Similarity and Difference between Magnetic- and Nonmagnetic-Impurity Effects in Spin-Peierls Cuprate CuGeO$_3$

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We have measured the magnetic susceptibility of single-crystal Cu$_{1-x}$Ni$_x$GeO$_3$ to study doping effects of the magnetic impurity (Ni$^{2+}$ has S = 1 spin) on the inorganic spin-Peierls (SP) material CuGeO$_3$. We observed the disappearance of the SP transition and the abrupt increase of the Néel temperature from 2.5 to 3.4 K at $x \sim 0.020$, which indicates the first-order phase transition between the dimerized-antiferromagnetic (D-AF) and the uniform-antiferromagnetic (U-AF) phases, as was discovered in Mg-doped (Mg$^{2+}$ is nonmagnetic) system [T. Masuda et al., Phys. Rev. Lett. 80, 4566 (1998)]. This indicates that this transition is universal for the doping to Cu site. We also found another phase with the easy axis in the $a-c$ plane in low $x$ region.

The magnetic properties of CuGeO$_3$ have been extensively studied since Hase, Terasaki and Uchinokura reported that this is the first inorganic spin-Peierls (SP) material. The effects of Zn substitution for Cu were investigated by Hase et al. and the suppression of SP transition and the occurrence of another phase transition were reported. It has been established that the antiferromagnetic (AF) transition takes place below 5 K in Cu$_{1-x}$M$_x$GeO$_3$ ($M$ = Zn (Ref. 3), Ni (Ref. 3, 5), Mn (Ref. 3) and Cu$_{1-x}$Si$_x$O$_3$ (Ref. 3).

In particular Cu$_{1-x}$Zn$_x$GeO$_3$ and CuGe$_{1-x}$Si$_x$O$_3$ have been investigated in detail by means of magnetization measurements and neutron scattering measurements and so on. One of the most interesting phenomena observed in Zn- and Si-doped CuGeO$_3$ is the coexistence of the long-range order of the lattice dimerization, which is intrinsic to SP phase, and the AF long- and short-range order (AF-LRO) [1, 2]. Theoretical investigations of Si-doped CuGeO$_3$ have recently suggested that local strain around the doped Si reduces the SP lattice dimerization, so that AF-LRO appears [3]. This theory indicated that both the lattice order parameter and the spin order parameter can coexist, and then there is a first-order phase transition between them at $x \sim 0.023$ [4]. In the U-AF phase, the lattice dimerization is absent and the state is a conventional AF state. On the other hand, for $x < x_c$ the lattice is dimerized below the SP transition temperature ($T_{SP}$) and even below the Néel temperature ($T_N$), i.e., both of the order parameters coexist in the D-AF phase.

Here we must determine whether this transition is characteristic solely to Mg-doped CuGeO$_3$ or is universal at least for the substitution for Cu$^{2+}$. For this purpose it is necessary to examine single-crystal Cu$_{1-x}$M$_x$GeO$_3$ in detail, where $M$ is a magnetic impurity. One of the best candidates of magnetic impurities is Ni, because Ni$^{2+}$ ion has $S = 1$ (Ref. 5) and its radius (0.69 Å) is close to that of Cu$^{2+}$ ion (0.73 Å). Single-crystals grown by the floating-zone method contain almost the same Ni concentration as the starting powder materials. It has been reported that the AF transition takes place in polycrystalline Ni-doped CuGeO$_3$ by means of specific heat measurements in single-crystal Cu$_{0.967}$Ni$_{0.033}$GeO$_3$ by susceptibility measurements and 1.5% ~ 6.0% Ni-doped CuGeO$_3$ using neutron scattering techniques. Impurity concentration ($x$) dependences of $T_{SP}$ and $T_N$ of Cu$_{1-x}$Ni$_x$GeO$_3$ have not yet been determined.

In this paper we will study the temperature-vs-$x$ phase diagram of single-crystal Cu$_{1-x}$Ni$_x$GeO$_3$ in detail. The disappearance of $T_{SP}$ and the corresponding increase of the $T_N$ at $x \sim 0.020$, which indicate the first-order phase transition between the D-AF and U-AF phases, are observed. We also found that with decreasing $x$ the easy axis of Cu$_{1-x}$Ni$_x$GeO$_3$ in the D-AF phase changes from nearly the $a$ axis near $x_c$ to the direction containing the $a$ and $c$ components.

