The phase transition between dimerized-antiferromagnetic and uniform-antiferromagnetic phases in impurity-doped spin-Peierls cuprate CuGeO₃

T. Masuda,* A. Fujioka, Y. Uchiyama, I. Tsukada, and K. Uchinokura
Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN
(January 9, 1998)

We discovered a first-order phase transition between dimerized-antiferromagnetic and uniform-antiferromagnetic phases in impurity-doped spin-Peierls (SP) cuprate Cu₁₋ₓMgₓGeO₃. As impurity concentration increases, linear reduction of SP transition temperature (Tₛₚ) and linear increase of Néel temperature (Tₙ) are observed up to x ≈ 0.023. At this critical concentration (x_c) SP transition suddenly disappears and Tₙ jumps discontinuously. The peak of the susceptibility at x_c around Tₙ is not so sharp as those at other concentrations, which indicates the phase separation of low and high concentration phases. These results indicate the existence of the first-order phase transition between dimerized-antiferromagnetic and uniform-antiferromagnetic long-range orders.

75.10.Jm, 75.30.Kz, 75.50.Ee

Since Hase, Terasaki, and Uchinokura discovered the first inorganic spin-Peierls (SP) material CuGeO₃ in 1993 [1], this material has attracted much attention. Soon after that substitution effect of nonmagnetic impurity (Zn²⁺) for Cu²⁺ was studied by Hase et al. [2] and a new magnetic phase was discovered below the spin-Peierls transition temperature (Tₛₚ), which turned out to have antiferromagnetic long-range order (AF-LRO) [3]. The neutron scattering experiments were studied on Si- and Zn-doped CuGeO₃ 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 CuGe₁₋ₓSiₓO₃ using phase Hamiltonian [4]. According to their theory, both dimerization and ⟨S²⟩ of spins on Cu²⁺ ions have spatially inhomogeneous distribution. Recent μSR study on Zn- and Si-doped CuGeO₃ indicated the spatial inhomogeneity of ⟨S²⟩ of spins on Cu²⁺ ions in AF-LRO phase [5], which supports Fukuyama et al.’s theory.

Transition temperature vs impurity concentration (T-x) phase diagrams have been proposed on Zn- and Si-doped CuGeO₃ [4][5][6]. In both cases Néel temperature (Tₙ) increases gradually, reaches its maximum and decreases moderately. The Tₛₚ decreases linearly as x increases. However, in the case of Zn-doped CuGeO₃ Tₛₚ was reported to have a plateau in highly doped region [5], while in the case of Si-doped CuGeO₃ the corresponding plateau was not observed [4]. 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 T-x phase diagram in Cu₁₋ₓMgₓGeO₃ in detail and report (a) the clear disappearance of Tₛₚ, the corresponding jump of Tₙ 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 plasma source and perform quantitative analysis by calibration curve method. The x for Mg is over 80% of nominal concentration xₙom for 0 ≤ xₙom ≤ 0.1. This is in contrast to that in Zn-doped CuGeO₃ [6], where the ratio is below 80%. This means that Mg is more easily doped to 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 CuGeO₃. 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 (χ-MAG, Conductus Co., Ltd.) for 34 samples (0 ≤ 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 Zn₁₋ₓNiₓO₃ [14], Mn₁₋ₓO₃ [5], and Co-doped CuGeO₃ [6], and (c) the magnetic easy axis is along the c axis below Tₙ, which is the same as in the case of Zn-doped CuGeO₃ [5]. Both Tₙ and Tₛₚ were determined from the crossing points of linear functions fitted to the susceptibility in applied field parallel to the c axis (χₑ(Tₙ)) above and below the transitions.

Fisher reported that the magnetic heat capacity of a ‘simple’ antiferromagnet is proportional to ∂(χₑ(T))/∂T and Tₙ is best determined by the maximum in ∂(χₑ(T))/∂T (χₑ is the susceptibility along the easy axis, which corresponds to χₑ in this case) [6]. The maximum in χₑ, therefore, occurs at a temperature slightly higher than Tₙ. We analyzed some of the data by this way and get, e.g. Tₙ = 4.3 K for the sample of x = 0.035, (Note that the temperature step was 0.1 K). This value is closer
to the \( T_N \), 4.2 K, which was determined from our heat capacity measurement than 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 above 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 the change of \( T_N \) with \( x \) but not the absolute value of \( T_N \) is essential in the present study.

