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Effects of oxygen nonstoichiometry on the stability of antiferromagnetic phases of $CuFeO_{2+\delta}$ single crystals

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Effects of oxygen nonstoichiometry on stabilities of the antiferromagnetic (AF) phases of $CuFeO_2$ with a delafossite-type structure have been investigated. Temperature dependence of the magnetic susceptibility between 5 and 300 K in 0.1 T parallel to the c axis, and magnetic-field dependence of the magnetization below 40 T parallel to the c axis at 4.2 K are clarified using $CuFeO_{2+\delta}$ single crystals with stoichiometry varying from oxygen deficiency ($\delta = -0.026$, -0.061) to oxygen excess ($\delta = 0.14$, 0.085). It is found that the stabilities are strongly affected by the oxygen defects, depending on their type, i.e., oxygen deficiency or oxygen excess. The transition temperature between the four-sublattice AF phase (low-temperature AF phase) and the partially disordered phase (high-temperature AF phase) is increased by the oxygen deficiency, whereas it is decreased by the excess oxygen. It should be noted that both types of oxygen defects bring another metamagnetic transition around 23 T. Besides, all metamagnetic transition fields are increased by the oxygen defects. These effects are discussed from the viewpoints of crystal chemistry.

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I. INTRODUCTION

Since the two-dimensional Cu-O planes play an important role in the high-T_c cuprate superconductors, such low dimensional structures have been attractive in their exotic physical properties. Thus materials having the two-dimensional triangular structure become the next important targets. Magnetic and electric properties of these materials are usually quite sensitive for stoichiometry and impurity.

Cuprous ferrite $CuFeO_2$ with the delafossite structure is one of these attractive materials. It has a crystal structure with the space group $R\bar{3}m$ and the hexagonal lattice parameters of $a = 3.03$ Å and $c = 17.09$ Å,[1] as shown in Fig. 1. The structure consists of respective hexagonal layers of Cu, Fe, and O with Cu at (0, 0, 0), Fe at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and two O at $(\frac{1}{9}, \frac{1}{9}, \frac{1}{9})$ and $(-\frac{1}{9}, -\frac{1}{9}, -\frac{1}{9})$, which stack in the sequence of A-B-C [A(Cu),A(O),B(Fe),C(O),C(Cu),C(O),A(Fe), etc.] to form a layered triangular lattice antiferromagnet.

$CuFeO_2$ shows successive antiferromagnetic (AF) transitions at $T_{N1} = 16$ K and $T_{N2} = 11$ K in zero magnetic field and multistep metamagnetic transitions.[2–4] Fukuda *et al.* investigated submillimeter wave electron spin resonance (ESR) on $CuFeO_2$ in frequencies up to 762 GHz.[5] They observed changes of antiferromagnetic resonance (AFMR) mode corresponding to the metamagnetic transition below T_{N1}. Mitsuda *et al.* investigated magnetic states by neutron-diffraction measurements and determined the magnetic phase diagram.[6–8] They clarified that the magnetic phase transitions in zero magnetic field are four-sublattice antiferromagnetic (AF) phase⇒partially disordered AF phase⇒paramagnetic phase with increasing temperature and that the magnetic phase transitions in magnetic fields at low temperatures (for example, at 4.2 K) are four-sublattice AF phase⇒five-sublatticelike AF phase⇒five-sublattice AF phase with increasing magnetic field. They have also clarified the first and second magnetization steps in detail recently.[9] These studies have reported that the magnetic structures and magnetic transitions are complicated because of the spin frustration based on the two-dimensional triangular lattices. Therefore the magnetic state is expected to be affected by a slight disturbance of the spin structure, such as impurities and nonstoichiometry. Ajiro *et al.*[10] and Kasahara *et al.*[11] reported effects of impurity (nonmagnetic Al or magnetic Cr) ions substituting from Fe ions in $CuFeO_2$ on the stability of the ground-state spin configuration in the triangular lattice AF lattice.

