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Inelastic neutron scattering study of frustrated Heisenberg triangular magnet $CuFeO_2$

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Abstract

We have studied the magnetic excitation spectrum of the geometrically frustrated triangular lattice antiferromagnets of $CuFeO_2$ with collinear ground state and $CuFe_{1-x}Al_xO_2$ ($0.014 \leqslant x \leqslant 0.030$) with noncollinear ground state, using inelastic neutron scattering measurements on the single crystals. We have reported almost complete spin-wave dispersion relations and the temperature dependence of the magnetic excitation spectrum in both pure and slightly diluted samples. While the higher-energy spin-wave branches remain almost unchanged between the pure and diluted samples, the energy gap of the lowest-energy branch in $CuFeO_2$ becomes zero as a result of the dilution, suggesting the retrieval of the original Heisenberg spin character of the orbital singlet Fe^{3+}. Furthermore, by comparing with recent elastic neutron diffraction and x-ray measurements, we discuss the interrelation among the magnetic ordering, crystal lattice distortion and magnetic excitation qualitatively.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, interplay between spin and lattice degree of freedoms in geometrically frustrated systems has become a subject of renewed interest. Although such systems are prevented from ordering due to the macroscopic degeneracy of their ground state, the spin systems may achieve magnetic ordering with the help of a crystal lattice distortion which lifts the degeneracy of the magnetic exchange energy.

$CuFeO_2$ with delafossite crystal structure has been studied extensively in the last decade as one of the model materials of geometrically frustrated triangular lattice antiferromagnets (TLA) [1–3]. This material shows successive magnetic phase transitions at $T_{N1} \sim 14$ K and $T_{N2} \sim 11$ K [2]. Since the magnetic ion is Fe^{3+} ($S = \frac{5}{2}$, $L = 0$) with no orbital momentum,

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a significant anisotropy should not be expected in this material. However, in contrast to the three-sublattice 120° magnetic structure expected from the classical Heisenberg spin TLA, the collinear four-sublattice (↑↑↓↓) magnetic structure with *quasi*-Ising character is realized as the ground state [1, 2]. Recently, our x-ray diffraction measurements have revealed the superstructural 'scalene triangle' (ST) lattice distortion below T_{N2}, which causes the three different exchange interactions in the triangular lattice plane to lift the vast degeneracy of the strongly frustrated spin system and leads to the four-sublattice ground state [4].

The magnetic properties in the frustrated spin system are highly sensitive to chemical impurity, because the delicate balance of the competing exchange interactions should be disturbed by the chemical defects. We have studied the effect of nonmagnetic Al^{3+} impurity on the magnetic properties in $CuFe_{1-x}Al_xO_2$. The quasi-Ising four-sublattice ground state disappears at slight Al concentration ($x \sim 0.014$), and instead the low-temperature (LT) phase, which was expected to be a non-collinear magnetic structure [6], is *impurity*-induced.

Furthermore, we have also investigated the magnetic excitation spectrum in $CuFeO_2$ and $CuFe_{1-x}Al_xO_2$ with $x = 0.0208$ in our preliminary neutron scattering measurements [7]. The previous measurements reported that the spin-wave dispersion relations differ significantly from each other. However, due to the lack of knowledge of the crystal lattice distortions and the detail magnetic orderings of $CuFe_{1-x}Al_xO_2$, we could not discuss the interrelation among spin-wave excitations, crystal lattice distortions [4] and magnetic orderings [5, 6] at that time.

This time, keeping in mind the new knowledge for the lattice and magnetic orderings, we have reinvestigated the magnetic excitation spectrum of $CuFeO_2$ and $CuFe_{1-x}Al_xO_2$ ($0.014 \leqslant x \leqslant 0.030$), using inelastic neutron scattering measurements.

2. Experimental procedure and results

Single crystals of nominal composition of $CuFe_{1-x}Al_xO_2$ were prepared by the floating zone technique. For the purpose of investigation of the magnetic excitations in the diluted system, we chose $x = 0.0155$ as well as $x = 0.0208$ samples, which exhibit distinct successive magnetic phase transitions (paramagnetic (PM) → oblique partially disordered (OPD) → partially disordered (PD) → LT phases). For the $x = 0$ sample, we have performed the inelastic neutron scattering measurements using cold neutron triple-axis spectrometer 4F2 at Laboratoire Léon Brillouin (LLB) in Saclay, France. We also used the cold neutron triple-axis spectrometer HER and thermal neutron triple-axis spectrometer GPTAS at JRR-3M in the Japan Atomic Energy Research Institute, Tokai, Japan, for the $x = 0.0155$ and the $x = 0.0208$ samples. For all measurements, the respective sample was mounted with the $\langle 1\bar{1}0 \rangle$ axis vertical in the ^{4}He-pumped cryostat so as to provide access to the (H, H, L) reciprocal lattice zone.

