Neutron scattering study of Ag, Mg and Al substitution effects on the magnetic excitations in CuCrO$_2$

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Abstract. CuCrO$_2$ is a quasi two-dimensional triangular-lattice antiferromagnet with \( S = \frac{3}{2} \). Recently, it was found that small amount of element substitution strongly affects magnetic and transport properties. In the present study, we studied magnetic excitations in powder samples of CuCrO$_2$, Cu$_{0.85}$Ag$_{0.15}$CrO$_2$, Cu$_{0.97}$Mg$_{0.03}$CrO$_2$ and Cu$_{0.85}$Al$_{0.15}$O$_2$ by inelastic neutron scattering using the chopper spectrometer AMATERAS at J-PARC. We observed a variety of the magnetic excitations induced by different types of the element substitutions, and they should be keys to understand the magnetic and transport properties.

1. Introduction

CuCrO$_2$ has triangular-lattice layers of magnetic Cr$^{3+}$ ions (3d$^3$) separated from each other by non-magnetic layers of Cu$^+$ ions (3d$^{10}$), which makes this compound a quasi two-dimensional triangular-lattice antiferromagnet with \( S = \frac{3}{2} \). With decreasing temperature \( (T) \), the Cr spins form a proper screw structure whose wave vector is \((q,q,0)\) with \( q \sim 1/3 \) [1–3]. Recently, it was found that element substitution strongly affects magnetic and transport properties. For example, substitution of the inter-layer Cu$^+$ ions with Ag$^+$ ions (4d$^{10}$) enhances the two-dimensionality in the magnetic correlation, and may induce some unusual magnetic excitations [4]. Substitution of the intra-layer Cr$^{3+}$ ions with non-magnetic Mg$^{2+}$ ions introduces holes, which slightly increases the transition temperature of the three-dimensional magnetic ordering \( (T_N) \) and drastically enhances the electric conductivity [5, 6]. On the other hand, substitution of the Cr$^{3+}$ ions with isovalent non-magnetic Al$^{3+}$ ions does not change \( T_N \), but induces a large increase in the two-dimensionality in the magnetic correlations [7].

In the present study, we have studied magnetic excitations in Ag, Mg and Al substituted CuCrO$_2$ in addition to CuCrO$_2$ by inelastic neutron scattering to elucidate the substitution effect on the spin dynamics in CuCrO$_2$.

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2. Experiments

About 3 cm$^3$ polycrystalline samples of CuCrO$_2$ (CCO), Cu$_{0.85}$Ag$_{0.15}$CrO$_2$ [(CA)CO], CuCr$_{0.97}$Mg$_{0.03}$O$_2$ [C(CM)O] and CuCr$_{0.85}$Al$_{0.15}$O$_2$ [C(CA)O] were synthesized by a standard solid-state reaction method [4–7]. They have rhombohedral crystal structures (space group $R\bar{3}m$) with the lattice constants $a \sim 3.0$ Å and $c \sim 17$ Å [4, 5, 7]. Their $T_N$’s determined by specific heat measurements are 24 K (CCO), 13 K [(CA)CO], 26 K [C(CM)O] and 24 K [C(CA)O] [7]. The neutron scattering measurements were performed with the time-of-flight technique using the cold neutron disk-chopper spectrometer AMATERAS installed on the BL14 beamline in the Materials and Life Science Experimental Facility (MLF), the Japan Proton Accelerator Research Complex (J-PARC) [8]. The power of the accelerator was $\sim$120 kW. The incident energy of neutrons ($E_i$) of 15 meV with the elastic energy resolution of 1 meV [9] were utilized. We analyzed all the data with the software suite Utsusemi [10] to obtain the powder averaged scattering function $S(Q, E)$ ($Q$ is the amplitude of the momentum transfer and $E$ is the energy transfer) [9]. The difference in utilized neutron flux between data was normalized by the counts of the protons injected into the neutron target. The difference in volume between the samples was normalized by intensities of nuclear Bragg peaks [CCO and (CA)CO] or the mole numbers [CCO, C(CM)O and C(CA)O].

3. Results and Discussions

Figure 1 shows elastic scattering profiles of the four samples measured at the base temperatures [6 K for CCO, 5 K for (CA)CO, 5 K for C(CM)O and 4 K for C(CA)O]. These data were obtained by cutting the $S(Q, E)$ data at $E = 0$ meV with an energy width $\pm 1$ meV. CCO shows magnetic Bragg peaks, which are indexed as $(q, q, 0), (q, q - 1, 1), (q - 1, q, 2), (q, q, 3)$ and $(q, q - 1, 4)$ with $q \sim 1/3$ (closed circles). The Mg substitution decreases the intensities of the magnetic Bragg peaks (open circles). Interestingly, the decrease is too large to be accounted for by the spin dilution of 3%. As for the peak widths, they are almost similar to those of CCO. On the other hand, the Ag substitution much decreases the intensities of the magnetic Bragg peaks and increases their widths (closed triangles), which originates from the increase in two-dimensionality in the magnetic correlations [4, 9]. Further decrease in the intensity and broadening of the peak widths are observed in the Al substituted sample (open triangles). Each of the magnetic Bragg peaks are hardly distinguished from each other, and they merge into one broad asymmetric profile, which is characteristic of two-dimensional correlations. Therefore, the decrease in intensity and the peak broadening in C(CA)O should reflect the large increase of the two-dimensionality in the magnetic correlation, though there may be the contribution of randomness in the Cr spins introduced by the spin dilution of 15% [7].
Figure 2. $S(Q, E)$ maps with $E_i = 15$ meV of (a) CCO, (b) (CA)CO, (c) C(CM)O and (d) C(CA)O measured at $T = 6, 5, 5$ and $4$ K, respectively.