In the present paper, effects of oxygen nonstoichiometry on stabilities of the AF phases in $CuFeO_2$ against temperature and magnetic field parallel to the c axis are clarified

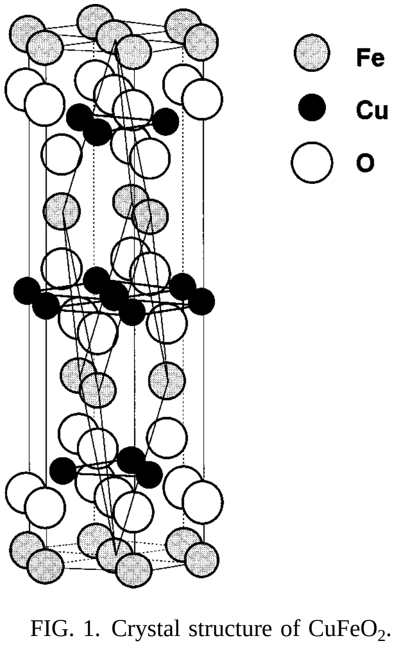

FIG. 1. Crystal structure of $CuFeO_2$.

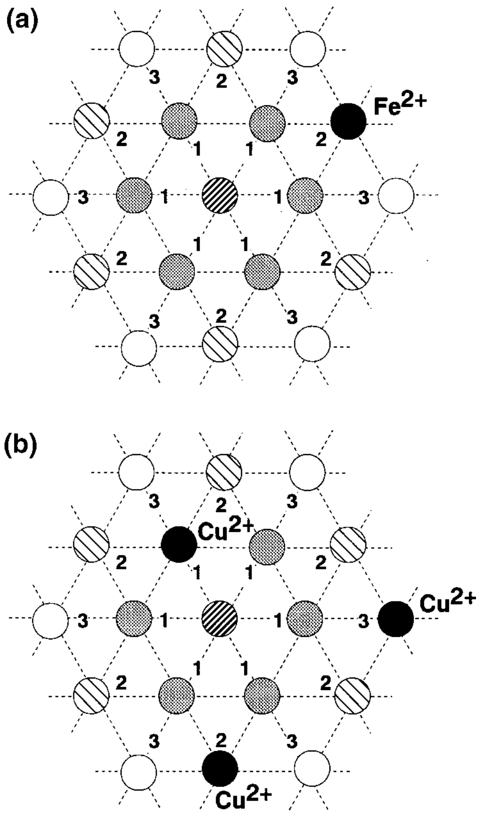

FIG. 2. Schematic illustration of two-dimensional Fe or Cu layer in oxygen nonstoichiometric $CuFeO_{2+\delta}$. Hatched circle indicates a noted original ion (Fe^{3+} or Cu^{+}). Marks ● indicate induced divalent ions (Fe^{2+} or Cu^{2+}). Each mark with number, (dotted circle) 1, (hatched circle) 2, (open circle) 3, indicates first, second, and third nearest-neighboring ions (Fe^{3+} or Cu^{+}) to the noted ion, respectively. (a) Fe ion layer of $\delta=-0.026$. (b) Cu ion layer of $\delta=0.085$.

using high quality $CuFeO_{2+\delta}$ single crystals with stoichiometry varying from oxygen deficiency ($\delta=-0.026$, -0.061) to oxygen excess ($\delta=0.014$, 0.085).