Figure 3 shows Mg concentration dependence of \( T_{SP} \) and \( T_N \): \( T-x \) phase diagram. \( T_N \) increases from 3.4 K to 4.2 K abruptly at \( x \simeq 0.23 \) and reaches its maximum. We define this critical concentration as \( x_c \). \( T_N \) has a plateau at \( x < x_c \leq 0.04 \) and decreases smoothly at \( x > 0.04 \). 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)–(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), (d), and (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 \( T_N \) is 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 a 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 K and 3.98 K at \( x = 0.23 \) (Fig. 3(c)).

According to the susceptibility data we can explain Fig. 3 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 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\(_x\)GeO\(_3\), it becomes important to review \( T-x \) phase diagrams of Cu\(_{1-x}\)Mg\(_x\)GeO\(_3\) \((M = \) 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. [8]). This suggests that the first-order phase transition also exists in this system. However the jump of \( T_N \) and the corresponding vanishment 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 K to 3.6 K at \( x = 0.020 \) were clearly observed [3]. This corresponds to the phase transition observed in Cu\(_{1-x}\)Mg\(_x\)GeO\(_3\). However, the behavior is more complex owing to the difference of the easy axis (nearly parallel to the \( a \) axis in Ni-doped CuGeO\(_3\)) [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\(_3\) [14]. This may also be explained by spatial variation of Zn concentration. Scattering from low concentration \((i.e., \text{dimerized})\) 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 Cu site.

The results of antiferromagnetic resonance [14] and of angular dependence of magnetization vs magnetic field [14] on Zn-doped (4%) CuGeO\(_3\) were explained very well using mean-field sublattice model [15]. 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 has classical AF-LRO, which arises because the interchain exchange interaction of CuGeO\(_3\) is not so weak [21] 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 dimer-
ization 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 be also explained.

M. Weiden et al. also reported $T$-$x$ phase diagram of Mg-doped CuGeO$_3$ from susceptibility measurements. But they have neither shown the susceptibility data nor clarified how they determined the concentration $x$. On the other hand we, first, checked that of emission spectra of Cu (327.396 nm), Ge (209.423 nm), and Mg (279.553 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$_x$GeO$_3$ for 0.001 $\leq x$) 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 future 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. As to Zn-doped CuGeO$_3$ we are planning to reinvestigate the phase diagram around $x \approx 0.017$ 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 problem is whether the phase transition exists in Si-doped CuGeO$_3$, in other words, whether it is unique to the doping to Cu-site or not. Detailed studies on the $T$-$x$ phase diagram of CuGe$_{1-x}$Mg$_x$O$_3$ are needed.

In summary we studied in detail the $T$-$x$ phase diagram of Cu$_{1-x}$Mg$_x$GeO$_3$ 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 Cu-site and we can explain some of the unsolved problems in impurity-doped CuGeO$_3$ by this $T$-$x$ phase diagram.

We thank G. Shirane, Y. Fujii, H. Nakao, M. Nishi, and K. Hirota for neutron diffraction measurement on Mg-doped CuGeO$_3$. This work was supported in part by Grant-in-Aid for Scientific Research (A), Grant-in-Aid for Scientific Research on Priority Area “Anomalous Metallic State near the Mott Transition”, Grant-in-Aid for COE Research “Phase Control of Spin-Charge-Photon (SCP) Coupled System” from the Ministry of Education, Science, Sports, and Culture, and NEDO (New Energy and Industrial Technology Development Organization) International Joint Research Grant.

