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Spin-Peierls State versus Néel State in Doped CuGeO₃

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The competition between nonmagnetic spin-Peierls (SP) and magnetic Néel ground states has been investigated in CuGeO₃ doped with Zn, Ni, Mn, and Si. The analysis of specific heat, $C_p$, data in CuGeO₃, measured as a function of magnetic field, supports a SP transition at $T_{SP} = 14$ K. The replacement of Cu⁺ by Zn²⁺, Ni²⁺, or Mn²⁺ reduces $T_{SP}$ and stabilizes a Néel state, not a spin-glass phase as previously suggested. No significant difference in $C_p$ was observed for Zn- and Ni-doped samples. We suggest that the Néel state depends on $|S'| - 3$, where $S'$ is the spin of the dopant and $S = \frac{1}{2}$.

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Quantum magnetism in low-dimensional (D) and low-spin ($S$) Heisenberg systems is a perennially attractive subject. Particularly, doping in quantum magnets has drawn great attention in recent years [1]. The linear structure of CuGeO₃ suggests that it is a good realization of a 1D $S = \frac{1}{2}$ antiferromagnet (AF). Furthermore, the inorganic nature of this compound allows different spin substitutions. From the isotropic and rapid drop of the magnetic susceptibility ($\chi$), Hase, Terasaki, and Uchinokura concluded that the compound undergoes a spin-Peierls (SP) transition at 14 K [2]. The SP transition can be described as a progressive dimerization of $S = \frac{1}{2}$ AF chains coupled to the 3D lattice. As the temperature ($T$) is lowered, the assembly of uniform AF chains undergoes a second-order phase transition at $T = T_{SP}$ to a system of alternating-bond-length AF chains. The main feature of this state is the appearance of an energy gap between the new ground state, a spin singlet, and a band of spin-triplet states. Such a transition has been reported in a few organic compounds, such as TTF-Cu(Au)BDT and [MME(TCNQ)₄], where the unpaired electrons are localized on the TTF⁺ and TCNQ⁻ units of the structure, respectively [3]. In CuGeO₃, the $S = \frac{1}{2}$ spin is localized on the Cu²⁺ ions. CuGeO₃ forms in an orthorhombic structure with a Cu-Cu distance of 4.793, 4.251, and 2.942 Å along the a, b, and c axes, respectively [4]. AF chains of Cu²⁺ along the c axis are coupled through O²⁻ ions and separated by Ge-O chains. This structure suggests 1D AF magnetic coupling. Recent neutron scattering data [5] have been interpreted as due to a continuous twisting of the oxygens connecting the Cu atoms to the a-b plane between room temperature and $T = T_{SP}$. This structural distortion was claimed to abruptly end at $T_{SP}$, suggesting that it drives the SP transition, i.e., the motion of the oxygens modulates the spin-spin interaction along the c axis, and they are responsible for the coupling between the singlet spin pairs and phonons. A model proposed by Imada [6], using the concept of the resonating valence bond (RVB) introduced by Anderson [7], may describe the SP phase in CuGeO₃. In his model, the spin gap is not a consequence of a static lattice dimerization, but the result of dynamic SP fluctuations. Nevertheless, two-magnon scattering data are not in agreement with the SP interpretation [8], but agree with a strong interchain ferromagnetic (FM) interaction in CuGeO₃, contrary to the negligible interchain interaction expected for SP systems.

CuGeO₃ is interesting because it can be used in order to address the problem of doping in one-dimensional magnetic systems. This is a subject of current interest where little experimental work is available [9], primarily because of the difficulty of finding chain magnets that can be doped without large changes in their symmetry and magnetic interactions. CuGeO₃ is a unique system because it allows us to study the effects of partial replacement of Cu by $S \neq \frac{1}{2}$ ions. The effect of doping has not been investigated in organic SP systems because of the low solubility of dopants. Hase et al. recently reported [10] a rapid decrease of $T_{SP}$ in CuGeO₃ upon doping with Zn and the appearance of a new magnetic state for concentrations of Zn ≈ 0.02. From their $\chi$ data, they concluded that the new state is a spin-glass (SG) phase. On the other hand, Lu, Su, and Yu [11] suggested that Zn doping results in the collapse of the spin gap, and predicted the existence of a gapless SP state for Zn ≈ 0.03.

