)+}$, below T_{N2}, the valence state deviates from the isotropic ionic state Fe^{3+}. The deviation might create the uniaxial single-ion anisotropy through the spin-orbit coupling; however, at the present stage, we cannot mention that the deviation could give the uniaxial anisotropy without any theoretical calculations. The absolute value of the magnetic moment could be reduced on both Fe1 and Fe2 sites, because d^5 of Fe^{3+} splits into $d^{5+\delta}$ and $d^{5-\delta}$. The value of magnetic moment in the 4SL state was determined to be $4.17\mu_B$ by the previous neutron diffraction measurements,[8] which is considerably smaller than the theoretical value of $5\mu_B$ of the high spin state Fe^{3+}. The reduction in the magnetic moment in the 4SL state supports the CD model.

IV. CONCLUSION

We have performed the RXD measurements on the delafossite CuFeO$_2$ near the Fe-K absorption edge. The resonant enhancement of the space-group-forbidden superlattice 010 reflection was observed below $T_{N2} = 11$ K at which the four-sublattice ground state is stabilized. The significant azi-

muthal angle dependence of the superlattice reflection was not observed. The energy spectrum can be explained by the CD model, $2Fe^{3+} \leftrightarrow Fe^{(3+\delta)+} + Fe^{(3-\delta)+}$. We also discuss the relationship between the CD state and the unconventional 4SL ground state. We argued that the CD plays an important role for the appearance of the uniaxial anisotropy that is not expected by the orbital singlet Fe^{3+}. For further investigation of the origin of the CD phenomenon, the other measurements that can directly probe the electronic states of Fe^{3+}, such as x-ray photoemission spectroscopy and Fe $L_{2,3}$ XAS, and the theoretical calculation are required.

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