# Phase Transition between Dimerized-Antiferromagnetic and Uniform-Antiferromagnetic Phases in the Impurity-Doped Spin-Peierls Cuprate $CuGeO_3$

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We report a first-order phase transition between dimerized-antiferromagnetic and uniform-antiferromagnetic phases in impurity-doped spin-Peierls (SP) cuprate $Cu_{1-x}Mg_xGeO_3$. As Mg concentration increases, linear reduction of the SP transition temperature ($T_{SP}$) and linear increase of the Néel temperature ($T_N$) are observed for $x$ up to $x_c \simeq 0.023$. At $x_c$ the SP transition suddenly disappears and $T_N$ jumps discontinuously. The peak of the susceptibility at $x_c$ around $T_N$ is not as sharp as those at other concentrations, which indicates the separation of low and high concentration phases. These results indicate the existence of a first-order phase transition between dimerized-antiferromagnetic and uniform-antiferromagnetic long-range orders. [S0031-9007(98)06165-1]

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Since Hase, Terasaki, and Uchinokura discovered the first inorganic spin-Peierls (SP) material $CuGeO_3$ in 1993 [1], this material has attracted much attention. Soon after that, the substitution effect of nonmagnetic impurity ($Zn^{2+}$) for $Cu^{2+}$ was studied by Hase *et al.* [2], and a new magnetic phase was discovered below the spin-Peierls transition temperature ($T_{SP}$), which turned out to have antiferromagnetic long-range order (AF-LRO) [3,4]. The neutron scattering experiments were studied on Si- [5] and Zn-doped [6,7] $CuGeO_3$, and both dimerization superlattice peak and AF magnetic peak were observed. Fukuyama *et al.* explained the coexistence of the dimerization and the AF-LRO in $CuGe_{1-x}Si_xO_3$ using phase Hamiltonian [8]. According to their theory, both dimerization and $\langle S^z \rangle$ of spins on $Cu^{2+}$ ions have spatially inhomogeneous distribution. Recent $\mu$SR study on Zn- and Si-doped $CuGeO_3$ indicated the spatial inhomogeneity of $\langle S^z \rangle$ of spins on $Cu^{2+}$ ions in AF-LRO phase [9], which supports the theory of Fukuyama *et al.*

Transition temperature vs impurity concentration ($T$-$x$) phase diagrams have been reported on Zn- and Si-doped $CuGeO_3$ [6,10–12]. In both cases Néel temperature ($T_N$) increases gradually, reaches its maximum, and decreases moderately. The $T_{SP}$ decreases linearly as $x$ increases. However, in the case of Zn-doped $CuGeO_3$, $T_{SP}$ was reported to have a plateau in highly doped region [6], while in the case of Si-doped $CuGeO_3$ the corresponding plateau was not observed [11]. The $T$-$x$ phase diagram is controversial in the relatively highly doped region, and the study on the substitution by other species of impurities is needed.

In this paper we study the $T$-$x$ phase diagram in $Cu_{1-x}Mg_xGeO_3$ in detail and report (a) the clear disappearance of $T_{SP}$, the corresponding jump of $T_N$, and (b) the existence of different AF-LRO's with and without the lattice dimerization.

All single crystals were grown by a floating-zone method. A typical dimension of the grown crystals is about 4–5 mm in diameter and about 4–8 cm in length. The true concentration of impurity $x$ was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). We use Ar gas as a plasma source and perform quantitative analysis by the calibration curve method. The $x$ for Mg is over 80% of nominal concentration $x_{nom}$ for $0 \leq x_{nom} < 0.1$. This is in contrast to that in Zn-doped $CuGeO_3$ [7], where the ratio is below 80%. This means that Mg is more easily doped to the Cu site and is expected to be a more adequate impurity than Zn for the study of the substitution effect of nonmagnetic ions. This is one of the reasons why we have reinvestigated the $T$-$x$ phase diagram in detail in Mg-doped $CuGeO_3$. The absence of impurity phase or structure change with $x$ was confirmed by x-ray diffraction after pulverization of the single crystals at room temperature.