Oxygen nonstoichiometry accompanies changes of cation valences and lattice parameters. In the present case, the oxygen deficiency induces a mixed-valence state of Fe ions, i.e., dominant Fe^{3+} and slight Fe^{2+}, while the excess oxygen induces a mixed-valence state of Cu ions, i.e., dominant Cu^{1+} and slight Cu^{2+}. For example, an oxygen deficiency of $\delta=-0.026$ induces 5.2% Fe^{2+} ions in Fe ions which is almost equal to $\frac{1}{18}$ in total Fe. This means that one Fe ion in the first, second, and third nearest-neighbor Fe ions changes to be Fe^{2+} from Fe^{3+}, as shown in Fig. 2(a). Besides, it should be noted that excess oxygen of $\delta=0.085$ induces 17% Cu^{2+} ions which is more than $\frac{1}{6}$ $(=\frac{3}{18})$ in total Cu. This means that one of the first nearest-neighboring Cu ions (three of the first, second, and third nearest-neighbor Fe ions) changes Cu^{+} to Cu^{2+}, as shown in Fig. 2(b). In addition, it was reported that the lattice parameters of $CuFeO_{2+\delta}$ depended on the oxygen nonstoichiometry.[12,13] Figure 3 shows δ dependence of a ratio between the lattice parameters c/a in $CuFeO_{2+\delta}$. It should be noted that changes of the ratio depend on the type of oxygen defect. In the case of oxygen deficiency the ratio increases slightly with increasing deficient oxygens, while in the case of oxygen excess the ratio decreased considerably with increasing the excess oxygen content. From these points of view on crystal chemistry of $CuFeO_{2+\delta}$, it is easily expected that disturbances induced by the oxygen nonstoichiometry in $CuFeO_2$ affect stability of antimagnetic phases of $CuFeO_2$.

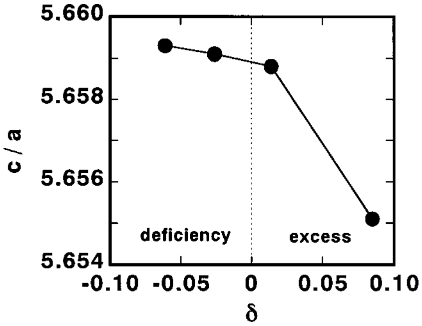

FIG. 3. Oxygen defect content, δ dependence of a ratio c/a between lattice parameters a and c of $CuFeO_{2+\delta}$ ($\delta<0$: oxygen deficiency; $\delta>0$: oxygen excess).

II. EXPERIMENT

All samples were as-grown single crystals. They had been grown by means of the traveling Cu_2O-solvent floating-zone method in an infrared radiation furnace under CO_2, Ar, Ar $+0.5\%O_2$, Ar$+2\%O_2$ atmosphere, respectively. Compositions of the single crystals were inspected by a scanning electron microscope with an electron probe microanalyzer (SEM-EPMA) using metal copper and iron as standards. The densities were also measured by a so-called Archimedean method. The chemical formula of each sample was determined from these measurements as $CuFeO_{1.974}$ ($\delta=-0.026$), $CuFeO_{1.939}$ ($\delta=-0.061$), $CuFeO_{2.070}$ ($\delta=0.014$), and $CuFeO_{2.085}$ ($\delta=0.085$). The crystal structures were investigated by an x-ray powder diffraction and precession camera method. The sharpness of the diffraction patterns revealed that the single crystals were found to be in good qualities. Details of the crystal growth and characterizations have been described elsewhere.[14–17]

Each sample to measure magnetic properties was cut from the respective single crystal. The Laue back-reflection pattern was used to establish the orientation of the single crystals. Magnetic susceptibilities were measured in the magnetic field of 0.1 T parallel to the c axis by a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS). The high-field magnetization was measured by an induction method using pulse magnetic fields parallel to the c axis up to about 40 T at 4.2 K. The transition magnetic field was determined from differential magnetization curves $[dM(H)/dH]$.

III. RESULTS AND DISCUSSION

A. Effects of oxygen nonstoichiometry on temperature stabilities of four-sublattice antiferromagnetic phase

Temperature dependence of the magnetic susceptibility of a $CuFeO_{1.974}$ ($\delta=-0.026$) single crystal in 0.1 T parallel to