Single crystals of pure CuGeO$_3$ and Cu$_{1-x}$Ni$_x$GeO$_3$ with $0.005(1) \leq x \leq 0.060(2)$ were prepared by the floating-zone method. The concentrations $x$ of Ni were determined by electron-probe microanalysis (EPMA).
Unexpected impurities or structural change with x were not observed by means of x-ray diffraction after pulverization of the single crystals at room temperature. The a-axis lattice parameter measured in single-crystal samples decreases monotonically as x increases. This fact supports that impurity ions are truly substituted in this system.

The magnetization measurements of the prepared samples were carried out using SQUID magnetometer from 2 to 300 K. Below 2 K, we measured the ac susceptibility of 0.5% Ni-doped samples using the $^3$He-$^4$He dilution refrigerator down to 20 mK. Experimental details are described elsewhere.

At first we show the temperature dependence of the susceptibility along the a, b and c axes ($\chi_a(T)$, $\chi_b(T)$ and $\chi_c(T)$) of 3.8% Ni-doped CuGeO$_3$ under $H = 0.1$ T below 15 K in the inset of Fig. 1. $\chi_a(T)$ has a cusp around 4.0 K and the magnitude of $\chi_a(T)$ decreases below 4.0 K, while the cusp around 4.0 K is less evident in $\chi_b(T)$ and $\chi_c(T)$. The magnetic field dependence of the magnetization in three directions ($M_a(H)$, $M_b(H)$ and $M_c(H)$) were also measured and only $M_a(H)$ changes rapidly around 1.1 T, i.e., the spin-flop transition occurs (not shown here). These behaviors indicate that the AF-LRO appears below the transition temperature $T_N \approx$ 4.0 K. However the easy axis is nearly along the a axis but all the spins do not align exactly along the a axis, because $\chi_a(T)$ does not tend to zero as $T \to 0$ K and moreover $\chi_a(T \to 0$ K) has a significant value (see the inset of Fig. 1). On the contrary, in Zn- or Mg-doped CuGeO$_3$ $\chi_c(T)$ tends to zero as $T \to 0$ K and therefore the easy axis is exactly along the c axis. This difference of spin orderings between Zn(Mg)- and Ni-doped CuGeO$_3$ is caused by that Ni$^{2+}$ ions carry spin $S = 1$ and accordingly have the single-ion anisotropy, while Zn$^{2+}$ (Mg$^{2+}$) ions are nonmagnetic, as will be discussed later in more detail.

Next, we show the T - x phase diagram of single-crystal Cu$_{1-x}$Ni$_x$GeO$_3$ in Fig. 1. We determined $T_{SP}$ as the temperature of the kink of $\chi(T)$ and $T_N$ as the temperature of the cusp of $\chi_a(T)$ with roughly estimated errors. Figure 1 shows (a) the disappearance of the SP transition and (b) the abrupt increase of the $T_N$ from 2.5 to 3.4 K at nearly the same x $\sim$ 0.020. We define this critical concentration as $x_c$. These behaviors indicate the first-order phase transition between the D-AF and U-AF phases, as was discovered in Mg-doped systems. We also observed the broadening of the peaks of $\chi_a(T)$’s at $x \sim x_c$, while the peaks are very sharp in both $x < x_c$ and $x > x_c$. This is due to the coexistence of two phases near the first-order phase boundary, as is always the case with a first-order phase transition.

To clarify the existence of the first-order phase transition, we show the x dependence of $\Delta \chi_{max}$ in Fig. 2. Here $\Delta \chi_{max}$ is defined as the maximum of the difference between the linear extrapolation to $T < T_{SP}$ from $\chi_a(T)$ ($T > T_{SP}$) and $\chi_a(T)$ (see the inset of Fig. 2). $\Delta \chi_{max}$ can be taken as a measure of the magnitude of the dimerization. A steep decrease of $\Delta \chi_{max}$ around $x \sim 0.02$ can be explained by the sudden disappearance of $T_{SP}$ at $x_c$.