In this Letter we present specific heat, $C_p$, data measured as a function of magnetic field ($H$) in pure CuGeO₃ and the effects of Zn, Ni, Mn, and Si doping. Magnetic specific heat has been useful in understanding organic SP systems [12]. The data are analyzed in terms of a mean-field model and compared with $\chi$ and EPR measurements on the same samples [13]. Polycrystalline materials were prepared by the standard solid-state reac-
tion in air. Large single crystals were grown by the slow cooling of stoichiometric melts. The specific heat was measured between 1.4 and 20 K using a small-sample relaxation calorimeter [14].

Data for $C_p/T$ vs $T$ for several compounds are shown in Fig. 1. A $\lambda$-type anomaly is observed in every case. $C_p$ is similar for 4% Ni or Zn doping. A more rapid reduction of $T_{SP}$ was found for Mn than for Ni or Zn doping. In contrast, Si which substitutes for Ge has little effect on $T_{SP}$. Applied fields of up to 10 T shift $T_{SP}$ by ~1.7 K. As seen in the inset of Fig. 1, Cu$_{0.99}$Zn$_{0.01}$GeO$_3$ exhibits anomalies at $\sim$3 and $\sim$10 K. In order to separate the lattice contribution, $C_L$, from the magnetic contribution, $C_m$, we have assumed that the magnetic transition, the applied magnetic field, and the doping have only minor effects on $C_L$. It is a reasonable assumption because independent fits for the different samples provide comparable values for $C_L$. This is clear from a simple inspection of the curves shown in Fig. 1 which remain essentially parallel everywhere except close to the anomalies. The data for $T \ll T_{SP}$ have been fitted by

$$C_p = \beta_1 T^3 + c \exp(-b T_{SP}/T),$$  
(1)

where the first term accounts for $C_L$. A better fit for $T > 4$ K is obtained by adding a term $\beta_2 T^5$. The data can then be represented above and below $T_{SP}$ by means of the same $C_L$. A mean-field analysis of an SP system is analogous to a BCS analysis for the superconducting state; thus we fit the magnetic specific heat data below $T_{SP}$ using a BCS-like exponential gap function [15]. The data above $T_{SP}$ were fitted by

$$C_p = \beta_1 T^3 + \beta_2 T^5 + \gamma T,$$  
(2)

where the linear term $\gamma T$ is characteristic of 1D homogeneous AF systems with $\gamma = 2Nk_B^2/3J [3,12]$. More weight was given to the parameters obtained for Eq. (1) using CuGeO$_3$ data. A larger $T$ range is covered when $T < T_{SP}$ for the undoped sample; consequently, the errors are smaller. Using the same argument, the parameters obtained from fitting the 4% Zn and Ni data by Eq. (2) were given more weight for $T > T_{SP}$. These parameters were determined independently for each compound and fell within experimental error of each other. The best fits were obtained with $\beta_1 = 0.66 \pm 0.05$ mJ/mol K$^4$, $\beta_2 = -0.00077 \pm 10^{-5}$ mJ/mol K$^6$, and $\gamma = 45 \pm 5$ mJ/mol K$^2$. $\beta_1$ corresponds to a Debye temperature $\Theta_D \sim 240$ K. In Fig. 1 we display the fit by Eq. (1) of the CuGeO$_3$, and by Eq. (2) of Cu$_{0.99}$Zn$_{0.01}$GeO$_3$ data, with $H = 0$. For the sake of clarity, fits to the other samples are not given. If $\gamma = 45 \pm 5$ mJ/mol K$^2$ is substituted in the expression $\gamma = 2Nk_B^2/3J$, a value of $J/k_B \sim 123$ K is obtained that is in agreement with the value of $\sim 125$ K derived from high magnetic field data [16]. The discrepancy with $J/k_B = 88$ K, obtained from $\chi$ data [2], may be associated with the poor agreement between the $\chi$ data and the model used to fit them [17].

