Substitution Effect on the Magnetic State of
Delafossite CuCrO$_2$ Having a Spin-3/2
Antiferromagnetic Triangular Sublattice

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Abstract. We have investigated substitution effects on transport, magnetic, and thermal properties of delafossite CuCrO$_2$ having a spin-3/2 antiferromagnetic triangular sublattice by measurements of resistivity, magnetization, specific heat, and neutron scattering. In the proceeding, we show unique effects of hole-doping by a substitution of nonmagnetic Mg$^{2+}$ ions for magnetic Cr$^{3+}$ ions ($S = 3/2$), randomness introduced between CrO$_2$ layers by a substitution of Ag$^+$ ions for Cu$^+$ ions, and spin-defect introduced into CrO$_2$ layers by a substitution of nonmagnetic Al$^{3+}$ ions for Cr$^{3+}$ ions upon the magnetic state in CuCrO$_2$.

1. Introduction

Quasi two-dimensional (quasi-2D) antiferromagnetic (AF) triangular lattice (ATL) is one of typical models with geometrical frustration and provides a platform to search for exotic quantum phenomena such as spin liquid[1], anomalous Hall effect[2], superconductivity[3], and so on. According to theoretical works, a so-called 120$^\circ$ spin structure is realized in an ATL Heisenberg model with a nearest neighbor bilinear coupling. However, the actually realized phase is controversial if a quantum fluctuation is enhanced by low dimensionality, quantum spin nature, and geometrical frustration.

Delafossite oxide CuCrO$_2$ is one of such quasi-2D ATL compounds. It has a rhombohedral lattice with the space group of $R3m$, where the edge-shared CrO$_6$ octahedral (CrO$_2$) layers and Cu layers alternatively stack (Fig. 1). The Cr$^{3+}$ ions ($3d^3$, $S = 3/2$) form ATLs and the compound shows a noncollinear 120$^\circ$ AF order at the Néel temperature ($T_N$).[4] In order to clarify the ground state and explore a novel phenomenon in a quasi-2D ATL, we have investigated various substitution effects on the electronic, magnetic, and thermal properties of CuCrO$_2$ having a spin-3/2 ATL.[5, 6, 7, 8, 9, 10] In this proceeding, we summarize our studies for the effects of

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various substitutions on the physical properties of CuCrO\textsubscript{2} together with some recent reports by other groups.

2. Results

2.1. Effect of Hole-doping on the transport and magnetic properties of CuCrO\textsubscript{2}

At first, we present the effect of hole-doping by the Mg\textsuperscript{2+} substitution for Cr\textsuperscript{3+} on the transport and magnetic properties for CuCrO\textsubscript{2}. The Mg substitution ideally induces the hole-doping, which is evidenced by the dramatic decrease of the resistivity ($\rho$) (the inset of Fig. 2) and the Hall measurements (not shown). It enhances the magnetization ($M$) around $T_N$ (Fig. 2), slightly increases $T_N$ (Fig. 3), and sharpens the AF transition (Fig. 3), while it largely decreases the Curie-Weiss temperature ($\Theta_{\text{CW}}$ in $\chi = C/(T + \Theta_{\text{CW}}$).) (Fig. 4(b)). Furthermore, the neutron scattering measurements[11] indicate the noncollinear 120\degree AF order below $T_N$ in CuCr\textsubscript{1−$x$}Mg\textsubscript{$x$}O\textsubscript{2} and the Al substitution does not increase $T_N$. These results suggest that the 120\degree AF order is promoted by the itinerant hole doped by the Mg substitution, in spite of the introduction of spin defects into the ATL.

However, the intensity of the (1/3 1/3 0) magnetic Bragg peak observed by the neutron scattering measurements decreases with the Mg substitution and the low-energy AF magnon measured by the inelastic neutron scattering measurements seems to be suppressed by the Mg substitution.[12] Furthermore, according to the recent $\mu^+$SR measurements[13], no oscillatory component was observed below $T_N$ in the ZF-$\mu^+$SR time spectra of CuCr\textsubscript{0.97}Mg\textsubscript{0.03}O\textsubscript{2} and the asymmetry was fitted with dynamic Kubo-Toyabe function, indicating randomly oriented
magnetic moments. These results indicate that the introduced disorder certainly affects the static and dynamic magnetic state, suggesting that the AF order is promoted by an order by disorder mechanism[14] through the coupling between the localized spins and the itinerant holes.