FIG. 1. The x dependence of $T_{SP}$ (closed circles) and $T_N$ (closed squares) of single-crystal Cu$_{1-x}$Ni$_x$GeO$_3$. Paramagnetic, spin-Peierls, dimerized-antiferromagnetic, and uniform-antiferromagnetic phases are abbreviated as P, SP, D-AF and U-AF, respectively. The inset shows the temperature dependence of $\chi(T)$'s below 15 K under $H = 0.1$ T of single-crystal Cu$_{0.962}$Ni$_{0.038}$GeO$_3$.

FIG. 2. The x dependence of $\Delta \chi_{max}$ of single-crystal samples of Cu$_{1-x}$Ni$_x$GeO$_3$. The inset shows the method of the determination of $\Delta \chi_{max}$.
Near $x_c$ the SP and paramagnetic phases coexist because of the first-order nature of the phase boundary at the vertical line at $x_c$ in the phase diagram of Fig. 1, which is the reason why $\Delta \chi_{\text{max}}$ changes almost vertically at $x_c$ in Fig. 2. This is consistent with the existence of the first-order phase transition between the D-AF and U-AF phases.

To study the anisotropy of the D-AF phase of $\text{Cu}_{1-x}\text{Ni}_x\text{GeO}_3$ in detail, we measured ac susceptibilities $\chi_a(T)$ and $\chi_c(T)$ of 0.5% Ni-doped one down to 20 mK (Fig. 3). These measurements were carried out under an magnetic field ($\sim 0.05$ Oe, 16 Hz) applied parallel to the $a$ and $c$ axes. Unfortunately the absolute values of the ac susceptibilities were not able to be determined, but the AF transition was clearly observed. In this sample, the SP and AF transitions occurred at 13.4 K and near 0.4 K, respectively. We can see that $\chi_c(T)$ has a cusp around $T_N \sim 0.4$ K and the magnitude of $\chi_c(T)$ decreases below $T_N$, while the cusp around 0.4 K is less evident in $\chi_a(T)$. This indicates that the sublattice magnetizations of $\text{Cu}_{0.995}\text{Ni}_{0.005}\text{GeO}_3$ have the components both along the $a$ and along the $c$ axes.

In $\text{Cu}_{0.983}\text{Ni}_{0.017}\text{GeO}_3$ (which has the D-AF phase but $x \sim x_c$) only $\chi_a(T)$ shows a cusp at $T_N$. This definitely shows that the samples with $x \sim x_c$ in the D-AF phase have the easy axis nearly along the $a$ axis. Combining these two experimental results we may think that another phase transition occurs in the D-AF state. One of the phases is a D-AF phase with the easy axis nearly along the $a$ axis when the Ni concentration $x$ is relatively high. This is caused by the single-ion anisotropy of the $S = 1$ spins on Ni$^{2+}$ ions and by sufficiently strong exchange interaction between $S = 1$ spins on Ni$^{2+}$ ions and neighboring $S = 1/2$ spins on Cu$^{2+}$ ions. The other is a D-AF state with the easy axis in the $a-c$ plane. This can be compared with the oblique antiferromagnetic (OAF) phase, which appears in the mixture of two anisotropic AF states with perpendicular easy axes.

In Fig. 3 we observe that $\chi_a(T)$ decreases and $\chi_c(T)$ increases as temperature decreases below 0.1 K. This behavior is reproducible and is not able to be explained by the experimental errors. It is one of the interesting problems to understand the reasons of these phenomena at ultra-low temperatures.

We have established that there occurs a first-order phase transition between the U-AF and D-AF phases in Ni-doped CuGeO$_3$. This transition occurs without the change of the direction of the easy axis. The easy axis remains nearly along the $a$ axis during the transition. Recently Coad et al. reported that the SP gap of 3.2% Ni-doped CuGeO$_3$ had collapsed almost completely, while that of 1.7% sample had coexisted with the AF order. Their results are consistent with our observations.