Measurements of dc magnetic susceptibility were performed with commercial SQUID magnetometer ($\chi$-MAG, Conductus Co., Ltd.) for 34 samples ($0 \leq x < 0.089$).

The susceptibility changes anisotropically at low temperatures as shown in Fig. 1. We can see that (a) Mg can be doped [12,13], (b) Mg-doping induces AF-LRO as in Zn- [4], Ni- [10,14], Mn- [3], and Co-doped $CuGeO_3$ [15], and (c) the magnetic easy axis is along the $c$ axis below $T_N$, which is the same as in the case of Zn-doped $CuGeO_3$ [4]. Both $T_N$ and $T_{SP}$ were determined from the crossing points of linear functions fitted to the susceptibility in applied field parallel to the $c$ axis [$\chi_c(T)$] above and below the transitions.

Fisher theorized that the magnetic heat capacity of a "simple" antiferromagnet is proportional to $\partial(\chi_\parallel T)/\partial T$ and $T_N$ is best determined by the maximum in $\partial(\chi_\parallel T)/\partial T$ ($\chi_\parallel$ is the susceptibility along the easy axis, which corresponds to $\chi_c$ in this case) [16]. The maximum in $\chi_\parallel$, therefore, occurs at a temperature slightly higher than $T_N$. Experimental verification of this suggestion has been reported in several antiferromagnets [16]. We analyzed some of the data by this method and get, e.g., $T_N = 4.3$ K

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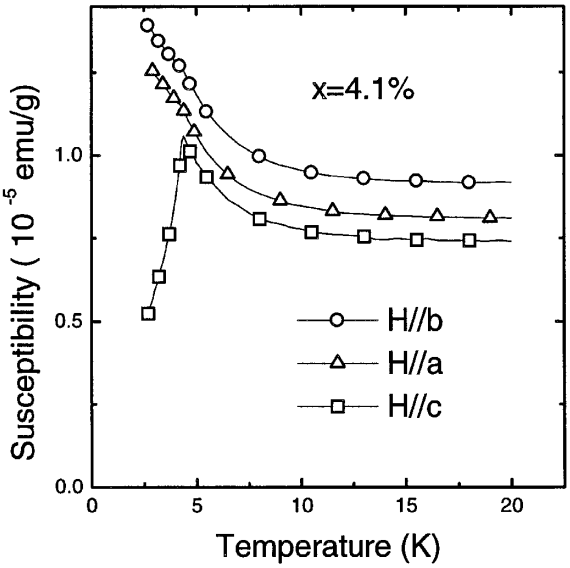


FIG. 1. Temperature dependence of susceptibility on the sample of $x = 0.041$ in the field applied parallel to the three principal axes. Néel transition at 4.4 K is observed.

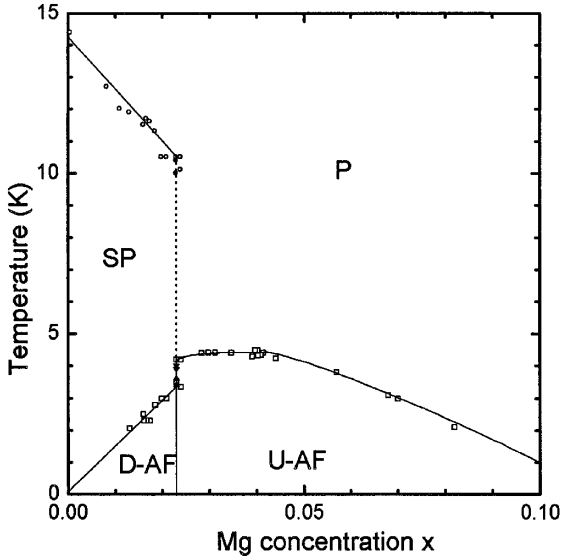


FIG. 2. The $T$-$x$ phase diagram of $Cu_{1-x}Mg_xGeO_3$. Circles and squares indicate $T_{SP}$ and $T_N$, respectively. At $x = 0.023$ jump of $T_N$ and sudden disappearance of $T_{SP}$ are observed. Filled triangles represent $T_1$ (upward triangle) and $T_2$ (downward one) at $x_c$, which are determined as shown in Fig. 3(c). SP and P mean spin-Peierls and paramagnetic states. The meanings of D-AF and U-AF are explained in the text.

