Magnetic phase diagram of multiferroic delafossite

CuFe$_{1-y}$Ga$_y$O$_2$

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Abstract. We report magnetic susceptibility measurements on nonmagnetic impurity-doped multiferroic CuFe$_{1-y}$Ga$_y$O$_2$ with $0 \leq y \leq 0.08$. The temperature versus Ga concentration magnetic phase diagram was obtained. Comparing the presently obtained phase diagram of CuFe$_{1-y}$Ga$_y$O$_2$ with that of CuFe$_{1-x}$Al$_x$O$_2$, we find that the stability of 4SL ground state for substitution of nonmagnetic ions does not depend on the nonmagnetic ionic radius significantly. On the other hand, the FEIC phase in CuFe$_{1-y}$Ga$_y$O$_2$ exists in a wider region of $0.02 \leq y \leq 0.05$ than CuFe$_{1-x}$Al$_x$O$_2$. We thus find that the local lattice distortion caused by large difference in ionic radii between Al$^{3+}$ and Fe$^{3+}$ affects the stability of the FEIC phase for nonmagnetic ion substitution significantly.

1. Introduction

For a long time, the delafossite CuFeO$_2$ has been extensively studied as a triangular lattice antiferromagnet,[1, 2] because of its unconventional spin behaviors, such as magnetic field-induced multistep magnetization changes[3] and novel magnetoelastic coupling.[4] Since the recent discovery of the magnetic field-induced ferroelectric phase transition,[5] the magnetoelastic coupling in this compound has attracted much attention as well. CuFeO$_2$ is a unique multiferroic material that exhibits both magnetic-field-induced[5] and impurity-induced[6, 7] ferroelectric phase transitions. In addition, unlike well-known multiferroic materials, such as TbMnO$_3$[8] and CoCr$_2$O$_4$[9], that exhibit noncollinear magnetic ordering with “cycloidal” components, the ferroelectricity in CuFeO$_2$ and CuFe$_{1-x}$Al$_x$O$_2$ is induced by “proper helical” ordering.[10, 11] Recently, Arima has argued that the coupling between spin and electric dipole moment in CuFeO$_2$ can be explained by the combined effect of $d-p$ hybridization between Fe 3$d$ and O 2$p$ orbitals and spin orbit coupling,[12] which is based on the theory developed by Jia et al.[13] The experimental evidence for the $d-p$ hybridization mechanism has not, however, been obtained so far.

The ferroelectric state in the pure CuFeO$_2$ occurs when an external magnetic field higher than 7 T. On the other hand, in the doped CuFe$_{1-x}$Al$_x$O$_2$, the ferroelectric and magnetically incommensurate (FEIC) phase develops without an external magnetic field that coexists with the paraelectric and partially disordered (PD) phase.[10] The single FEIC phase without the PD phase can be obtained when the system is cooled under an external magnetic field higher than 4 T.[10]
Recently, we have succeeded in obtaining the single FEIC phase without magnetic field by substituting nonmagnetic Ga$^{3+}$ ions with Fe$^{3+}$ ions in the chemical composition of CuFeO$_{0.963}$Ga$_{0.037}$O$_2$. The phase transition temperatures in this compound are almost the same as those observed in CuFe$_{0.005}$Al$_{0.02}$O$_2$, which indicates that the Al$^{3+}$-doping has larger effects on the magnetic properties of CuFeO$_2$. This might be due to the different local lattice distortions for Al$^{3+}$ and Ga$^{3+}$ ions that originate from their different ionic radii. In order to reach a better understanding of their doping effects, we have systematically performed magnetic bulk susceptibility measurements on single crystals of CuFe$_{1−y}$Ga$_y$O$_2$ with various Ga concentrations.

2. Experimental detail

Single crystals of CuFe$_{1−y}$Ga$_y$O$_2$ with $y = 0.010, 0.013, 0.016, 0.020, 0.037, 0.050, 0.060$ and $0.080$ were grown by the floating zone technique.[14] The sample with $y = 0.037$ was chemically analyzed by the inductively coupled plasma-optical emission spectrometry and was confirmed the Ga concentration to be equal to the nominal value, 0.037.[14] Thus, we assume that the Ga concentration in other samples are also the same as their nominal values. Magnetic susceptibility measurements were performed using the Magnetic Property Measurement System of Quantum Design.

3. Results and Discussion

Temperature dependence of the magnetic susceptibility of CuFe$_{1−y}$Ga$_y$O$_2$ is shown in figure 1. In CuFeO$_2$, with decreasing temperature from paramagnetic (PM) phase, a small peak anomaly appears at $T_{N1}(y = 0.000) = 14$ K in the susceptibility data obtained with a weak magnetic field (100 Oe) that is applied parallel and perpendicular to the crystallographic $c$-axis, $\chi_{||c}$ and $\chi_{\perp c}$, that indicates the second order magnetic phase transition from the PM phase to the PD phase. Below $T_{N1}$, $\chi_{||c}$ is slightly smaller than $\chi_{\perp c}$ in the PD phase. With further decreasing temperature, $\chi_{||c}$ reduces rapidly at $T_{N2}(y = 0.000) = 10.7$ K; at the same time, a relatively small step anomaly is observed in $\chi_{\perp c}$. These anomalies correspond to the first order phase transition from the PD phase to the 4SL phase. In the samples with $y \leq 0.016$, the anomalies mentioned above are observed, indicating that the 4SL ground state remains up to $y = 0.016$.