2.1. $CuFeO_2$

The 4F2 spectrometer was operated in the constant $k_f = 1.30$ Å^{-1} or 1.55 Å^{-1} mode with horizontal collimations 60′–60′–60′. The higher-order contaminations of scattered neutrons were removed by the nitrogen-cooled Be filter placed on the back of a sample.

The spin-wave dispersion relation for the four-sublattice ground state of $CuFeO_2$ was shown in figures 1(a)–(c). The dispersion relation consists of three spin-wave branches — the lowest-energy (LE) branch, the middle-energy (ME) branch, and the highest-energy (HE) branch — which are illustrated in figure 1(a). In addition to the LE and ME branches in the low-lying energy region around the magnetic zone centre, which were reported in our previous work [7], we newly observed the HE branch and the fine structure around the zone boundary in the present measurements. We confirmed that the LE branch has the two bottom

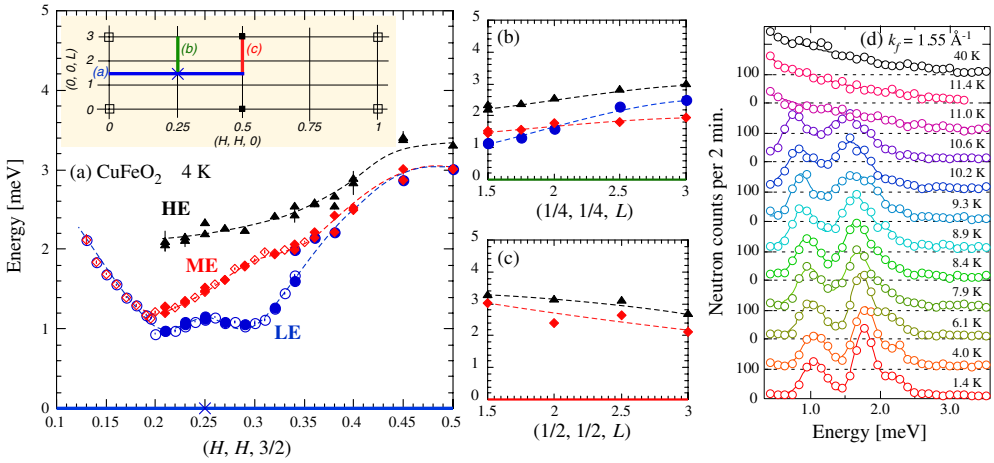

Figure 1. The spin-wave dispersion relation of $CuFeO_2$ at 4 K along (a) $(H, H, \frac{3}{2})$, (b) $(\frac{1}{4}, \frac{1}{4}, L)$ and (c) $(\frac{1}{2}, \frac{1}{2}, L)$ lines. The open and closed symbols denote the data for the previous and present measurements, respectively. The dotted lines are guides for the eye. The inset in (a) shows the reciprocal lattice map of the (H, H, L) zone. The cross, open square and solid square symbols denote the reciprocal lattice positions of magnetic, nuclear and superlattice reflections, respectively. (d) Temperature dependence of the constant-Q scan profiles at $\mathbf{Q} = (0.29, 0.29, \frac{3}{2})$.

positions which correspond to the two wavenumbers $q \sim 0.21$ and $\frac{1}{2} - q \sim 0.29$ characteristic of the impurity-induced noncollinear magnetic structure in the LT phase in $CuFe_{1-x}Al_xO_2$ ($0.014 \leqslant x \leqslant 0.030$). This suggests that, although $CuFeO_2$ does not show the original Heisenberg character of the orbital singlet Fe^{3+} in the magnetic ordering, the Heisenberg character might be hidden in the low-lying magnetic excitation energy spectrum.