for the sample with $x = 0.035$ (note that the temperature step was 0.1 K). This value is closer to the $T_N = 4.2$ K, determined from our heat capacity measurement, than to the value 4.5 K, determined from the maximum in $\chi_c$. In the present paper, however, we determine $T_N$ by the method described previously because Fisher's method can be applied to a simple antiferromagnet, to which the low-concentration antiferromagnetic phase in Mg-doped $CuGeO_3$ does not belong and because in the present study the change of $T_N$ with $x$ is more important than the absolute value of $T_N$.

Figure 2 shows Mg concentration dependence of $T_{SP}$ and $T_N$: $T$-$x$ phase diagram. $T_N$ increases from 3.4 to 4.2 K abruptly at $x \simeq 0.023$ and reaches its maximum. We define this critical concentration as $x_c$. $T_N$ has a plateau at $x_c < x \lesssim 0.04$ and decreases smoothly at $x \gtrsim 0.04$. The Néel transition was not observed in the sample of $x = 0.089$ above 1.9 K. On the other hand, $T_{SP}$ reduces linearly from 14.2 K of pure $CuGeO_3$ and suddenly disappears at $x_c$ around 10 K and is not observed at $x > x_c$.

Figure 3(a) shows $\chi_c(T)$ of Mg-doped $CuGeO_3$ [$x = 0.019$, $0.023(\simeq x_c)$, 0.028, and 0.082]. Figures 3(b)–3(e) show the same data as in Fig. 3(a) near $T_N$. Below and even above $x_c$ sharp transitions are observed in Figs. 3(b), 3(d), and 3(e). The measurements were done in the steps of 0.1 K, and the broadening of the peaks was not observed. Therefore the errors of $T_N$ are less than 0.05 K at these $x$'s. At $x_c$, however, the broadening of the peaks is observed as shown in Fig. 3(c). This behavior indicates the existence of two transition temperatures $T_1$ and $T_2$, which is caused by a phase separation into low and high concentration phases. It is noted that a phase separation always appears in the case of a first-order phase transition. Here we analyzed the data by fitting three linear functions of $T$ and determined crossing points as $T_1$ and $T_2$. These are 3.43 and 3.98 K at $x = 0.023$ [Fig. 3(c)].

According to the susceptibility data we can explain Fig. 2 as follows. First, the jump of $T_N$ at $x = x_c$ indicates that AF-LRO at $x < x_c$ and $x > x_c$ belong to essentially different phases, and there is a distinct phase transition between them.

Second, the disappearance of the SP transition at $x_c$ implies that the lattice dimerization is absent; i.e., the lattice is uniform in the region of $x > x_c$. Therefore it is inferred that at $T < T_N$ the lattice remains uniform. We define this phase as the uniform-antiferromagnetic phase (U-AF phase). The U-AF phase is supposed to be classical; there is no spatial inhomogeneity of $\langle S^z \rangle$ of the spins on $Cu^{2+}$ ions. In the sample of $x = 0.041$ the absence of dimerization was confirmed by neutron diffraction measurement down to 1.3 K [17]. On the other hand, in the region of $x < x_c$ the lattice is dimerized below $T_{SP}$. It is expected that the lattice is dimerized below $T_N$, which was also confirmed by neutron scattering measurement on the sample of $x = 0.017$ [17]. There should be spatial inhomogeneity of Cu spins as is claimed so far in Si-doped $CuGeO_3$ [8]. Here we define this phase as dimerized-antiferromagnetic phase (D-AF phase).