Our recent neutron diffraction and bulk property measurements on the $y = 0.037$ sample have determined, upon cooling, the phase transition temperatures for the successive transitions (PM ↔ oblique PD(OPD) ↔ PD ↔ FEIC), as $T_{N1}$ (PM → OPD), $T_{N2}^{low}$ (OPD → PD) and $T_{N2}^{high}$ (PD → FEIC).[14] In the magnetic susceptibility, a small peak anomaly appears at $T_{N1}(y = 0.037) = 14$ K, which corresponds to the second order magnetic phase transition from the PM phase to the OPD phase. In the OPD phase, isotropic magnetic susceptibility is observed, i.e. $\chi_{||c} = \chi_{\perp c}$. At the phase transition from the OPD phase to the PD phase, with decreasing temperature, $\chi_{||c}$ and $\chi_{\perp c}$ bifurcate at $T_{N2}^{high}(y = 0.037) = 10$ K. At $T_{N2}^{low} = 7.1$ K where the magnetic phase transition from the PD phase to the FEIC phase, discontinuous reductions are observed in both $\chi_{||c}$ and $\chi_{\perp c}$. Note that these reductions observed at $T_{N2}^{low}$ are much tinier than those observed at the phase transition from the PD phase to the 4SL phase in $y \leq 0.016$.

Guided by the anomalies observed at the phase transitions in the $y = 0.037$ sample, we have identified the phase transitions in the samples with $y \geq 0.020$. In the $y = 0.020$ sample, a small peak anomaly is observed at $T_{N1}(y = 0.020) = 14$ K, which is the same as the case of $y = 0.037$. However, unlike the $y = 0.037$ sample, $\chi_{||c}$ is not the same as $\chi_{\perp c}$ just below $T_{N1}(y = 0.020)$. Since the observed anisotropic susceptibility corresponds to not the OPD phase but the PD phase, the phase transition at $T_{N1}(y = 0.020)$ is concluded to be from the PM phase to the PD phase. With further cooling in the $y = 0.020$ sample, both $\chi_{||c}$ and $\chi_{\perp c}$ reduce discontinuously at $T_{N2}^{low}(y = 0.020) = 8.6$ K, which corresponds to the phase transition from the PD phase to the
**Figure 1.** Temperature dependence of the magnetic susceptibility in CuFe$_{1-y}$Ga$_y$O$_2$. The dotted line denotes the phase transition temperature (PM $\rightarrow$ PD or OPD), $T_{N1}$. Single, double and triple arrows denote the phase transition temperatures, $T_{N2}$ (4SL $\rightarrow$ PD), $T_{N2}^{high}$ (OPD $\rightarrow$ PD) and $T_{N2}^{low}$ (PD $\rightarrow$ FEIC).

FEIC phase. The anomalies observed in the $y = 0.050$ sample are the same as those observed in the $y = 0.037$ sample apart from the shift of each transition temperature. The transition temperatures are $T_{N1}(y = 0.050) = 13.6$ K, $T_{N2}^{high}(y = 0.050) = 5.4$ K and $T_{N2}^{low}(y = 0.050) = 4.6$ K. In the $y = 0.080$ and $y = 0.060$ samples, isotropic magnetic susceptibility is observed below $T_{N1} = 13.5$ K, which means that the OPD phase remains at the lowest temperature.

Figure 2(b) shows the phase diagram of CuFe$_{1-y}$Ga$_y$O$_2$ as a function of the Ga concentration and temperature. Let us compare this phase diagram with that of CuFe$_{1-x}$Al$_x$O$_2$ shown in figure 2(a). In CuFe$_{1-x}$Al$_x$O$_2$, the 4SL ground state survives up to $x = 0.015$ and the FEIC phase exists in $0.015 \leq y \leq 0.030$ with the coexistence of the PD phase, as shown in figure 2(a). In CuFe$_{1-y}$Ga$_y$O$_2$, as shown in figure 2(b), the 4SL phase remains up to $y = 0.016$, which is almost the same as the case of the Al-substitution. This result indicates that the stability of
4SL ground state for substitution of nonmagnetic ions does not depend on whether ion radius of nonmagnetic ion is close to magnetic Fe$^{3+}$ or not significantly. On the other hand, the FEIC phase in CuFe$_{1-y}$Ga$_y$O$_2$ exists in a wider region of $0.02 \leq y \leq 0.05$. In addition, the FEIC is realized without the coexistence of the PD phase, which has been revealed by the recent neutron diffraction study.[14] We thus conclude that the local lattice distortion caused by a large difference in ionic radii between Al$^{3+}$ and Fe$^{3+}$ affects the stability of the FEIC phase for nonmagnetic ion substitution significantly. We add that the stability of the OPD phase is also affected by the local distortion significantly.

4. Summary
We have performed magnetic susceptibility measurements on nonmagnetic impurity-doped multiferroic CuFe$_{1-y}$Ga$_y$O$_2$ with $0 \leq y \leq 0.08$. The temperature versus Ga concentration phase diagram was obtained. Comparing the presently obtained phase diagram of CuFe$_{1-y}$Ga$_y$O$_2$ with that of CuFe$_{1-x}$Al$_x$O$_2$, we found that the stability of 4SL ground state for substitution of nonmagnetic ions does not depend on the nonmagnetic ionic radius significantly. On the other hand, the FEIC phase in CuFe$_{1-y}$Ga$_y$O$_2$ exists in a wider region of $0.02 \leq y \leq 0.05$ than CuFe$_{1-x}$Al$_x$O$_2$. We also found that the large local lattice distortion, caused by the nonmagnetic dopant with the difference in ionic radius between magnetic and nonmagnetic ions, affects significantly the stability of the FEIC phase.

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