Effects of substitution on quantum spin system having a nearly non-magnetic state and antiferromagnetic long-range order

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Abstract. The cuprate Cu$_2$CdB$_2$O$_6$ has two Cu sites (Cu1 and Cu2). Cu1 spins are in a nearly non-magnetic state because of formation of AF dimers, while Cu2 spins form antiferromagnetic (AF) long-range order. We investigated effects of substitution of Zn for Cu on magnetism of this cuprate. The reduction in AF transition temperature per Zn is small in comparison with other quasi-one-dimensional antiferromagnets. We consider that the system of the Cu2 spins is a two-leg ladder.

1. Introduction
Studies of substitution effects have contributed to developments of solid state physics. We can investigate properties of host materials by substitution of impurities. For example, the superconducting transition temperature decreases more rapidly with increasing amount of magnetic impurities than with increasing amount of non-magnetic impurities in conventional superconductors. This result is now understood to be caused by destruction of Cooper pairs due to magnetic impurities and demonstrates clearly validity of BCS theory. Unpredicted phenomena sometimes emerge in substances doped with impurities. For example, antiferromagnetic (AF) long-range order (AF-LRO) can appear in several quantum spin systems, which have originally spin-singlet ground state accompanied by a spin gap, when impurities are substituted. Such AF-LRO has been confirmed in CuGeO$_3$ [1, 2, 3, 4, 5], SrCu$_2$O$_3$ [6] and PbNi$_2$V$_2$O$_8$ [7].

In antiferromagnets, reduction of the AF transition temperature with increasing impurity concentration depends strongly on dimensionality of their spin systems. The transition temperature decreases drastically and gradually in quasi-one-dimensional and three-dimensional systems, respectively. Consequently, it is possible to obtain information on spin systems from investigations of substitution effects.

We studied effects of substitution of Zn for Cu on an antiferromagnet Cu$_2$CdB$_2$O$_6$. Figure 1 shows schematically the spin system derived from magnetization and specific-heat results [8]. There are two kinds of Cu$^{2+}$-ion sites (Cu1 and Cu2) having spin-1/2 and three kinds of dominant AF exchange interactions ($J_1$, $J_2$ and $J_3$). Values of $J_1$, $J_2$ and $J_3$ were evaluated as 160, 38.8 and 9.7 K, respectively. Because $J_1$ is largest, AF dimers of spins on Cu1 sites are formed and therefore the Cu1 spins are in a nearly non-magnetic state. On the contrary, the Cu2 spins form AF-LRO below 9.8 K. We emphasize that the states of Cu1 and Cu2 spins differ.
Figure 1. An illustration of Cu sites and dominant interactions in Cu$_2$CdB$_2$O$_6$. Red and blue circles indicate Cu1 and Cu2 sites. Red, green and blue bars represent Cu-Cu bonds of the $J_1$, $J_2$ and $J_3$ interactions. These interactions are defined in $H = \sum_i [J_1 S_i,2 \cdot S_i,3 + J_2 (S_i,1 \cdot S_i,2 + S_i,3 \cdot S_i,4) + J_3 (S_i,1 \cdot S_{i+1,1} + S_i,4 \cdot S_{i+1,4})]$. Ellipses show AF dimers of the Cu1 spins. An effective interaction ($J_{\text{eff}}$) between two Cu2 spins is caused by the AF dimer.

much from each other, although adjacent Cu1 and Cu2 spins are coupled by the $J_2$ interaction. The system of the Cu2 spins seems to be an AF uniform chain with the $J_3$ interaction. However, this speculation is not acceptable undoubtedly because the AF transition temperature (9.8 K) is close to the intrachain ($J_3$) interaction (9.7 K). Accordingly, we reconsider the system of the Cu2 spins based on results of substitution effects.

2. Methods of experiments
Crystalline powders of Cu$_2$CdB$_2$O$_6$ were synthesized using solid-state reaction method. We performed X-ray diffraction measurements to confirm the formation of Cu$_2$CdB$_2$O$_6$ and the absence of other materials. We measured magnetic susceptibility using a superconducting quantum interference device (SQUID) magnetometer (MPMS-5S; Quantum Design).