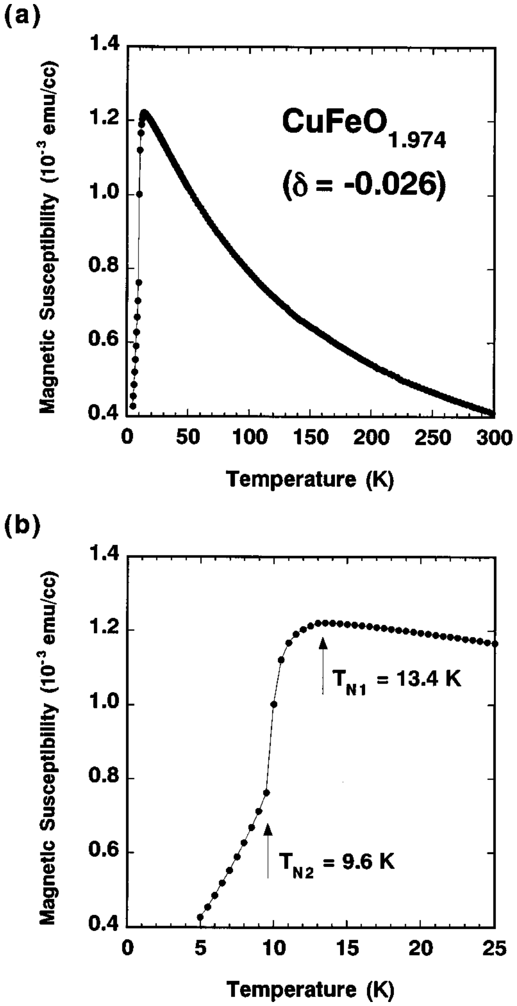

FIG. 4. Temperature dependence of the magnetic susceptibilities parallel to the c axis of $\mathrm{CuFeO}_{1.974}$ ($\delta = -0.026$); (a) below 300 K, (b) below 25 K.

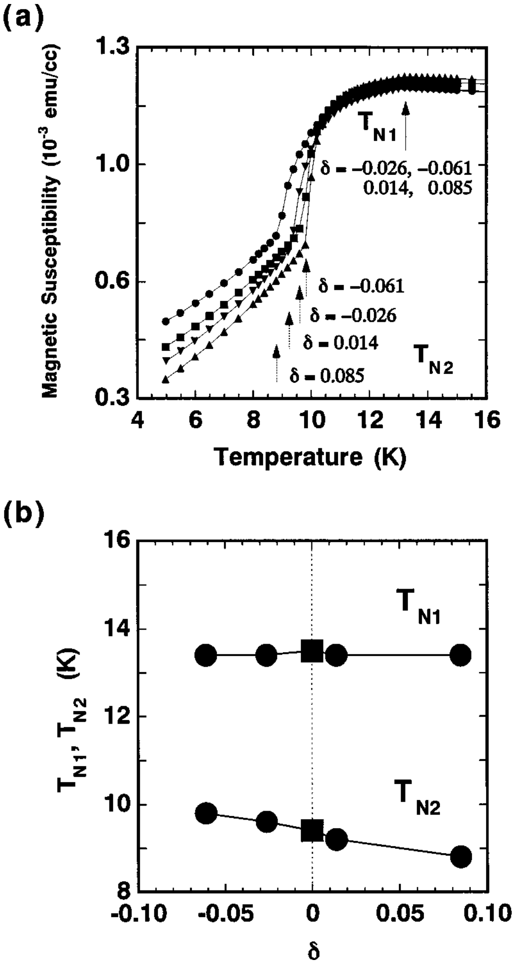

FIG. 5. (a) Temperature dependence of the magnetic susceptibilities parallel to the c axis of $\mathrm{CuFeO}_{2+\delta}$ below 16 K. The applied magnetic field is 0.1 T. Each mark indicates as follows: ■: $\delta = -0.026$; ▲: $\delta = -0.061$; ▼: $\delta = 0.014$; ●: $\delta = 0.085$. (b) Oxygen defect content, δ dependence of antiferromagnetic transition temperatures T_{N1} and T_{N2} of $\mathrm{CuFeO}_{2+\delta}$ ($\delta < 0$: oxygen deficiency; $\delta > 0$: oxygen excess). Each mark indicates as follows: ●: data of present study; ■: data of stoichiometric CuFeO_2 determined from temperature dependence of magnetic susceptibility under 1 T by Ajiro *et al.* (Ref. 4).