One of the most important issues in this Letter is whether the first-order phase transition between the D-AF and U-AF phases in Mg-doped CuGeO$_3$ found by Masuda et al. is universal or not. Our experimental results tell us that the same phenomenon occurs definitely in Ni-doped CuGeO$_3$. In Ni-doped CuGeO$_3$ this phenomenon occurs without the change of the direction of the easy axis. Considering the fact that Mg$^{2+}$ ion is nonmagnetic and Ni$^{2+}$ ion has $S = 1$ spin on it, we may infer that this type of the first-order phase transition is universal at least for the substitution for Cu$^{2+}$ ion. Of course we must still study the detailed phase diagrams by using other dopants, e.g., Zn and Mn, which is being done at present. A remaining problem is whether or not this transition occurs for the substitution for Ge$^{4+}$ ion by, e.g., Si$^{4+}$ ion. Recent report of the phase diagram of CuGe$_{1-x}$Si$_x$O$_3$ (see Fig. 8 of Ref. 18) may indicate that this does not occur for Si-doping. However, the temperature dependence of the magnetization of CuGe$_{1-x}$Si$_x$O$_3$ shown in Fig. 5 of Ref. 18 has broadening of the AF transition for $0.005 \leq x \leq 0.024$ ($T_{SP}$ was observed $x \leq 0.008$), in contrast to relatively sharp AF transition at $x = 0.002$ and 0.05. This is somewhat similar to that observed in Mg-doped CuGeO$_3$ (see Fig. 3 of Ref. 11), which indicated the coexistence of two phases (D-AF and U-AF phases) owing to a first-order phase transition. Therefore more detailed study on the phase diagram of this system is needed to reach a definite conclusion.

Here we will compare the phase diagrams of Ni-doped and Mg-doped (or Zn-doped) CuGeO$_3$ in more detail. In the U-AF phase and especially far from the phase boundary with the D-AF phase the phase boundary with the paramagnetic phase is almost the same in the two cases (see Fig. 2 of Ref. 11). This may be explained as follows. The U-AF phase is supposed to be a conventional AF phase except for the existence of the disorder. Every spins either on Cu$^{2+}$, or on Ni$^{2+}$ ions have effective magnetic moments $\mu_{\text{eff}}$ reduced by the quantum fluctuation. Moreover in this concentration region the
easy axes do not change in both cases, although the directions are different. Therefore except for the existence of the $S = 1$ spins on Ni$^{2+}$ ions and the difference of the easy axes, both of the U-AF phases can be treated as classical Neél states, which are expected to be described by the mean-field theory. This may be the reason why both of the U-AF phases behave similarly despite the difference of the easy axis. To explain the decrease of $T_N$ with increasing $x$, we must consider the effect of the disorder, which plays an important role in AF materials into which the disorder is introduced.

Next we shall consider the competing effect of the anisotropies. In Mg-doped (also Zn-doped) CuGeO$_3$ the direction of the easy axis along the $c$ axis can be only explained by the small anisotropy of the exchange interaction between the spins on Cu$^{2+}$ ions, because the spins have $S = 1/2$ and do not have single-ion anisotropy and because Zn$^{2+}$ and Mg$^{2+}$ ions are nonmagnetic. On the other hand, spins on Ni$^{2+}$ ions have $S = 1$ and single-ion anisotropy. When $x$ is large enough, $S = 1$ spins on Ni$^{2+}$ drive the whole $S = 1/2$ spins on Cu$^{2+}$ ions to orient nearly along the $a$ axis. This can be attained by sufficiently strong exchange interaction between $S = 1$ spins on Ni$^{2+}$ ions and neighboring $S = 1/2$ spins on Cu$^{2+}$ ions. This explains the spin configurations of Mg- and Ni-doped CuGeO$_3$ at large $x$.

