Observation of the Spin-Peierls Transition in Linear Cu^{2+} (Spin-$\frac{1}{2}$) Chains in an Inorganic Compound $CuGeO_3$

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(Received 4 January 1993)

The magnetic susceptibility of single-crystal $CuGeO_3$, a linear Cu^{2+} (spin-$\frac{1}{2}$) chain compound, was measured. The susceptibilities in all the directions rapidly drop to small constant values with decreasing temperature below a phase transition temperature near 14 K. The magnetic-field dependence of the transition temperature quantitatively agrees with both theoretical predictions and experimental results for organic spin-Peierls systems. This Letter is the first report of an unambiguous determination of the existence of the spin-Peierls transition in an inorganic compound.

PACS numbers: 75.10.Jm, 75.40.Cx, 75.50.Ee

Magnetic properties of low-dimensional systems of quantum spins with antiferromagnetic (AF) interactions have attracted much attention because of their various interesting phenomena, e.g., the spin-Peierls transition in alternating Heisenberg chains [1], the appearance of the Haldane gap in Heisenberg chains with integer spins [2–5], and the high-temperature superconductivity occurring in layered cuprates including CuO_2 planes [6]. In particular, AF oxides containing Cu^{2+} have been extensively studied [7] since the discovery of cuprate superconductors, because the two-dimensional (2D) CuO_2 planes are responsible for the high-temperature superconductivity. Our motivation to study the magnetic properties of $CuGeO_3$ including linear chains with Cu^{2+} is to compare one-dimensional (1D) Cu^{2+} based antiferromagnets with 2D cuprate superconductors. This compound is suitable for magnetic studies because only Cu^{2+} is magnetic ($S=\frac{1}{2}$).

The crystal structure of $CuGeO_3$ has an orthorhombic unit cell [8]. Each Cu^{2+} ion is equivalent at room temperature. The distance between nearest neighbor Cu^{2+} ions, which are located along the c direction, is much shorter than that between next nearest ones along the b direction. Adjacent Cu^{2+} ions in the c direction are coupled through two O^{2-} ions. Considering this structure, we expect a 1D AF interaction between spins on adjacent Cu^{2+} ions in the c direction.

In this Letter, we report the magnetic susceptibility of single-crystal $CuGeO_3$, which clearly exhibits the characteristic properties of the spin-Peierls transition. As far as we know, the existence of this transition is discovered for the first time in inorganic materials, while it has been observed so far only in a few organic compounds. The spin-Peierls transition occurs when a system of uniform Heisenberg AF linear chains undergoes a transformation to a system of dimerized or alternating AF linear chains [1]. This dimerization is mainly caused by the spin-phonon coupling between the 1D spin system and the three-dimensional (3D) phonon system. Below the transition temperature (T_{sp}), the ground state is spin singlet (nonmagnetic), and a finite energy gap opens in the excitation spectrum.

The samples were grown by a self-flux method. They were confirmed to be single-crystal $CuGeO_3$ by x-ray diffraction patterns and the Weissenberg method. The obtained single crystals are transparent with light-blue color and insulating. A typical dimension is about 0.05, 0.2, and 2 mm parallel to the a, b, and c axes, respectively. We also made polycrystalline $CuGeO_3$ by a usual sintering method. The x-ray diffraction patterns of the polycrystalline samples show the existence of the $CuGeO_3$ crystals and no trace of other impurity phases. Magnetic susceptibility was measured by a SQUID magnetometer.

The temperature dependence of the magnetic susceptibility of single-crystal $CuGeO_3$ is shown in Fig. 1. Measurement was performed from 4.5 to 300 K under the magnetic field H of 1 T in the configurations with H parallel to three principal axes. The most striking feature is that the susceptibilities in all the directions $\chi_i(T)$ ($i=a$, b, and c) exponentially drop to small constant values below 14 K. The data measured in zero-field cooling and field cooling processes are identical. As usual we assume that the orbital part of the susceptibility χ_i^{orb} ($i=a$, b, and c) is independent of temperature, because it consists of a Van Vleck paramagnetic susceptibility and a diamagnetic one of core electrons. Although an accurate value of χ_i^{orb} is unknown, it is estimated to be of the order of 1×10^{-4} emu/mole, comparable with the magnitude of the 4.5-K susceptibilities. Since the spin parts of the susceptibilities $\chi_i^{spin}(T)$ ($i=a$, b, and c) can be obtained as $\chi_i^{spin}(T)=\chi_i(T)-\chi_i^{orb}$, the observed data strongly indicate that $\chi_i^{spin}(T)$ rapidly reduces to zero with decreasing temperature.