the c axis is shown in Fig. 4. The magnetic susceptibilities increase with decreasing temperature almost following the Curie-Weiss law between room temperature and about 15 K. They suddenly decrease at T_{N1} and more at T_{N2}, as shown in Fig. 4(b). These drops correspond to the successive AF transitions (T_{N1} four-sublattice AF phase⇒partially disordered AF phase, and T_{N2}, partially disordered AF phase ⇒paramagnetic phase) reported in the previous papers.[2] All samples showed almost the same profile of temperature dependence of the magnetic suceptibilities.

The temperature dependence of magnetic susceptibilities of all samples below 16 K in a magnetic field of 0.1 T parallel to the c axis is shown in Fig. 5(a). The oxygen defect content dependence of the AF phase transition temperatures T_{N1} and T_{N2} is also shown in Fig. 5(b). It is found that the low transition temperature T_{N2} depends on the oxygen defect concentration although the high transition temperature T_{N1} is not affected. It should be noted that the effects of the oxygen nonstoichiometry on the stability of the four-sublattice AF phase (low-temperature AF phase) is definitely different in accordance with the defect type of either deficiency or excess ($\delta < 0$ or $\delta > 0$) of oxygen. In the case of oxygen deficiency, T_{N2} moves towards a high-temperature region with increasing deficient oxygen content. On the other hand, in the case of oxygen excess T_{N2} shifts towards the low-temperature region with increasing excess oxygen content. These results mean that oxygen deficiency and excess, respectively, stabilize and destabilize the four-sublattice AF phase.

As mentioned in the introduction, in the case of the oxygen deficiency iron ions are in the mixed-valence state of Fe^{3+} and Fe^{2+}, whereas the valence state of copper is kept monovalent. In addition, the change of the ratio c/a is small ($\delta < 0$ region in Fig. 3). Therefore the magnetic configuration in CuFeO_2 with layered frustrated triangular spin lattices is almost kept even in oxygen deficient $\mathrm{CuFeO}_{2+\delta}$. This indicates that disturbance in the spin structure of the four-sublattice AF phase is effectively induced by the subordinate Fe^{2+} ions which have magnetic moments different from

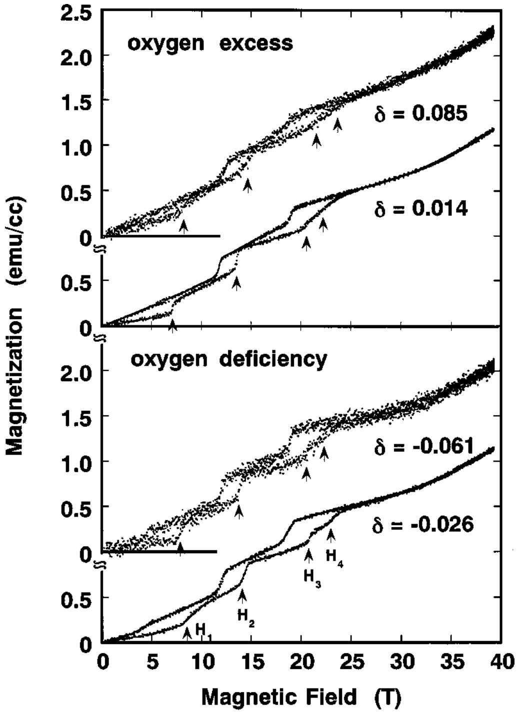

FIG. 6. Magnetization curve parallel to the c axis of $CuFeO_{2+\delta}$ ($\delta<0$: oxygen deficiency; $\delta>0$: oxygen excess) at 4.2 K.

Fe^{3+}. Accordingly, it can be considered that they relieve the spin frustration in the four-sublattice AF phase and result in stabilizing this phase against temperature.

