Effects of Substitution of Zn for Cu in the Spin-Peierls Cuprate, $CuGeO_3$: The Suppression of the Spin-Peierls Transition and the Occurrence of a New Spin-Glass State

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The magnetic susceptibilities of polycrystalline $Cu_{1-x}Zn_xGeO_3$ were measured to study the effects of nonmagnetic impurities on the spin-Peierls transition. The transition temperature drastically reduces upon Zn doping and the spin-Peierls state collapses around $x=0.03$. The Zn doping causes another phase transition in the samples with $0.02 \leq x \leq 0.08$, which proved to be spin-glass-like. The present Letter provides the first study of the spin-Peierls system with impurities.

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The impurities doped in the antiferromagnetic (AF) quantum spin system significantly affect its physical properties. For example, Cu doped in the Haldane material causes the $S=\frac{1}{2}$ degrees of freedom at the edges [1], while Zn doped in the high-T_c cuprate drastically suppresses its superconductivity [2]. On the contrary, the effect of impurities for the spin-Peierls (SP) system has never been investigated. The SP transition is known to occur in only a few organic compounds, e.g., TTF-CuBDT [3] or MEM-$(TCNQ)_2$ [4], where unpaired electrons on TTF^+ or $TCNQ^-$ ions are responsible for localized spins ($S=\frac{1}{2}$). Thus the value of S on a part or all of these ions cannot be easily changed.

Recently some of the present authors have discovered that an insulating inorganic compound, $CuGeO_3$, exhibits the SP transition [5]. The crystal structure of $CuGeO_3$ has an orthorhombic unit cell and each Cu site is equivalent at room temperature [6]. Localized spins exist only on Cu^{2+} ions ($S=\frac{1}{2}$). The AF linear chains parallel to the c axis consist of Cu^{2+} ions coupled with one another through O^{2-} ions and are separated from one another by Ge-O chains. The values of the SP transition temperature (T_{SP}) and the intrachain exchange interaction (J_{intra} [7]) are 14 and 88 K, respectively [5]. One expects that Cu^{2+} in $CuGeO_3$, as well as in the high-T_c cuprates, can be substituted by other metal elements. Therefore this compound is suitable for a study of impurity doping in the SP system.

To study the effects of impurities, we chose Zn as the best dopant. First of all, Zn is expected to be substituted only for Cu, because the ionic radius of a Zn^{2+} ion (0.75 Å) is similar to that of a Cu^{2+} ion (0.73 Å), but is larger than that of a Ge^{4+} ion (0.40 Å) [8]. Second, the value of S on Cu sites will be unchanged, because both Cu and Zn cations are divalent. Third, Zn^{2+} ions are nonmagnetic; that is, the magnetic susceptibility is mainly determined by the magnetic properties of Cu spins.

Thirteen samples of polycrystalline $Cu_{1-x}Zn_xGeO_3$ with $x=0$, 0.002, 0.005, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, and 0.1 were prepared by an ordinary solid-state reaction method. The x-ray diffraction patterns of the samples show that there is no trace of other impurity phases, and that the lattice constants are almost independent of x. Magnetic susceptibility was measured by a SQUID magnetometer.

The temperature dependence of the magnetic susceptibility per 1-mol Cu ions [$\chi(T,x)$] of $Cu_{1-x}Zn_xGeO_3$ is shown in Fig. 1. Measurement was performed in the magnetic field H of 0.01 T in the field-cooling process. The SP transition characterized by a rapid drop of $\chi(T,x)$ near 10–14 K was observed in the samples with