It is necessary to seek a possible origin of the rapid decrease of the susceptibility below 14 K. First of all, we emphasize that neither a 3D AF long-range order (LRO) nor a 1D Ising-like antiferromagnetic [9] can explain the observed data, because in these two cases the susceptibility decreases to zero as $T\rightarrow0$ K only in one direction of the crystal and remains finite in other directions. Second, we also exclude a Haldane system because $CuGeO_3$ has linear spin chains with a half-integer spin of Cu^{2+}. (An

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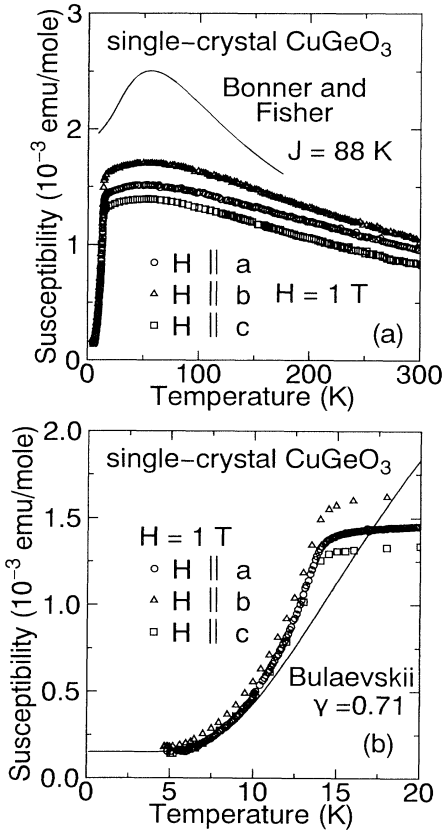

FIG. 1. The magnetic susceptibility of single-crystal $CuGeO_3$ measured under $H=1$ T. (a) The susceptibility from 4.5 to 300 K. The solid curve is a theoretical one calculated by Bonner and Fisher with $J=88$ K (from Ref. [9]). (b) The susceptibility below 20 K. The solid curve is a theoretical one calculated by Bulaevskii (from Ref. [10]). The value of J and the ratio between two alternating J's (γ) are 103 [$=88(1+0.17)$] K and 0.71, respectively, which are estimated in the text. The value of χ_i^{orb} is assumed to be 1.5×10^{-4} emu/mole.

integer-spin chain is essential to a Haldane system.) Nonetheless the susceptibility of $CuGeO_3$ is very similar to that of Haldane materials, suggesting that the excitation spectrum of $CuGeO_3$ has a finite energy gap with a nonmagnetic ground state below 14 K.

There exists another system which shows a nonmagnetic ground state and a finite energy gap between the ground and excited states. It is a system of Heisenberg AF chains with alternating exchange interactions [10]. If the distance between $S=\frac{1}{2}$ spins located on Cu^{2+} ions changes alternately, the AF exchange integral J will also change alternately. The susceptibility of this system is theoretically calculated and shows a rapid decrease slightly below a temperature at which the susceptibility is maximum [10]. As mentioned previously, positions of Cu^{2+} ions in $CuGeO_3$ are equivalent at room temperature [8], indicating that the AF interaction is uniform at room temperature. However, an abrupt change of the susceptibility at 14 K in Fig. 1 strongly suggests some kind of phase transition. This may cause the change of the homogeneous AF chain to an alternating AF chain.

To confirm the existence of a phase transition at 14 K we have measured the specific heat in cooperation with Sekine's group at Sophia University. The experimental results clearly show an anomaly due to a second-order phase transition around 14 K. (These results will be published separately [11]). This definitely shows the existence of a phase transition at this temperature. Then there remain two possibilities. One is the case that a simple structural phase transition accidentally occurs with the doubling of the c length, which then induces the alternation of the AF couplings among the Cu^{2+} spins. The other is a spin-Peierls transition, which has been confirmed to exist only in organic compounds. The difference between the two is whether the AF interaction is essential to the phase transition or not.