3. Results and discussion
Figure 2(a) represents temperature ($T$) dependence of magnetic susceptibility $\chi(T, x)$ of Cu$_2$(1−x)Zn$_2x$CdB$_2$O$_6$ in the magnetic field of $H = 0.1$ T. The susceptibility at low $T$ increases with increasing $x$. Figure 2(b) shows $1/\Delta \chi(T, x) \equiv 1/\{\chi(T, x) - \chi(T, 0)\}$, which does not obey the Curie law. Accordingly, spins engendering the increase of the susceptibility are not isolated. When a Zn ion enters a Cu1 site, an AF dimer is destroyed and a spin on a Cu1 site neighboring upon Zn becomes an unpaired spin. The unpaired spin generates the increase of the susceptibility. However, the unpaired spin is not isolated, because the $J_2$ interaction affects the unpaired spin. Consequently, $1/\Delta \chi(T, x)$ does not obey the Curie law. On the contrary, it is considered that the susceptibility does not increase so much by substitution of Zn ions for Cu2 sites, because the numbers of eliminated up and down Cu2 spins are nearly equal.

The derivative of $\chi [d\chi(T, x)/dT]$ in Fig. 2(c) shows a lambda-type behavior, indicating appearance of the AF transition. Figure 3 depicts $x$ dependence of $T_N(x)/T_N(0)$ of Cu$_2$(1−x)Zn$_2x$CdB$_2$O$_6$, where $T_N(x)$ is the AF transition temperature. We also show results of quasi-one-dimensional antiferromagnets BaCu$_2$(1−x)Zn$_2x$Ge$_2$O$_7$ and Cu$_3$(1−x)Zn$_{3x}$Mo$_2$O$_9$ [9]. The value of $T_N(x)/T_N(0)$ decreases with increasing $x$ in all the substances, but the rate of the decrease depends on substance. We compare firstly the results between BaCu$_2$(1−x)Zn$_2x$Ge$_2$O$_7$...
and Cu$_3$(1−x)Zn$_x$Mo$_2$O$_9$. The average of absolute values of interchain exchange interactions ($J_\perp$) was estimated as $zJ_\perp/J_\parallel = 0.028$ and 0.058 for BaCu$_2$Ge$_2$O$_7$ [10] and Cu$_3$Mo$_2$O$_9$ [11], respectively. Here, $J_\parallel$ and $z$ are the intrachain interaction and the number of neighboring chains, respectively. Because $zJ_\perp/J_\parallel$ of BaCu$_2$Ge$_2$O$_7$ is smaller than that of Cu$_3$Mo$_2$O$_9$, $T_N(x)/T_N(0)$ reduces more drastically in BaCu$_2(1−x)$Zn$_x$Ge$_2$O$_7$ than Cu$_2(1−x)$Zn$_x$CdB$_2$O$_6$.

The reduction of $T_N(x)/T_N(0)$ per Zn in Cu$_2(1−x)$Zn$_x$CdB$_2$O$_6$ is very small in comparison with the others. Because the AF transition temperature should decrease rapidly with increasing impurity concentration in quasi one dimensional antiferromagnets, it is natural to consider that the spin system of the Cu2 spins is not quasi one dimensional. As described in [8], an effective interaction between two Cu2 spins through an AF dimer of Cu1 spins is possible theoretically. The value of the effective interaction was roughly estimated as $J_{\text{eff}} \sim J_2^2/J_1 = 9.4$ K. Recently, such an effective interaction has been experimentally confirmed to exist in Cu$_2$Fe$_2$Ge$_2$O$_{13}$ [12]. Accordingly, the spin system of Cu2 spins should be considered to be a two-leg ladder, where the $J_3$ and $J_{\text{eff}}$ interactions are leg and rung ones, rather than the AF chain. Probably, inter-ladder interaction is not so small. Such a spin system can explain qualitatively that the value of $T_N(0)$ is close to the $J_3$ and $J_{\text{eff}}$ values.

Figure 2. (a) Magnetic susceptibility $\chi(T,x)$ of Cu$_2(1−x)$Zn$_x$CdB$_2$O$_6$. (b) Representative results of $1/\Delta \chi(T,x)$. (c) Representative results of $d\chi(T,x)/dT$. In (b) and (c), results of the other $x$’s are qualitatively same as the shown results.
Figure 3. The $x$ dependence of $T_N(x)/T_N(0)$ in the three substances. The circles and squares are the results obtained in susceptibility and specific-heat measurements. The values of $T_N(x)/T_N(0)$ in Cu$_2$Zn$_x$Cd$_{1-x}$B$_2$O$_6$ and Cu$_3$Zn$_x$Mo$_{2-x}$O$_9$ are fit to lines whose formulas are described in this figure.

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