Last, the broad peak of $\chi_c(T)$ in the sample of $x \simeq x_c$ indicates the transition from D-AF to U-AF phases is the first order as $x$ is varied. The displacement of $Cu^{2+}$ ion, $\delta$, from a uniform lattice changes abruptly from finite value to zero at $x = x_c$. As briefly mentioned previously

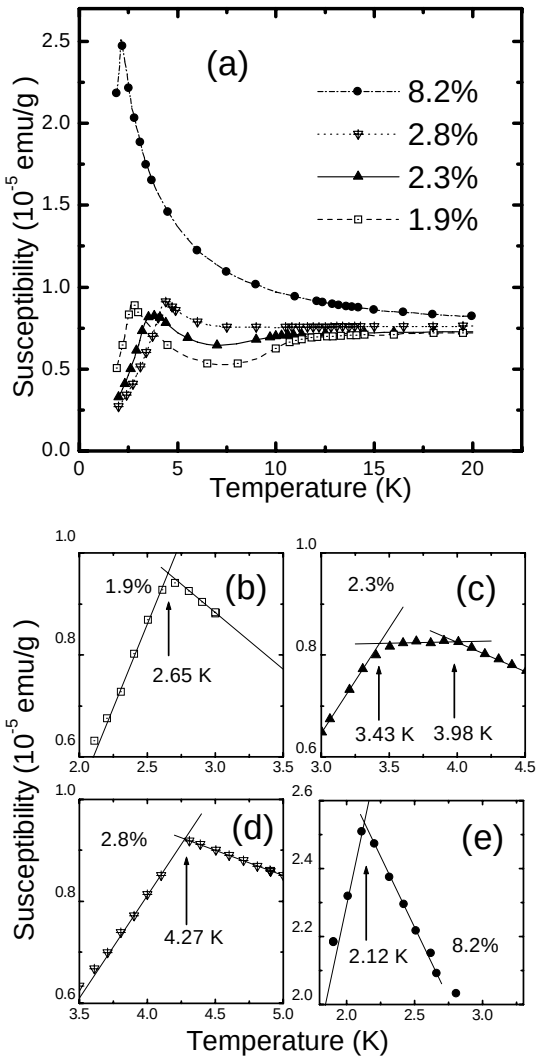


FIG. 3. (a) $\chi_c(T)$ of $Cu_{1-x}Mg_xGeO_3$ with $x = 0.019$, 0.023 ($\simeq x_c$), 0.028, and 0.082. (b)–(e) $\chi_c(T)$ near $T_N$. While below and above $x_c$ the peaks are sharp as shown in (b), (d), and (e), at $x \simeq x_c$ the peak is broad as shown in (c). We determined the transition temperatures $T_1$ and $T_2$ at $x = x_c$ as crossing points of fitted three linear functions of $T$. $T_1 = 3.43$ K and $T_2 = 3.98$ K in (c).

the absence of the structure change with $x$ was confirmed by x-ray diffraction at room temperature.

Once we know the presence of the first-order phase transition in $Cu_{1-x}Mg_xGeO_3$, it becomes important to review $T$-$x$ phase diagrams of $Cu_{1-x}M_xGeO_3$ ($M$ = impurity). In the case of Zn-doped $CuGeO_3$, the absence of $T_N$ between 3.0 and 4.2 K at $x \sim 0.017$ was observed (see Fig. 2 of Ref. [18]). This suggests that the first-order phase transition also exists in this system. However, the jump of $T_N$ and the corresponding disappearance of the SP transition have not been clearly confirmed so far. This, we think, is because the distribution of Zn in the sample is not so uniform as that of Mg, and the phase boundary was disturbed by this effect. In the case of Ni-doped $CuGeO_3$, sudden disappearance of $T_{SP}$ and abrupt increase of $T_N$ from 2.5 to 3.6 K at $x = 0.020$ were clearly observed [14]. This corresponds to the phase transition observed in $Cu_{1-x}Mg_xGeO_3$. However, the behavior is more complex owing to the difference of the easy axis (nearly parallel to the $a$ axis in Ni-doped $CuGeO_3$) [10,14], and the detail will be discussed separately [14].