Before reaching a conclusion let us discuss the magnetic properties above the transition temperature. The temperature dependences of the susceptibilities in the a, b, and c axes shown in Fig. 1 are almost identical with one another except for a weak anisotropy. The spin parts of the susceptibilities $\chi_i^{\text{spin}}(T)$ can be obtained as discussed before. The ratios $\chi_a^{\text{spin}}(T)/\chi_c^{\text{spin}}(T)$ and $\chi_b^{\text{spin}}(T)/\chi_c^{\text{spin}}(T)$ are 1.10 and 1.22, respectively, in the temperature region between 4.5 and 300 K. This suggests that the magnetism of this compound can be described by a Heisenberg model,

$$H=J\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j\,. \tag{1}$$

The susceptibility has a broad maximum near 56 K and slowly decreases above 56 K with increasing temperature. This broad maximum strongly indicates the existence of an AF exchange interaction [9]. As was discussed already, a magnetic interaction of the spins in $CuGeO_3$ is expected to be 1D. The value of J is calculated to be about 88 K according to the model of uniform Heisenberg AF linear chains [9]. However, as is seen in Fig. 1(a), the experimental results do not quantitatively agree with the theory. The magnitude of the former is smaller than that of the latter, and the temperature dependence of the former is weaker than that of the latter. We cannot at present determine the reason for this discrepancy but the weak interchain coupling between the spins or the temperature dependence of the exchange interaction may be possible reasons. The discrepancy between the measured susceptibility above the transition temperature and the theories must be studied in more detail.

We will prove that the phase transition of $CuGeO_3$ is really the spin-Peierls transition. In Fig. 2 we show the temperature dependence of the susceptibility of a polycrystalline sample under various magnetic fields. It can be seen that the transition temperature shifts to lower temperature with increasing magnetic field. We cannot expect the shift of the transition temperature to lower

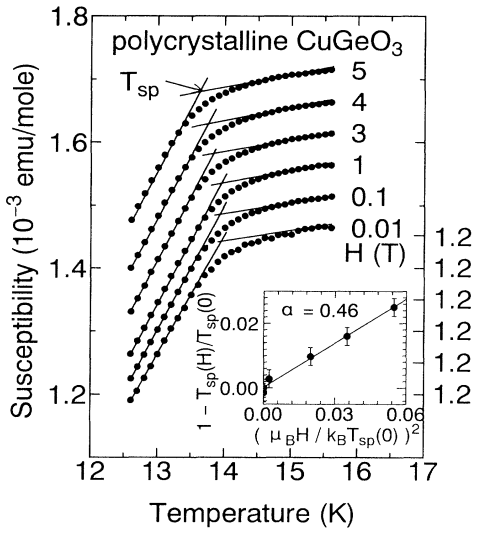

FIG. 2. The magnetic susceptibility of polycrystalline $CuGeO_3$ measured near the phase transition temperature, $T_{sp}(H)$, under $H=0.01\sim5$ T. As is seen in this figure, each value of $T_{sp}(H)$ is defined as the temperature of the intersection of two lines along each curve. The vertical position of each data point is shifted as indicated on the right-hand side of the figure. Inset: $1-T_{sp}(H)/T_{sp}(0)$ vs $[-\mu_B H/k_B T_{sp}(0)]^2$.

temperature in a simple structural phase transition. Therefore the possibility of a simple structural phase transition can be excluded in $CuGeO_3$ and it is concluded that the spin-Peierls transition occurs around 14 K.

Now let us compare the experimental results with theories and the experimental results of the already known organic spin-Peierls systems. According to the Hartree-Fock theory of Bulaevskii, Buzdin, and Khomskii (BBK) [12] and also to the Luther-Peschel-type treatment of the spin-correlation functions of Cross [13], the magnetic field dependence of T_{sp} $[T_{sp}(H)]$ is expressed as follows when $2\mu_B H \ll k_B T_{sp}(0)$:

$$1-\frac{T_{sp}(H)}{T_{sp}(0)}\sim\alpha\left[\frac{\mu_B H}{k_B T_{sp}(0)}\right]^2, \tag{2}$$