In very low Zn concentration region of Cu$_{1-x}$Zn$_x$GeO$_3$, Manabe et al. experimentally showed that there is no critical concentration for the occurrence of AF-LRO and also showed that the easy axis remains parallel to the $c$ axis down to $x = 1.12(2) \times 10^{-3}$. The latter is easily understandable because there is only one kind of anisotropy in Zn-(or Mg-)doped CuGeO$_3$. At low $x$ in Ni-doped CuGeO$_3$, however, two kinds of the anisotropic energies compete, because the effect of the single-ion anisotropy diminishes with decreasing $x$. Therefore at very low $x$ slightly anisotropic AF exchange interaction between the spins on Cu$^{2+}$ ions dominates. This is expected to drive the easy axis toward the $c$ axis with decreasing $x$ and is the reason why we found the “OAF state” at $x \sim 0.005$ in Ni-doped CuGeO$_3$.

The occurrence of the first-order phase transition between the D-AF and U-AF phases and its universality do not seem to have been theoretically explained conclusively. Based on the phase Hamiltonian formulation applied to the explanation of the coexistence of dimerization and AF-LRO in Si-doped CuGeO$_3$ at $T = 0$ K, Saito proposes a model of a transition, which, however, derives a second-order phase transition. Further considering the 3-dimensional interaction explicitly, she claims that the first-order transition could be obtained. To construct a theory we must consider the fact that this transition is universal for the substitution for Cu$^{2+}$. It also depends on whether this transition occurs for the substitution for Ge$^{4+}$ or not.

In summary we have found that the first-order phase transition observed in Mg-doped CuGeO$_3$ occurs also in Ni-doped CuGeO$_3$ with the different directions of the easy axis. From this we infer that this transition occurs universally for the substitution for Cu$^{2+}$. Competing anisotropies cause more complex phase diagram in Ni-doped CuGeO$_3$ than in Mg- or Zn-doped CuGeO$_3$ in the low concentration region.

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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. B. 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 (Amsterdam) 215B, 164 (1995).
5 J-G. Lussier, S. M. Coad, D. F. McMorrow and D. McK Paul, J. Phys. Condens. Matt. 7, L325 (1995).
6 J. P. Renard, K. Le. Dang, P. Veillet, G. Dhalenne, A. Revecovschi, and L.-P. Regnault, Europhys. Lett. 30, 475 (1995).
7 M. Hase, K. Uchinokura, R. J. Birgeneau, K. Hirota, and G. Shirane, J. Phys. Soc. Jpn. 65, 1392 (1996).
8 Y. Sasago, N. Koide, K. Uchinokura, M. C. Martin, M. Hase, K. Hirota, and G. Shirane, Phys. Rev. B 54, R6835 (1996).
9 M. C. Martin, M. Hase, K. Hirota, G. Shirane, Y. Sasago, N. Koide, and K. Uchinokura, Phys. Rev. B 56, 3173 (1997).
10 H. Fukuyama, T. Tanimoto, and M. Saito, J. Phys. Soc. Jpn. 65, 1182 (1996).
11 T. Masuda, A. Fujioka, Y. Uchiyama, I. Tsukada, and K. Uchinokura, Phys. Rev. Lett. 80, 4566 (1998), cond-mat/9803163.
12 N. Koide, Y. Sasago, T. Masuda, and K. Uchinokura, Czech. J. Phys. 46(S2), 1981 (1996).
13 S. Coad, J-G. Lussier, D. F. McMorrow, and D. McK Paul, J. Phys. Condens. Matter 8, 6251 (1996).
14 S. Coad, O. Petrenko, D. McK. Paul, B. Fäk, J-G. Lussier, and D. F. McMorrow, Physica (Amsterdam) 239B, 350
K. Manabe, H. Ishimoto, N. Koide, Y. Sasago, and K. Uchinokura, to be published in Phys. Rev. B, Rapid Communication, cond-mat/9805072.

K. Uchinokura, N. Koide, Y. Uchiyama, T. Hayashi, and T. Masuda, in preparation.

F. Matsubara and S. Inawashiro, J. Phys. Soc. Jpn. 42, 1529 (1977).

B. Grenier, J.-P. Renard, P. Veillet, C. Paulsen, R. Calemczuk, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B 57, 3444 (1998).

K. Uchinokura, T. Ino, I. Terasaki, and I. Tsukada, Physica (Amsterdam) 205B, 234-248 (1995).

M. Saito, submitted to J. Phys. Soc. Jpn.

M. Saito, private communication.