In the case of the oxygen excess, the valence state in copper appears in the mixed state of Cu^{+} and Cu^{2+} although the valence state of all iron ions is kept trivalent, as mentioned in the introduction. Since the divalent copper ions posses magnetic moment, the perfect nonmagnetic copper layers below and above the iron layers in $CuFeO_{2+\delta}$ disappear. In addition, the oxygen excess induces considerable shrinkage of the distances between the Fe and Cu layers (Fig. 3). As a result, the magnetic configuration and interaction in the frustrated triangular spin lattices are changed by excess oxygen. These situations promote the instability of the four-sublattice AF phase.

Kasahara *et al.* reported that the four-sublattice AF phase disappeared by the substitution of nonmagnetic Al ions of only less than 1 at. % to Fe ions.[11] In the present study all samples keep the four-sublattice AF phase although content of the divalent ions as ''impurities'' is 17% in maximum. This distinct difference between Kasahara's results and ours suggests different impurity effects between Al^{3+} (Kasahara's) and Fe^{2+} or Cu^{2+} (ours) in the magnetic disturbance in the delafossite.

It is reasonable that the high transition temperature T_{N1}, which corresponds to the transition between the paramagnetic and partially disordered AF phases, is not affected in any oxygen defect cases. Because the partially disordered AF phase already includes a lot of disturbance in the spin structure.

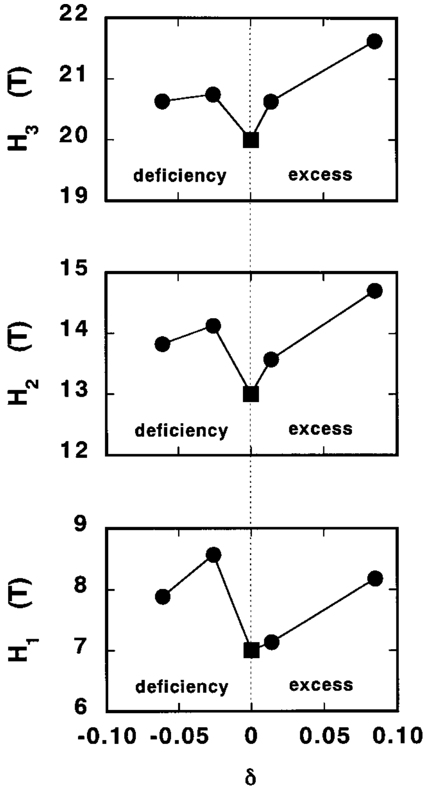

FIG. 7. Oxygen defect content, δ dependence of the metamagnetic transition magnetic fields H_1, H_2, and H_3 parallel to the c axis of $CuFeO_{2+\delta}$ ($\delta<0$: oxygen deficiency; $\delta>0$: oxygen excess). Each mark indicates as follows: ●: data of present study; ■: data of stoichiometric $CuFeO_2$ by Ajiro *et al.* (Ref. 4).

B. Effects of oxygen nonstoichiometry on magnetic-field stabilities of antiferromagnetic phase below 40 T

Figure 6 show magnetization curves parallel to the c axis of $CuFeO_{2+\delta}$ below 40 T at 4.2 K for all samples. Analyses of the differential magnetization curves exhibited four step anomalies with apparent hystereses for all samples at H_1, H_2, H_3, and H_4, as shown in Fig. 6. Ajiro *et al.* reported three clear metamagnetic transitions in the curves below 40 T parallel to the c axis using a single-crystal sample of stoichiometric $CuFeO_2$.[10] They reported three distinct transitions at about 7, 13, and 20 T with increasing and decreasing magnetic field below 40 T. On the other hand, in our results of nonstoichiometric $CuFeO_{2+\delta}$, there is another small transition around 23 T for all samples, as clearly observed in the case of $\delta=-0.026$ in Fig. 6 (indicating H_4). This result means that this transition is attributable to the oxygen nonstoichiometry and that the oxygen nonstoichiometry strongly affects the stability of the spin structure around 23 T at 4.2 K.