The superstructural 'scalene triangle type' (ST) lattice distortion, which doubles the unit cell along the hexagonal $\langle 110 \rangle$ and causes the change of the translational symmetry of the exchange bonds, has recently been reported by our x-ray diffraction study [4]. Reflecting the ST lattice distortion, the LE branch reverses at the reciprocal lattice point of $(\frac{1}{4}, \frac{1}{4}, \frac{3}{2})$. On the other hand, in spite of the superstructural lattice distortion, the ME and HE branches do not reverse at this point, and instead they reverse at the Brillouin zone boundary of the conventional hexagonal cell.

We should also mention the dispersion curves along the hexagonal c-axis direction. As shown in figures 1(b) and (c), significant dispersion behaviours were observed along the c-axis, suggesting that the inter-plane exchange interactions are almost comparable to the in-plane interactions. This feature has been pointed out by Petrenko *et al* [3].

In order to investigate how the successive magnetic phase transitions correspond to the magnetic excitation spectrum, we measured the temperature dependence of the inelastic scattering profiles. The results are shown in figure 1(d). Any inelastic peaks corresponding to the spin-wave branches were not observed in the PD phase as well as the PM phase. This result is consistent with the partial disorder picture characterized by thermal spin fluctuations in the PD phase [2]. In the four-sublattice phase, a decrease in temperature slightly reduces the lattice constant c [4, 8]; therefore, reflecting a change in Fe–O–Fe bond angle toward 180°, the antiferromagnetic super exchange interactions were expected to increase. However, the reflection of the expected change was not observed in the magnetic excitation energy significantly.

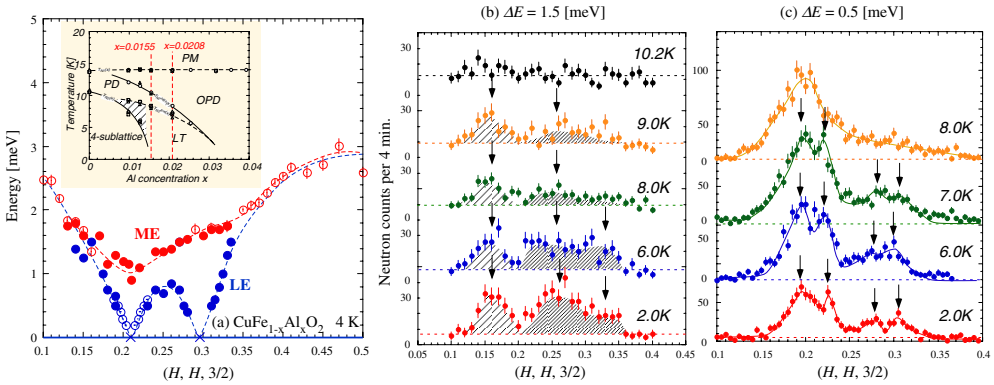

Figure 2. The spin-wave dispersion relation for the LT phase of $CuFe_{1-x}Al_xO_2$. Solid and open symbols denote the data measured for the $x = 0.0155$ and the $x = 0.0208$ sample, respectively. The dotted lines are guides for the eye. The inset shows the x–T magnetic phase diagram of $CuFe_{1-x}Al_xO_2$, which was taken from [5]. Temperature dependence of the reciprocal lattice scans at the fixed energy transfers (b) 1.5 meV and (c) 0.5 meV in the $x = 0.0155$ sample.

2.2. $CuFe_{1-x}Al_xO_2$

The HER spectrometer was operated in the constant $k_i = 1.25$–1.55 Å^{-1} mode with almost relaxed horizontal collimations 40′–80′–80′. The higher-order contaminations of incident neutrons were removed by the cooled Be filter placed in front of a sample. Since the reachable energy transfer was ∼2.3 meV in this mode, we also used the thermal neutron spectrometer GPTAS to determine the excitation energy around the zone boundary. The GPTAS spectrometer was operated in the constant $k_f = 2.57$ Å^{-1} mode with collimations 80′–40′–40′.

The spin-wave dispersion relation at 4 K for the LT phase was shown in figure 2(a). In contrast to the case of the $x = 0$ sample, the LE branch has no energy gap. It starts from the two magnetic Bragg points, $(q, q, \frac{3}{2})$ and $(\frac{1}{2} - q, \frac{1}{2} - q, \frac{3}{2})$ with $q \sim 0.21$, strongly suggesting the retrieval of the original Heisenberg spin character of the orbital singlet Fe^{3+}, which was also stated in our previous work [7].