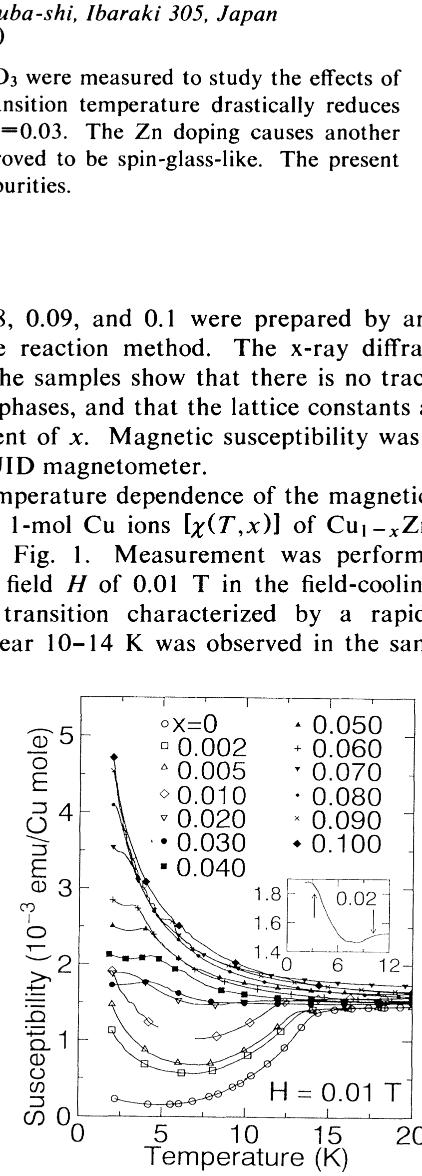

FIG. 1. The magnetic susceptibilities of polycrystalline $Cu_{1-x}Zn_xGeO_3$ below 20 K measured under $H=0.01$ T in the field-cooling process. We measured the data at an interval of 0.2 K in general. Many experimental points have been suppressed in order to improve the clarity of the figure. The susceptibility for $x=0$ was derived from that of single-crystal $CuGeO_3$ measured under $H=1$ T, because polycrystalline Cu-GeO_3 includes a small amount of divergent term. Inset: The susceptibility of the sample with $x=0.02$. Arrows indicate the positions of the phase transitions.

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$x \leq 0.02$. The value of T_{SP} defined as the onset temperature of the drop reduces with doping and disappears around $x=0.03$. The magnitude of $\chi(T,x)$ increases upon doping below 20 K. We also measured $\chi(T,x)$'s from 20 to 300 K, which show only a weak x dependence. This suggests that the spin and orbital parts of the susceptibility [$\chi^{spin}(T)$ and χ^{orb}, respectively] remain unchanged by Zn doping from 20 to 300 K. Since in general the value of χ^{orb} is independent of temperature, we can see that $\chi^{spin}(T)$ below about 20 K drastically changes with doping. As is seen in $\chi(T,x)$'s for $0.002 \leq x \leq 0.02$, the value of $\chi^{spin}(T)$ does not become zero in the SP state, in contrast to that of $x=0$. These finite $\chi^{spin}(T)$'s are mainly caused by spins which do not become singlet because of the existence of Zn ions.