It is also found that the oxygen nonstoichiometry affects the three metamagnetic transition fields of stoichiometric $CuFeO_2$. Figure 7 shows the metamagnetic transition fields H_1, H_2, and H_3 of $CuFeO_{2+\delta}$, as a function of δ in both cases of deficiency ($\delta<0$) and excess ($\delta>0$). Stoichiometric $CuFeO_2$ data by Ajiro *et al.* are also plotted in this figure.[10] It should be noted that the oxygen defect in both types shifts these three transitions to the higher magnetic-field region with increasing the defect content. This means that it stabilizes every AF phase against magnetic field. However, the effects slightly depend on the type of oxygen defect. Although excess oxygen simply stabilizes these AF phases, a large amount of deficient oxygen makes them unstable.

Since the metamagnetic transition is strongly related to the magnetic anisotropy energy, the results in Fig. 7 reflect the effect of the nonstoichiometry on the magnetic anisotropy of $CuFeO_2$. It is interesting that both types of the oxygen defects in the present oxygen content region stabilize every AF phase in magnetic field parallel to the *c* axis. This means that both types of oxygen defects increase magnetic anisotropy. Especially, the stabilization by the oxygen excess is interesting because the fundamental magnetic configuration of $CuFeO_2$ is destroyed by decreasing the ratio c/a and appearing Cu^{2+} magnetic ions in nonmagnetic Cu^+ layers due to the excess oxygens, as mentioned in the previous section.

Although it is difficult to explain these results explicitly, they may be related to the change in the lattice parameters, the site of deficient or excess oxygens. Besides, the magnetic anisotropy of the induced divalent cations, Fe^{2+} ($L=2$, $S=2$) in the case of oxygen deficiency and Cu^{2+} ($L=2$, $S=\frac{1}{2}$) ions in the case of oxygen excess may be also effective, because the former ions are in the octahedrally coordinated Fe site and have a magnetic anisotropy due to the residual orbital angular moments induced by the residual orbital degeneracies.[18] The latter ions are in the linearly coordinated Cu site and have a magnetic anisotropy due to the magnetic dipole interaction and anisotropic exchange interaction.[19]

IV. SUMMARY

Effects of oxygen nonstoichiometry on stabilities of the AF phases of $CuFeO_2$ with a delafossite-type structure have been investigated using $CuFeO_{2+\delta}$ single crystals with stoichiometry varying from oxygen deficiency ($\delta=-0.026$, -0.061) to oxygen excess ($\delta=0.014, 0.085$). The temperature dependence of the magnetic susceptibility between 5 and 300 K in 0.1 T parallel to the *c* axis and the magnetic-field dependence of magnetization below 40 T parallel to the *c* axis at 4.2 K has been clarified.

It is found that stabilities of the AF phases are strongly affected by the oxygen defects. The excess oxygen stabilizes the four-sublattice AF phase in magnetic fields against temperature. On the other hand, the deficient oxygen destabilized this AF phase. These results are explained by changes in the lattice parameters and induced divalent cations on the fundamental magnetic configuration of $CuFeO_2$.

It should be noted that both types of oxygen defects bring another metamagnetic transition around 23 T. Besides, they stabilize AF phases at 4.2 K against the magnetic field parallel to the *c* axis below 40 T. In the case of the oxygen deficiency, the effects are, however, not simple. That is, a large amount of deficiency destabilizes the AF phases. These results indicate that oxygen nonstoichiometry enhances magnetic anisotropy in both cases of deficient and excess oxygens. The effects might be related to changes in the lattice parameters, site of deficient or excess oxygens, and magnetic anisotropy of the induced divalent cations, Fe^{2+} ($L=2$, $S=2$) and in the octahedrally coordinated site or Cu^{2+} ions ($L=2$, $S=\frac{1}{2}$) in the linearly coordinated site.

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In these references, the magnetic anisotropy energy of FeO in which Fe^{2+} ions were in the octahedral coordination site was discussed. In this case the orbital degeneracies of Fe^{2+} are not completely removed and the residual orbital angular momenta play an important role through the presence of the spin-orbit coupling and through the direct effect of the orbital magnetic moments.

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