In order to study the region of the transition in more detail we analyze it within the mean-field model, as in the case for the organic SP compounds [12]. In Fig. 2 we present $C_m = C_p - C_L$ for CuGeO$_3$. The A-shaped anomaly is approximated by means of a triangular function, with the same entropy gain under this function as under the measured anomaly. The baseline of the triangle, represented by the term $\gamma T$ for the 4% Zn and Ni specimens, shows the entropy gain as compared to the case where no transition occurs. The mean-field

![FIG. 1. Total specific heat, $C_p/T$, for pure CuGeO$_3$ measured at 0, 5, and 10 T, and for 4% Zn and 4% Ni doping, measured in $H = 0$. The inset shows data for Cu$_{0.99}$Zn$_{0.01}$GeO$_3$, where two anomalies are seen. The full lines are the best fits by Eqs. (1) and (2) for CuGeO$_3$ and Cu$_{0.99}$Zn$_{0.01}$GeO$_3$ data, respectively.](image)

![FIG. 2. Magnetic specific heat, $C_m$ (○), of CuGeO$_3$. The triangular function approximates the mean-field character of the transition leaving the entropy gain unaltered. The baseline of the triangle is defined by $C_m$ of Cu$_{0.99}$Zn$_{0.01}$GeO$_3$ (△) and Cu$_{0.99}$Ni$_{0.01}$GeO$_3$ (×) for $T > T_p$. The temperatures discussed in the text, $T_{SP}$ and $T_p$, are shown. The inset shows the best fit by $c \exp(-b T_{SP}/T)$ for CuGeO$_3$ measured in different fields.](image)
transition temperature, $T^{MF}_{SP}$, is found to be ~14 K, in excellent agreement with $T_{SP}$ obtained from $\chi$ and EPR data [2,13]. The temperature of the peak, $T_p$, is ~13.3 K, i.e., indicating a transition width of ~0.7 K. The jump in the triangular function, $-920 \pm 100$ mJ/mol K, can be compared with the jump predicted by the BCS model, $\Delta C_m = 1.43\gamma T_{SP}$. This expression yields a value of $\gamma \sim 46 \pm 5$ mJ/mol K$^2$, in excellent agreement with the value of $\gamma$ obtained by extrapolation above $T_{SP}$. Below $T_{SP}$, the magnetic term $C_m$ was fitted by $c \exp(-bT_{SP}/T)$. The fit yields $c \sim 20$ J/mol K and $b \sim 2.6$. These values can be compared with those expected for a BCS model, $c \sim 10\gamma T_{SP}$ and $b \sim 1.5$ [15]. For CuGeO$_3$, values of $c \sim 6$ J/mol K and $b \sim 1.5$ are obtained by using $\gamma \sim 45$ mJ/mol K$^2$ and $T^{MF}_{SP} \sim 14$ K, these values are smaller than the experimental ones. Similar discrepancies were found in organic SP systems [12].