Most unexpectedly, we discovered an occurrence of another phase transition characterized by a cusp of $\chi(T,x)$ around 2–5 K for $0.02 \leq x \leq 0.08$. We emphasize that the sample with $x=0.02$ has two phase transitions. On the other hand, the $\chi(T,x)$'s for $x=0.09$ and 0.10 monotonically increase as temperature is lowered below 20 K and show no transitions. In order to see the novel phase transition more clearly, the data for $x=0.04$ measured in various H's below 5 K are shown in Fig. 2. A remarkable hysteresis is observed between the zero-field-cooling (ZFC) and field-cooling (FC) processes in the data in 0.01 T below 4.7 K. The transition temperature is defined as the temperature at which the irreversibility begins, and is slightly higher than the temperature at which the susceptibility has the cusp. As the magnetic field increases, the hysteresis becomes less evident and the susceptibility reduces both below and above the transition temperature at low temperatures. We measured the magnetization for $x=0.04$ at various temperatures and observed that the magnetization curve at 7.8 K was almost a linear function of H up to 15 T [9]. The above-mentioned properties of the susceptibility strongly indicate that a spin-glass-like (SG-like) phase transition [10] occurs in $Cu_{1-x}Zn_xGeO_3$ for $0.02 \leq x \leq 0.08$. However, the ZFC susceptibility of $Cu_{1-x}Zn_xGeO_3$ is different from that of an ordinary spin-glass material which monotonically diminishes with decreasing temperature below the transition temperature. We cannot at present determine the reason for this difference. This SG-like transition has characteristic properties; that is, a small amount of impurities cause the phase transition and the SG-like transition temperature (T_{SG}) is much smaller than J_{intra}. Analogous results were obtained in other quasi-one-dimensional magnetic systems. For example, an anomaly was observed around 3 K in the magnetic susceptibility of $CsCo_{1-x}M_xCl_3$ [$M=$Mg or Zn: $x \sim 0.01$, $J_{intra} \sim 75$ K (AF)], and interpreted by the random field [11]. The SG-like transition was seen around 1.8 K in the differential susceptibility of $C_6H_{11}NH_3Cu_{1-x}Mn_xCl_3$ [$x=0.009$, $J_{intra} \sim -70$ K (ferromagnetic)] [12]. In these materials, the interchain exchange interaction is considered to play an important role in the occurrence of the random field or SG-like transition. On the other hand, a Haldane material with impurities shows neither a phase transition nor an anomaly. It should be emphasized that the value of $|J_{inter}/J_{intra}|$ (J_{inter} is the value of the interchain exchange interaction) is very small ($\sim 10^{-4}$) in the Haldane material [13].

The x dependences of T_{SP} [$T_{SP}(x)$] and T_{SG} [$T_{SG}(x)$] are shown in Fig. 3. The value of $T_{SP}(x)/T_{SP}(0)$ linearly reduces up to $x \leq 0.02$, which is expressed as $1-13.7x$, and the SP state collapses around $x=0.03$. This means that the value of T_{SP} drastically decreases by a small amount of Zn doping [14]. On the other hand, the SG-like transition is seen in the samples with $0.02 \leq x \leq 0.08$, and the value of $T_{SG}(x)$ has a maximum around

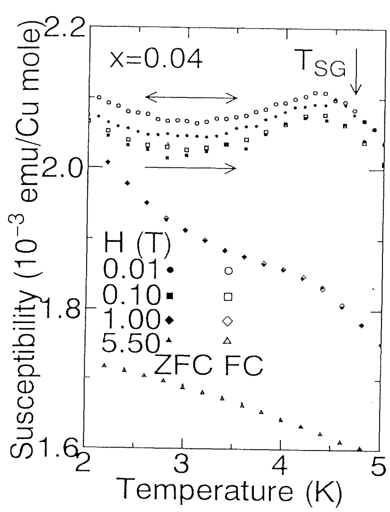

FIG. 2. The magnetic susceptibility of the sample with $x=0.04$ below 5 K measured in various H's. ZFC and FC indicate the zero-field-cooling and field-cooling processes, respectively. Horizontal solid arrows mean the directions of the temperature scan.

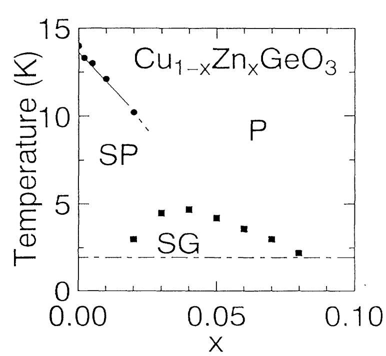

FIG. 3. The x dependences of $T_{SP}(x)$ (closed circles) and $T_{SG}(x)$ (closed squares). Spin-glass-like, spin-Peierls, and paramagnetic states are abbreviated to SG, SP, and P, respectively. The dot-dashed line represents the position of 2 K, which is the limit of temperature of the susceptibility measurement.

