Hole-doping effect on the magnetic state of delafossite oxide CuCrO$_2$

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Abstract. We investigated the substitution effects of Mg$^{2+}$, Ca$^{2+}$, and Al$^{3+}$ for Cr$^{3+}$ on the magnetic, transport and thermal properties of delafossite oxide CuCrO$_2$, which possesses a quasi-2D Heisenberg triangular antiferromagnetic (AF) lattice. Magnetization and specific heat measurements indicated that AF ordering is promoted by the substitution of nonmagnetic Mg$^{2+}$ for Cr$^{3+}$ ($S = 3/2$), despite the fact that a spin vacancy is introduced in a 120$^\circ$ spin structure at the Cr sites. These results suggest that the residual magnetic frustration is partially broken by spin fluctuations, which are enhanced through the interaction between the itinerant hole introduced by Mg doping and the localized spin at the Cr site.

1. Introduction

The delafossite oxide CuRO$_2$ ($R =$ trivalent cation) is one of a number of systems possessing an antiferromagnetic triangular sublattice. CuRO$_2$ has a layered structure with a space group of $R3m$, which is viewed as the alternate stacking of edge-shared RO$_6$ octahedral (RO$_2$) layers and Cu layers (Fig.1 in ref.1). The magnetic properties of these layered compounds have attracted much attention, since the geometrical frustration in the magnetic triangular sublattice at the $R$ sites causes intriguing properties, such as field induced multistep magnetization change [2] and multiferroics [3]. The introduction of charge carriers, which is possible in some delafossite compounds, may further induce novel phenomena arising from the coupling between the magnetic and transport properties in the quasi-two-dimensional frustrated triangular lattice.

Among such delafossite oxides, CuCr$_{1-x}$Mg$_x$O$_2$ [1] may possess a unique spin-charge coupling system. In the case of the end compound CuCrO$_2$, the Cr$^{3+}$ ions at the $R$ sites have magnetic moments ($S = 3/2$) [4]. According to neutron scattering studies carried out with CuCrO$_2$ [5, 6], the magnetic degeneracy was lifted and the noncollinear 120$^\circ$ magnetic structure was realized in the antiferromagnetic (AF) regime below the ordering temperature ($T_N$) to resolve the magnetic frustration. When some of the Cr$^{3+}$ ions were substituted by nonmagnetic Mg$^{2+}$ ions, however, the magnetic order seems to be promoted (as shown in Fig.1 (a)), despite the introduction of some degree of randomness into the compound that would usually suppress the order. In other words, the residual magnetic frustration appeared to be removed by the introduction of nonmagnetic impurities. In this study, to clarify in depth such a unique Mg-substitution effect,
we investigated in detail the effect of the substitution of \( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \) and \( \text{Al}^{3+} \) for \( \text{Cr}^{3+} \) on their magnetic, transport, and specific heat properties of \( \text{CuCrO}_2 \).

2. Experimental results

2.1. Magnetization

![Figure 1](image-url)

Figure 1. Temperature \((T)\) dependence of magnetization \((M)\) for (a) \( \text{CuCr}_{1-x}\text{Mg}_x\text{O}_2 \) [1], (b) \( \text{CuCr}_{1-x}\text{Ca}_x\text{O}_2 \) [4], (c) \( \text{CuCr}_{1-x}\text{Al}_x\text{O}_2 \) [4], and (d) \( \text{CuCr}_{0.98-y}\text{Mg}_{0.02}\text{Al}_y\text{O}_2 \).

Figure 1 shows the temperature \((T)\) dependence of magnetization \((M)\) for (a) \( \text{Mg}^{2+} \), (b) \( \text{Ca}^{2+} \), (c) \( \text{Al}^{3+}\)-doped, and (d) \( \text{Mg}^{2+} \) and \( \text{Al}^{3+} \) co-doped compounds. In the high temperature regime above about 150 K, all compounds obey Curie-Weiss law and the estimated \( S \) values are 1.4 - 1.5, which are almost consistent with the expected value \((S = \frac{3}{2})\). Around \( T_N \), an anomaly associated with a three dimensional AF magnetic order was observed. In the case of the \( \text{Ca}^{2+} \) doping in Fig.1 (b), the anomaly slightly changes in magnitude affording a better-resolved peak as well as in the Mg doping in Fig.1 (a). On the other hand, the \( \text{Al}^{3+} \) substitutions for \( \text{Cr}^{3+} \)
in (c) CuCrO$_2$ and (d) CuCr$_{0.98}$Mg$_{0.02}$O$_2$ seems to slightly suppress the anomaly around $T_N$ and to slightly decrease $T_N$. These Al$^{3+}$ doping induced changes are qualitatively different from those for the Mg$^{2+}$ and Ca$^{2+}$ dopings and are expected when only randomness is introduced.