A test for the SP model is to study the change of $T_{SP}$ with magnetic field. The behavior in a field can help in discriminating between a simple structural transition and a SP transition. A large difference in the decrease of $T_{SP}$ is expected between the two cases, $\Delta T \sim (H/J)^2$ for a structural transition and $\Delta T_{SP} \sim (H/T_{SP})^2$ for a SP transition [18]. In the inset of Fig. 2 we present the fits of the $C_m$ data measured at 0, 5, and 10 T by $c \exp(-bT_{SP}/T)$. The best fits are obtained with $c = 20 \pm 2$, $16 \pm 2$, and $9 \pm 2$; and $bT_{SP} = 37 \pm 1$, $32 \pm 1$, and $25 \pm 1$ K for $H = 0$, 5, and 10 T, respectively. When analyzing the data within the mean-field model, values of $T^{MF}_{SP}$ = 13.6 and 12.3 K and $T_p = 12.8$ and 11.5 K were found for $H = 5$ and 10 T, respectively. A decrease of $bT_{SP}$ with $H$ is expected because of the increase of the Zeeman energy and the reduction of the energy gap in the spin-wave spectrum. For fields with $\mu_B H < 0.5k_B T_{SP}$, a decrease of $T_{SP}$ by $\Delta T_{SP}/T_{SP} = \alpha x(1 + x + \ldots)$, where $x = (\mu_B H/2k_B T_{SP})^2$ and $g$ (gyromagnetic factor for Cu$^{2+}$) is ~2.17 for a powder sample [13], has been predicted [18–20]. The expression reduces to the first term for $\mu_B H \ll k_B T$. Using the $T^{MF}_{SP}$ and $T_p$ given above, values of $\alpha = 0.41$ and 0.40 for 5 and 10 T are obtained, respectively. They agree well with those derived from a Hartree-Fock approximation, which yields $\alpha = 0.44$ [18,19] and the calculation by Cross which predicts $\alpha = 0.38$ [20]. For fields larger than 5 T, the agreement is possibly fortuitous. A similar agreement was found in the organic SP systems when measuring at high fields [21]. Our data analysis supports a SP transition, in disagreement with the two-magnon scattering conclusions [8]. A strong FM interaction between chains, as suggested in Ref. [8], should produce large $g$ shifts of the Cu$^{2+}$ EPR line as a function of $T$, but they were not observed [13].

The influence of doping upon the magnetic specific heat can be observed in Fig. 3, in which $C_m/T$ ratios are plotted as a function of temperature. The anomaly associated with the SP transition shifts to lower $T$ with doping. As previously suggested by Hase et al. [10], and seen in Figs. 1 and 3, there is a second anomaly at ~3 K for Cu$_{0.09}$Zn$_{0.03}$GeO$_3$. For larger concentrations of Zn or Ni, the temperature of the second anomaly increases to ~4 K with the complete disappearance of the SP anomaly. There is no significant difference between the specific heat for 4% Zn and Ni materials. We calculated the excess entropies for 4% Zn and Ni with $|S' - S| = 1/2$. The fit yields $\Delta S \sim 0.15$ J/mol K, which accounts for ~4% of $R \ln(2|S' - S| + 1) = 5.76$ J/mol K. One would expect that replacing Cu by Zn would result in an increase of $\chi$ due to Cu ions that do not dimerize in a singlet ground state. However, only a small increase in $\chi$, that weakly depends on doping, is measured. This can be understood as follows: Zn can be thought of as an on-site spin vacancy that introduces a localized magnetic moment which is “polarized” by the staggered magnetization. As it sees the local field due to the staggered order, no Curie term appears [9]. The consequence of doping with nonmagnetic Zn$^{2+}$ or magnetic Ni$^{2+}$, $S = 1$, is almost the same. The increase in $\chi$ due to Ni doping is small compared with the contribution expected from Ni$^{2+}$ free ions. The effect of doping with Mn$^{2+}$, $S = \frac{3}{2}$, was studied by EPR. The EPR data can be explained as Mn$^{2+}$ doping depresses $T_{SP}$ about twice as rapidly as Zn and Ni. From these observations we may infer that the difference