[1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. 70, 3651 (1993).
[2] M. Hase, I. Terasaki, Y. Sasago, K. Uchinokura, and H. Obara, Phys. Rev. Lett. 71, 4059 (1993).
[3] S. Oseroff, S.-W. Cheong, B. Aktas, M. F. Hundley, Z. Fisk, and L. W. Rupp, Jr., Phys. Rev. Lett. 74, 1450 (1995).
[4] M. Hase, N. Koide, K. Manabe, Y. Sasago, K. Uchinokura, and A. Sawa, Physica B 215, 164 (1995).
[5] L. P. Regnault, J. P. Renard, G. Dhahane, and A. Revcolevschii, Europhys. Lett. 32, 579 (1995).
[6] Y. Sasago, N. Koide, K. Uchinokura, M. C. Martin, M. Hase, K. Hirota, and G. Shirane, Phys. Rev. B 54, R6835 (1996).
[7] M. C. Martin, M. Hase, K. Hirota, G. Shirane, Y. Sasago, N. Koide, and K. Uchinokura, Phys. Rev. B 56, 3173 (1997).
[8] H. Fukuyama, T. Tanimoto, and M. Saito, J. Phys. Soc. Jpn. 65, 1182 (1996).
[9] K. M. Kojima, Y. Fudamoto, M. Larkin, G. M. Luke, J. Merrin, B. Nachumi, Y. J. Uemura, M. Hase, Y. Sasago, K. Uchinokura, Y. Ajiro, A. Revcolevschii, and J.-P. Renard, Phys. Rev. Lett. 79, 503 (1997).
[10] S. Coad, J.-G. Lussier, D. F. McMorrow, and D. McK. Paul, J. Phys.: Condens. Matter 8, 6251 (1996).
[11] J. P. Renard, K. Le Dang, P. Veillet, G. Dhahane, A. Revcolevschii, and L. P. Regnault, Europhys. Lett. 30, 475 (1995).
[12] Y. Ajiro et al. reported the susceptibility measurement of Cu$_{1-x}$Mg$_x$GeO$_3$ on polycrystalline samples at $T > 5$ K and observed only the suppression of $T_{SP}$ (Y. Ajiro et al., Phys. Rev. B 14, 9399 (1995)). We also prepared the polycrystalline samples from stoichiometric mixture of starting oxides sintered at 1000$^\circ$C for 100 h. We did not observe $T_N$ at $T > 1.9$ K though the small suppression of $T_{SP}$ was observed on the susceptibility measurements. It suggests that only small amount of Mg can be doped in the case of polycrystalline samples.
[13] M. Weiden, W. Richter, R. Hauptmann, C. Geibel, and F. Steglich, Physica B 233, 153 (1997).
[14] N. Koide, Y. Uchiyama, T. Hayashi, T. Masuda, Y. Sasago, and K. Uchinokura, in preparation.
[15] P. E. Anderson, J. Z. Liu, and R. N. Shelton, Phys. Rev. Lett. 70, 11014 (1997).
[16] M. E. Fisher, Phil. Mag. 7, 1731 (1962).
[17] H. Nakao, Y. Fujii, M. Nishi, G. Shirane, K. Hirota, T. Masuda, and K. Uchinokura, private communication.
[18] N. Koide, Y. Sasago, T. Masuda, and K. Uchinokura, Czechoslovak J. Phys. 46 S4, 1981 (1996).
[19] M. Hase, M. Hagiwara, and K. Katsumata, Phys. Rev. B 54, R3722 (1996).
[20] M. Nishi, O. Fujita, and J. Akimitsu, Phys. Rev. B 50, 6508 (1994).
[21] J. W. Bray, H. R. Hart, Jr., L. V. Interrante, I. S. Jacobs, J. S. Kasper, G. D. Watkins, and S. H. Wee, Phys. Rev. Lett. 35 744 (1975).
[22] S. Huizinga, J. Kommandeur, G. A. Sawatzky, and B. T. Thole, Phys. Rev. B 19, 4723 (1979).

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$_x$GeO$_3$. 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 meaning of D-AF and U-AF are explained in the text.

FIG. 3. (a) $\chi_c(T)$ of Cu$_{1-x}$Mg$_x$GeO$_3$ with $x = 0.019, 0.023 (\approx x_c), 0.028$, and $0.082$. (b) $\sim$ (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 $x \approx x_c$ 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 $T$. $T_1 = 3.4$ K and $T_2 = 4.0$ K in (c).