Figure 2 shows $S(Q, E)$ maps of the four samples measured at the base temperatures. All the samples show well defined magnetic excitations. The magnetic excitations in CCO [figure 2(a)] consist of two kinds of components: one is a steep dispersive component at $Q \sim 1.4 \text{ Å}^{-1}$, whose value corresponds to the wave vector of the magnetic ordering $Q = (q, q, 0)$. The other is a less dispersive component (flat component) at $E \sim 5$ meV spreading over a wide range of $Q$. The dispersive component and the flat component may be dominated by fluctuations of the Cr spins within the spiral plane and those out of the spiral plane, respectively [9,11]. In (CA)CO [figure 2(b)], the dispersive component becomes more diffusive compared with CCO, which reflects the increase in the two-dimensionality in the magnetic excitations. The flat component much decreases its intensity and is hard to observe. This suggests that the flat component is intrinsic to the inter-layer correlations between the Cr spins [9].

The excitation spectrum of C(CM)O [figure 2(c)] is apparently similar to that of CCO. However, there are some distinctive differences between the excitation spectra of the two materials. First, the overall weight of the excitation spectrum of C(CM)O is smaller than that of CCO. Furthermore, the energy dependence of the dispersive component shows an interesting character. As the energy decreases, the weight of the dispersive component increases in CCO, while it decreases in C(CM)O. These clear differences cannot be explained solely by the 3% dilution of the Cr spins. Therefore, the holes introduced by the Mg substitution should play an important role for the suppression of the magnetic excitations especially at low energies, as well as for the dramatic increase in the electric conductivity. Though the detailed mechanism of the suppression of the magnetic excitations remains to be an open question, it may be the origin of the promotion of the magnetic ordering by the Mg substitution.

The excitation spectrum of C(CA)O [figure 2(d)] is completely different from that of C(CM)O. This is another evidence that the difference in the magnetic excitations between C(CM)O and CCO can not be explained by the spin dilution effect. The spectrum of C(CA)O looks similar to that of (CA)CO, which includes a diffusive dispersive component and a very weak flat component, though the overall weight of the spectrum is much smaller than that of (CA)CO due
to the spin dilution. This fact suggests that the Al substitution enhances the two-dimensionality in the magnetic excitations in the similar manner as the Ag substitution. However, there is a clear difference between (CA)CO and C(CA)O. In (CA)CO, the low energy excitations are much enhanced compensating for the decrease in the elastic scattering, which indicates the increase in the two-dimensionality in (CA)CO is followed by an enhancement of the dynamical character of the spin correlations. On the other hand, the enhancement of the low energy excitations is less evident in C(CA)O, which indicates that the disorder in the spin correlations induced by the Al substitution has a more static character than those by the Ag substitution. Okuda et al. reported that the Al substitution causes a \( T \)-linear spin-glass component in the low-\( T \) magnetic specific heat \( (C_{\text{mag}} \propto T^2) \) \[7\]. The spin-glass component in \( C_{\text{mag}} \) should contribute the \( S(Q, E) \) in a very low-energy region, lower than the energy resolution of the neutron scattering measurement.

4. Conclusion

We have studied magnetic excitations in CuCrO\(_2\), Cu\(_{0.85}\)Ag\(_{0.15}\)CrO\(_2\), CuCr\(_{0.97}\)Mg\(_{0.03}\)O\(_2\), and CuCr\(_{0.85}\)Al\(_{0.15}\)O\(_2\) by inelastic neutron scattering to elucidate the element substitution effects on the spin dynamics in the quasi 2D triangular-lattice antiferromagnet CuCrO\(_2\). We found a variety of the magnetic excitations induced by different types of the element substitutions: The Ag substitution of the inter-layer Cu sites enhances the dynamical and two-dimensional characters in the spin correlations. For the Mg substitution of the intra-layer Cr sites, the doped holes decrease the low-energy part of the spin excitations, which may be closely connected to the promotion of the magnetic ordering as well as the dramatic increase in the electron conductivity. On the other hand, the Al substitution of the intra-layer Cr sites, which does not change the nominal valence in a Cr ion, shows completely different excitation spectrum from the Mg substituted sample. The spectrum rather looks similar to the Ag substituted sample, but the difference from the Ag substituted sample suggests the disorder in the spin correlations has substantial static character.

Acknowledgments

This work was partly supported by Grants-in-Aid for Scientific Research on Priority Areas “Novel States of Matter Induced by Frustration” of MEXT, Japan (19052001 and 19052004) and by a Grant-in-Aid for Scientific Research (B) of JSPS, Japan (20340097).

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