![FIG. 3. Magnetic specific heat, $C_m/T$, as determined from the subtraction of the lattice contribution, $C_L$. For pure CuGeO$_3$ measured at 0 (○), 5 (▼), and 10 (△) T, and at $H = 0$, for 2% (●) and 4% (△) Zn and 4% (★) Ni doping. Inset (a) shows $C_m (\Delta)$, and the zero-field-cooled (ZFC) (○) and field-cooled (FC) (▲) $\chi$ for Cu$_{0.09}$Zn$_{0.03}$GeO$_3$, measured in 50 Oe. Inset (b) shows $C_m (\propto)$ and $\chi (\Delta)$ for Cu$_{0.09}$Ni$_{0.01}$GeO$_3$ measured in 50 Oe.](image-url)
between the spin value of the doping impurity and the $S = \frac{1}{2}$ spin of Cu$^{2+}$ is an important parameter in determining the properties of the system. Furthermore, the size of the ion substituting for Cu$^{2+} = 0.73$ Å (Zn$^{2+} = 0.74$ Å, Ni$^{2+} = 0.69$ Å) does not seem to play a significant role. Replacing Ge$^{4+}$ by up to 10% of Si$^{4+}$ reduces $T_{SP}$ by just $\sim 1$ K.

Our data analysis does not agree with the speculation of Ref. [10] that a SG phase resulted from Zn doping. As seen in the insets of Fig. 3 for 4% of Zn or Ni, a peak in $C_m$ is found at the same $T$, within the experimental error, where $\chi$ shows a maximum. It is well known that the magnetic specific heat of a SG system shows no indication of a cooperative peak, discontinuity, or any broad anomaly close to the freezing temperature, $T_{SG}$, where $\chi$ displays its characteristic sharp peak [22]. For a SG system, $C_m$ increases linearly with $T$ showing only a rounded maximum at $T$ well above $T_{SG}$. Furthermore, contrary to Ref. [10], and as can be seen in inset (a) of Fig. 3, our low field $\chi$ measured in $H = 50$ Oe for Cu$_{0.996}$Zn$_{0.004}$GeO$_3$ does not display a difference between zero-field cooling and field cooling below the $\chi$ cusp, as would be expected for a SG compound [22]. Another argument against the SG description is that frustration is required for its occurrence, which is not possible within 1D chains, unless a strong interchain interaction is induced by doping [10]. The peak in $C_m$ and the drop in the $\chi$ below its maximum are strong indications of a Néel state, rather than a SG. The presence of two peaks in the $C_p$ of Cu$_{0.99}$Zn$_{0.01}$GeO$_3$ suggests the coexistence of a SP and a Néel state, for which we do not have an explanation.

In addition, the existence of the two peaks appears to be inconsistent with the gapless SP state proposed by Lu, Su, and Yu [11].

As mentioned above, neutron scattering data [5] indicate that the SP transition in CuGeO$_3$ is not a consequence of a static lattice dimerization, but is due to dynamic fluctuations of the oxygens, a possibility proposed earlier by Imada [6] using the concept of RVB [7]. Doping could destroy the fluctuations by pinning the impurities, which could explain the rapid decrease of $T_{SP}$ with Cu-site substitution. Inagaki and Fukuyama [23] studied the possibility of having a magnetic Néel or a SP as a ground state for a quasi-1D Heisenberg AF. They obtained a phase diagram where either the SP or the Néel state is the ground state depending on the ratio between the interchain and intrachain exchange interaction. As Cu substitution modifies the chain length, it changes the spin-phonon interaction, and possibly increases the intrachain-interchain ratio, then a Néel state ground state could be stabilized. For CuGeO$_3$ the boundary between the SP state and the Néel state is $\sim -3\%$ for Zn or Ni and $\sim -1\%$ for Mn.

New x-rays and neutron studies on CuGeO$_3$ were reported after the completion of this work [24]. Their authors postulate the existence of oxygen displacements in the $a$-$b$ plane and critical fluctuations above $T_{SP}$ for CuGeO$_3$. Their data analysis supports a SP transition [24].

In summary, the analysis of the field dependent specific heat data of CuGeO$_3$ indicates the occurrence of a SP transition, and the specific heat data suggest that the second magnetic anomaly observed for doped samples is associated to a Néel and not a SG ground state.

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