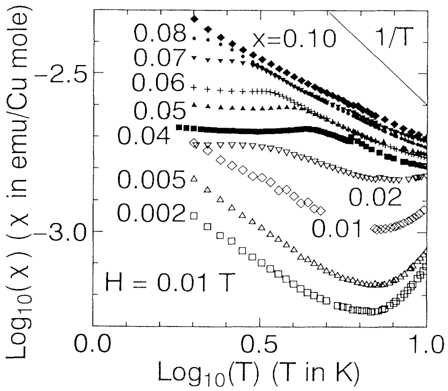

FIG. 4. $\log_{10}[\chi(T,x)]$ vs $\log_{10}(T)$ below 10 K measured under $H=0.01$ T in the field-cooling process.

$x=0.04$.

We point out that $\chi(T,x)$'s at low temperatures do not obey a simple Curie law. The data of $\log_{10}[\chi(T,x)]$ vs $\log_{10}(T)$ are shown in Fig. 4. The divergence of $\chi(T,x)$'s is weaker than $1/T$ in each data. The slope of the curve changes outside the region where the SG-like transition occurs; that is, the slope for $x \leq 0.01$ is larger than that for $x=0.10$. Bulaevskii [15] has calculated the susceptibility of the uniform AF Heisenberg linear chain with defects, which diverges as $1/T$. On the other hand, Bulaevskii *et al.* [16] have also calculated the susceptibility of the one-dimensional (1D) system with a distributed AF interaction, which diverges weaker than $1/T$. These theories strongly suggest that the AF interaction is not uniform at low temperatures in all the samples. The nonuniformity may come from a local lattice distortion and/or a disorder of AF interactions in these samples, although the SP transition is not observed in the samples with $0.03 \leq x \leq 0.10$. We point out as another feature of the divergent term that the total amount of spins contributing to it increases with x. Suppose that $\chi(T,x)$ is roughly expressed as $C(x)T^{-\gamma(x)}[\gamma(x)<1]$ at low temperatures. To explain the increase of the magnitude of $\chi(T,x)$ with x, we conclude that only the value of $C(x)$ increases with x, because the slope, $\gamma(x)$, is nearly constant or slightly decreases with x. The value of $C(x)$ is in general proportional to the total amount of spins, although an exact expression depends on a theoretical model. As is mentioned, the strong x dependence was observed in $\chi(T,x)$'s below 20 K, which indicates that Zn homogeneously distributes in the AF chains in each sample.

Before the discussion about the effects of impurities on the SP transition, we summarize theories of this transition. The Hamiltonian for the SP system is changed into that expressed in terms of spinless-fermion operators by the Jordan-Wigner [17] and Fourier transformations. To treat the SP transition properly, it is necessary to include accurately interactions between spinless fermions. Cross and Fisher have developed a theory of the SP transition using boson representations of fermion operators [18]. Nakano and Fukuyama have obtained a phase Hamiltonian, and succeeded in treating properly the ground state and the low-lying excitation in the SP state [19]. According to the theory of Cross and Fisher [18], the value of T_{SP} is determined from the following equations: $0=\Omega_0^2(2k_F)+\Pi(2k_F,T_{SP})$ and $\Pi(2k_F,T) = -1.04|g(2k_F)|^2T^{-1}$, where $\Omega_0(q)$, $\Pi(q,T)$, $g(q)$, and k_F denote the phonon frequency in the absence of the spin interactions, the polarizability, the coupling constant between the 1D spin and three-dimensional (3D) phonon systems, and the Fermi wave vector, respectively.