2.2. Effect of disorder on the magnetic property of CuCrO$_2$

Next, we show the effects of disorder introduced by the substitutions of Ag$^+$ (4$d^{10}$, $S=0$) for Cu$^+$ (3$d^{10}$, $S=0$) and Al$^{3+}$ (3$d^0$, $S=0$) for Cr$^{3+}$ on the magnetic and specific heat properties.

The Ag substitution for Cu introduces the randomness between the ATLs, which weakens the magnetic interactions between the ATL layers and induces the dimensional crossover from anisotropic-three-dimensional (3D) AF magnon to short-range 2D AF low-energy excitations.[7] The gradual crossover is evidenced by the gradual change of power ($\alpha$) of the T dependence of low-T $C_{mag}$ from 3 to 2, as shown in the inset of Fig. 3 and Fig. 4(c). Furthermore, the Ag

Figure 3. (Color online) $T$ dependences of magnetic specific heat ($C_{mag}$) around $T_N$ for CuCrO$_2$, CuCr$_{0.97}$Mg$_{0.03}$O$_2$ (Mg 3%), Cu$_{0.85}$Ag$_{0.15}$CrO$_2$ (Ag 15%), and CuCr$_{0.8}$Al$_{0.2}$O$_2$ (Al 20%). The arrows show the Néel temperatures ($T_N$ and $T_{N2}$). The inset shows the $C_{mag}/T$ vs. $T^{-1}$ for CuCrO$_2$, Cu$_{0.85}$Ag$_{0.15}$CrO$_2$, and CuCr$_{0.8}$Al$_{0.2}$O$_2$. The dotted lines are the results of fitting to the formula, $C_{mag}/T = \gamma + \beta T^{-\alpha}$. The substitution dependences of $\alpha$ are shown in Fig. 4(c). These data are from refs. 6, 7 and 9.

Figure 4. Mg, Ag, and Al substitution ($x$) dependences of (a) the Néel temperature ($T_N$ and $T_{N2}$), (b) the Curie-Weiss temperature ($\Theta_{CW}$), and (c) the power ($\alpha$) and $T$-linear coefficient ($\gamma$) of $T$ dependence of $C_{mag}$. These data are from ref. 9.
substitution increases the magnetic entropy below $T_N$, which is attributed to the enhancement of low-energy magnetic excitation in the inelastic regime of neutron scattering (not shown).[7] Taking into account these experimental results[7, 8, 9], this enhanced short-range 2D AF low-energy excitation may be from a spin-liquid[1, 15, 16] or spin-nematic states[17, 18, 19].

On the other hand, the Al substitution introduces both the randomness and spin defect into the ATLs. As shown in Fig. 3, $T_N$ little changes with the Al substitution but induces another magnetic transition ($T_{N2}$). As well as in Cu$_{1-x}$Ag$_x$CrO$_2$, the $T^a$ component of low-$T$ $C_{mag}$ exists and the $\alpha$ changes from 3 to 2 with the Al substitution, as shown in the inset of Fig. 3 and Fig. 4(c). The change suggests the appearance of the same low-energy magnetic excitation as that observed in Cu$_{1-x}$Ag$_x$CrO$_2$, while the spin-glass state manifested by the $T$-linear component of $C_{mag}$ also appears. The change of $\alpha$ by the Al substitution is more gradual than that of the Ag one, which may be because the randomness introduced by the Ag substitution between the ATLs produces the stronger disorder effect on the dynamic magnetic state than the randomness and spin-defect introduced by the Al substitution into the ATLs.

3. Summary

In the proceeding, we summarize our studies for substitution effects on transport, magnetic, and thermal properties of delafossite CuCrO$_2$ having a spin-3/2 antiferromagnetic triangular sublattice.

The hole-doping by the Mg substitution promotes the 120$^\circ$ AF order, although the introduced disorder certainly affects the static and dynamic magnetic states. One of possible mechanism to explain the observed phenomenon is an order by disorder mechanism through the coupling between the localized spins at the ATL and the doped itinerant holes.

The disorder introduced by substitutions of Ag for Cu and Al for Cr reduces the dimensionality of the low-energy magnetic excitations in the process of destruction of the 120$^\circ$ AF order. The short-range 2D AF low-energy excitation enhanced by the Ag and Al substitutions has both macroscopic and microscopic features of spin-liquid or spin-nematic states. The further experiments are eagerly desired to clarify the unusual magnetic state.

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