The plateau of $T_{SP}$ at relatively large $x$ is observed by the neutron diffraction, but only very weakly by the susceptibility measurement, in the case of Zn-doped $CuGeO_3$ [6,7]. This may also be explained by spatial variation of Zn concentration. Scattering from low concentration (i.e., dimerized) region can be observed by the neutron diffraction even though the volume of that region is small. On the other hand, the susceptibility measurement detects the average property of a sample. From the above discussion the first-order phase transition seems to be universal for all dopants, at least in the case of doping to the Cu site.

The results of antiferromagnetic resonance [19] and of angular dependence of magnetization vs magnetic field [14] on Zn-doped (4%) $CuGeO_3$ were explained very well using the mean-field sublattice model [14,19]. This may also be explained by the fact that the magnetic phase of these samples at $x > x_c$ is perfectly classical U-AF. Different behaviors are expected in the samples at $x < x_c$.

While D-AF phase has AF-LRO characteristic to SP state, U-AF phase has classical AF-LRO, which arises because the interchain exchange interaction of $CuGeO_3$ is not so weak [20] as that of other typical organic SP materials [21,22]. In other words, if SP transition had not occurred in $CuGeO_3$, even pure $CuGeO_3$ would be a classical AF material. The disappearance of lattice dimerization may induce the phase transition from D-AF to U-AF phases through spin-lattice coupling. The energies of D-AF and U-AF phases including both spin and lattice should be calculated in the ground state and sudden disappearance of SP transition should also be explained.

Weiden *et al.* also reported the $T$-$x$ phase diagram of Mg-doped $CuGeO_3$ from susceptibility measurements [12] in which an $x_c \simeq 0.04$ can be inferred. This disagreement in $x_c$ is most likely due to accurate measurement of $x$ or sample inhomogeneity. However, Weiden *et al.* [12] do not give any details in how $x$ and $T_N$ were measured. On the other hand, we first checked that the emission spectra of Cu (= 327.396 nm), Ge (= 209.423 nm), and Mg (= 279.533 nm) do not interfere with each other in ICP-AES measurement. Second, we made sure that the detection limit of the intensity of Mg spectrum is much smaller than the intensity of our usual samples (about 4 mg of $Cu_{1-x}Mg_xGeO_3$ for $0.001 \lesssim x$) for ICP-AES measurement. Third, we performed quantitative analysis on a few nearest neighboring samples, and we confirmed that the fluctuation of $x$ is within 0.001. The detailed composition analysis and the good choice of impurity make the discovery of the present phase transition possible.

As for unresolved problems, the properties of the two phases should be studied close to the first-order phase

boundary using various kinds of physical measurements: neutron diffraction and neutron inelastic scattering, $\mu$SR, specific heat, and x-ray diffraction at low temperatures. For the Zn-doped $CuGeO_3$, we are planning to reinvestigate the phase diagram around $x \sim 0.017$ in detail and to clarify whether the jump of $T_N$ really exists or not. Further theoretical explanation of the phase transition is also needed. Another question is whether the phase transition exists in Si-doped $CuGeO_3$; in other words, whether it is unique to the doping to the Cu site or not. Detailed studies on the $T$-$x$ phase diagram of $CuGe_{1-x}M_xO_3$ are needed.

In summary, we studied in detail the $T$-$x$ phase diagram of $Cu_{1-x}Mg_xGeO_3$ and discovered a first-order phase transition between D-AF and U-AF phases. At $x_c$ $\delta$ changes from finite value to zero and spatial distribution of $\langle S^z \rangle$ also changes from inhomogeneous to uniform distributions. The transition seems to be universal for the doping to the Cu site, and we can explain some of the unsolved problems in impurity-doped $CuGeO_3$ by this $T$-$x$ phase diagram.

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