Let us consider the SP transition in $Cu_{1-x}Zn_xGeO_3$. The rapid and linear decrease of T_{SP} reminds us of the reduction of the Peierls transition temperature (T_P) in a low-dimensional conductor with nonmagnetic impurities [20], e.g., $Ta_{1-x}Nb_xS_3$ [$T_P(x)/T_P(0) \sim 1-31.3x$: $T_P(x)$ is T_P for x] [21]. The Hamiltonian for the SP system expressed by spinless fermions is nearly equivalent to that for the Peierls system except for the interaction terms among spinless fermions. Thus we think that the reduction of T_{SP} originates from the disorder of the spinless-fermion band induced by Zn ions. Although an explicit expression of the polarizability in $Cu_{1-x}Zn_xGeO_3$ has not been obtained, it is considered that the absolute value of the polarizability becomes smaller upon Zn doping at the same temperature because of the disorder of the spinless-fermion band. Since the SP transition occurs at the temperature where the value of $-\Pi(2k_F,T)$ is equal to that of $\Omega_0^2(2k_F)$, the value of T_{SP} reduces with doping. Further investigations are necessary for the quantitative understanding of the reduction of T_{SP} both experimentally and theoretically.

We shall have a closer look at the newly discovered SG-like transition. As is seen above, the SP order is destroyed by Zn. The disappearance of the SP order leads to a development of the 1D AF correlation in each chain, which is considered to play an important role in the appearance of the SG-like transition. However, in addition to the 1D AF correlation, some other conditions are necessary for the occurrence of the SG-like transition: the frustration and/or randomness in the exchange interaction [10]. There is randomness, because Zn is randomly distributed in chains. However, whether or not there is frustration is not a simple problem. If the chain is strictly 1D, the frustration does not exist. On the other hand, a spin-glass transition occurs in a magnet, where the exchange interaction is 2D or 3D (e.g., 2D AF kagomé lattice [22]). Then we consider the following scenario. Even in a pure SP system, there should be a weak interchain exchange interaction at least in a paramagnetic state, which does not affect the SP state because most spins are singlet below T_{SP}. As a result, the 2D or 3D magnetic correlation exists and may produce frustration. We think that the interchain exchange interaction is necessary for the occurrence of the SG-like transition.

We consider the x dependence of the 2D or 3D magnetic correlation. The energy of the 2D or 3D magnetic correlation and then T_{SG} are roughly estimated to be proportional to $|\xi_{\parallel} J_{inter}|$ where $\xi_{\parallel}$ is the 1D AF correlation length in the chain. The value of $\xi_{\parallel}$ is proportional to T^{-1} in general [23], while that of J_{inter} is almost independent of T. Therefore a phase transition may occur when the magnetic energy, which increases with decreasing temperature, coincides with the thermal energy. The Zn doping hardly changes the value of J_{inter} dominated mainly by the interchain exchange interaction inherent in the undoped system, whereas the Zn doping changes $\xi_{\parallel}$. In the small x region, the value of $\xi_{\parallel}$ increases upon Zn doping because of the reduction of the SP order and the corresponding development of the 1D AF correlation. As a result, the value of $T_{SG}(x)$ increases. On the other hand, in the large x region, the value of $\xi_{\parallel}$ is limited to an average distance between two neighboring Zn ions in chains, because the two Cu spins located on opposite sides of Zn within a chain interact weaker than the two neighboring Cu spins within a chain. Since the average distance between two neighboring Zn ions in chains reduces with doping, the values of $\xi_{\parallel}$ and T_{SG} decrease. In order to understand the SG-like state and microscopic state of chains in more detail, more experiments, such as the differential susceptibility and electron nuclear double resonance, are needed.

In summary, we synthesized polycrystalline $Cu_{1-x}Zn_xGeO_3$ and measured the magnetic susceptibilities to study the effects of nonmagnetic impurities on the spin-Peierls system. The spin-Peierls transition temperature linearly reduces and the spin-Peierls state collapses around $x=0.03$. We also discovered a new spin-glass-like transition in the samples with $x=0.02$–0.08. This transition is caused by a small amount of Zn. This Letter is the first report of the effects of impurities on the spin-Peierls system.

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