In addition to the previously observed LE branch, the ME branch was newly observed in the present measurements, which remains almost unchanged from that of the $x = 0$ sample. It should be noted that the fine structure around the zone boundary and the HE branch seen in the $x = 0$ sample were not measurable, because of the use of thermal neutrons with worse energy resolution in the measurements for the diluted samples. In contrast to the significant change in the LE branch in the nonmagnetic dilution, the ME branch remains almost unchanged, as seen in figures 1(a) and 2(a).

Furthermore, as is similarly seen in the $x = 0$ sample, the LE branch in the LT phase reverses at the reciprocal lattice point of $(\frac{1}{4}, \frac{1}{4}, \frac{3}{2})$, reflecting the doubling of the unit cell along the hexagonal ⟨110⟩ axis; however, the ME branch does not reverse at this point and instead reverses at the zone boundary of the conventional hexagonal cell. Consequently, we found that, while the LE branch is highly sensitive to both the nonmagnetic impurity and the crystal lattice distortion, the higher ME branch is insensitive to them.

The successive magnetic phase transitions of $CuFe_{1-x}Al_xO_2$ ($0.014 \leqslant x \leqslant 0.030$) are rather complex. Nevertheless, using the $x = 0.0155$ sample whose phase transitions are relatively clear, we measured the temperature dependence of the magnetic excitation spectrum. As seen in the inset of figure 2(a), the phase transitions occur at $T_{N1} \sim 14$ K (PM → OPD), $T_{N2}^{high} \sim 10.5$ K (OPD → PD) and $T_{N2}^{low} \sim 8$ K (PD → LT).

In order to investigate the temperature dependence of the ME brach, we performed the reciprocal lattice scans at fixed energy transfer $\Delta E = 1.5$ meV. The spin-wave signals were observed below T_{N2}^{high} in the PD phase of the $x = 0.0155$ sample, as shown in figure 2(b). It should be noted that the ME branch was not observed in the PD phase of the pure system, in contrast to the diluted system. We thus found that, in spite of the same magnetic structure in the PD phase of both systems, the spin dynamics are significantly affected by a nonmagnetic impurity. As shown in figure 2(c), the reciprocal lattice scans at $\Delta E = 0.5$ meV show that the spin-wave signals corresponding to the LE branch were observed below $T_{N2}^{low} \sim 8$ K. From these experimental facts, we found that the LE branch was considered to be characteristic of the LT phase.

3. Summary

We have performed inelastic neutron scattering measurements on geometrically frustrated TLA $CuFeO_2$ and $CuFe_{1-x}Al_xO_2$, using single crystals. We obtained the almost complete spin-wave dispersion relations in both samples.

In the pure system, in addition to the LE and ME branches in the low-lying energy region around the magnetic zone centre, which were previously reported, we newly obtained the HE branch and the fine structure around the zone boundary in the present measurements. We also confirmed that the LE branch has the two bottom positions, which correspond to the two wavenumbers characteristic of the impurity-induced noncollinear LT ground state: this suggests that the $CuFeO_2$ does not show the original Heisenberg character of the orbital singlet Fe^{3+} in the magnetic orderings; the original character might be hidden in the low-lying magnetic energy spectrum.

The superstructural ST lattice distortion, which causes the change in the translational symmetry of the exchange bonds, has recently been reported by our x-ray study [4]. Reflecting this lattice distortion, the LE branch reverses at the magnetic zone centre $(\frac{1}{4}, \frac{1}{4}, \frac{3}{2})$; on the other hand, the higher ME and HE branches do not reverse at this point, and instead reverse only at the zone boundary of the conventional hexagonal cell. In the diluted systems, the energy gap of the LE branch becomes zero, suggesting the retrieval of the original Heisenberg spin character of Fe^{3+}. In contrast, the newly obtained ME branch in the diluted system remains almost unchanged from that in the pure system. We thus found that, while the LE branch is highly sensitive to both the nonmagnetic impurity and the crystal lattice distortion, the higher ME branch is insensitive to them.

In this work, compared with the results of our x-ray and neutron diffraction measurements, we have discussed the inter-relation among the magnetic ordering, crystal lattice distortion and magnetic excitation qualitatively. However, for further understanding of the experimental data, theoretical investigation is required.

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