2.2. Resistivity

![Figure 2](image_url)

Figure 2 shows the $T$ dependence of resistivity ($\rho$) for CuCrO$_2$, CuCr$_{1-x}$Mg$_x$O$_2$ ($x = 0.01, 0.02, 0.03$) [1], CuCr$_{0.96}$Ca$_{0.04}$O$_2$ [4], CuCr$_{0.9}$Al$_{0.1}$O$_2$ [4], and CuCr$_{0.96}$Mg$_{0.02}$Al$_{0.02}$O$_2$.

The substitutions of divalent ions (Mg$^{2+}$, Ca$^{2+}$) for Cr$^{3+}$ reduces $\rho$, indicating hole doping. On the other hand, the substitution of Al$^{3+}$ for Cr$^{3+}$ in (c) CuCrO$_2$ and (d) CuCr$_{0.98}$Mg$_{0.02}$O$_2$ simply increases $\rho$, which is perhaps due to the randomness introduced by the substitution. All of these experimental results of $M$ and $\rho$ suggest a correlation between the doped holes and the order of local spins at the Cr sites, i.e. the itinerant holes doped by the substitution of divalent ions seem to promote the magnetic order.

2.3. Specific heat

Figure 3 shows the $T$ dependence of $C_{\text{mag}}/T$ for CuCrO$_2$ and CuCr$_{1-x}$Mg$_x$O$_2$, and the inset summarizes the Mg doping dependence of the peak temperature ($T_{\text{peak}}$) of the AF transition with and without a magnetic field [4]. It is clearly observed that the peak becomes sharper and $T_{\text{peak}}$ increases as $x$ increases. Such $x$ dependence of $C_{\text{mag}}$ is apparently correlated with that of $M$ [1]. It is interesting that the change in $T_{\text{peak}}$ induced by a magnetic field of 9 T increases as $x$ increases, indicating that the AF transition is sensitive to a magnetic field only when the holes are present [4]. These results of $C_{\text{mag}}$ are also evidence that the AF transition becomes sharper and the transition temperature increases with the increase in $x$, although the Mg$^{2+}$ substitution for Cr$^{3+}$ is thought to introduce some randomness into the network of the Cr spins.

3. Discussion

One of the possible factors affecting the physical properties may be, in addition to the doped holes and magnetic randomness, a structural change of the lattice stemming from the substitution of the ions. Although a structural phase transition does not occur for any synthesized compounds.
at room temperature, the lattice constant certainly changes with the substitutions. However, the change in the lattice constants introduced by the Mg doping falls between the changes due to the Ca doping and the Al doping and are almost independent on $x$ [4]. The change of lattice constant dose not directly cause the change in $M$ and $\rho$, since the Mg-doped compound with the least change of lattice constant shows the largest change in $M$ and $\rho$ with the substitution [4].

According to the preliminary neutron scattering measurements [6], the spin state for the Mg-doped compound is almost identical to that for CuCrO$_2$. The peak position does not change within the experimental error, but the intensity at the low $2\theta$ is decreased and that at the high $2\theta$ is increased by the Mg$^{2+}$ substitution [6]. Taking into account the Mg$^{2+}$, Ca$^{2+}$, and Al$^{3+}$ substitution dependence of $M$, $\rho$ and $C_{mag}$, the main origin of the stabilization of the AF state is perhaps not the introduced randomness but the doped itinerant holes. The coupling between the local spins at the Cr sites and doped holes may enhance spin fluctuations at the Cr sites [1], which may break the residual magnetic degeneracy as fluctuation-induced symmetry breaking in a highly magnetic degenerate ground state manifold of some frustrated systems [7, 8]. Such partial relaxation of the magnetic frustration makes the AF transition sharper and $T_N$ higher. A detailed investigation of the spin dynamics of CuCr$_{1-x}$Mg$_x$O$_2$ by a neutron scattering measurement would be of great benefit.

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