where μ_B is the Bohr magneton and k_B is the Boltzmann constant. The value of α is about 0.44 and 0.38 according to BBK and Cross, respectively. The left-hand side of Eq. (2) of the experimental results is plotted as a function of $[\mu_B H/k_B T_{sp}(0)]^2$ in the inset of Fig. 2. It shows the expected H^2 dependence and the value of α obtained in our sample is about 0.46, which is in excellent agreement with the theories. In organic spin-Peierls systems it has been established that the phase boundaries are expressed by a universal phase diagram [14], which in particular at low magnetic-field range coincides with the theories of BBK as well as Cross. This means that the phase boundary between the spin-Peierls and the uniform states in $CuGeO_3$ agrees with that of the organic spin-Peierls systems, although the measured range of the magnetic field is very narrow in this Letter. The measurement in the wider magnetic-field region is currently being done.

Below T_{sp} two alternating J's $[J_{1,2}(T)]$ are formed and expressed as follows [15]:

$$J_{1,2}(T)=J\{1\pm\delta(T)\}. \tag{3}$$

According to the mean-field theory of Pytte the relationship between $\delta(T)$ and the excitation energy gap $\Delta(T)$ at temperature T is expressed as [16]

$$\delta(T)=\frac{\Delta(T)}{pJ}, \tag{4}$$

where the value of p is 1.637. Bulaevskii has calculated the susceptibility of the system of the Heisenberg AF linear chains with temperature-independent alternating J in the Hartree-Fock approximation [10]. The value of $\delta(T)$ and therefore $\Delta(T)$ can be obtained by combining Bulaevskii's theory with Eqs. (3) and (4). By this method we obtained $\delta(0)=0.17$ [i.e., $J_2(0)/J_1(0)=0.71$] and $\Delta(0)=24$ K. These values are isotropic, because $\chi_i^{spin}(T)$'s are almost identical if they are normalized by their maximum values as was discussed before. It should be noted that the experimental data cannot be simply explained by the model of the Heisenberg AF linear chains with temperature-independent alternating J. In Fig. 1(b), we show a theoretical curve of this model with estimated parameters. The discrepancy between the theoretical curve and the experimental data becomes evident above 10 K, which is due to a temperature dependence of $J_{1,2}(T)$. The value of $2\Delta(0)/k_B T_{sp}$ is 3.43, which is close to the values of organic spin-Peierls materials (3.53, 3.7, and 3.16 for TTF-CuBDT [16], TTF-AuBDT [1], and MEM-$(TCNQ)_2$ [17], respectively). According to the theory of Cross and Fisher [18], T_{sp} is given by

$$T_{sp}=0.8J\eta', \tag{5}$$

where η' is the spin-lattice coupling constant. From Eq. (5) we obtain $\eta'=0.20$. The values of η' and $\Delta(0)$ in $CuGeO_3$ are surprisingly close to those of TTF-CuBDT [16] or MEM-$(TCNQ)_2$ [17].

The properties of $CuGeO_3$ can be well described by the existing theories of the spin-Peierls transition and no inconsistencies with the theories have been found. Moreover the agreement with the experimental results in organic spin-Peierls systems is very good. The present authors think that they have firmly proven the existence of the spin-Peierls transition in Cu^{2+} linear chains in an inorganic compound, $CuGeO_3$.

After we observed the anomalous behavior of the susceptibility in $CuGeO_3$, we found out that there had been a report on the magnetic and resonance properties of crystalline and amorphous $CuGeO_3$ [19]. General features of the temperature dependence of the susceptibility of the crystalline $CuGeO_3$ are very similar to our results except for the existence of a sharp rise of $T<7$ K and

larger and different anisotropy [$\chi_c(T) < \chi_b(T) < \chi_a(T)$]. They claimed that a magnetic LRO (Néel order) exists in the $CuGeO_3$ system below 7 K and did not attribute the sharp drop of the susceptibility to any kind of phase transitions. Since we have not observed a sharp rise of the susceptibility in our samples, we think that the rise of the susceptibility at low temperature should be attributed to some extrinsic effect. Here we emphasize that the essential property of $CuGeO_3$ is the occurrence of a spin-Peierls transition, as we have already shown.

In conclusion, we measured the magnetic susceptibility of single-crystal $CuGeO_3$. The susceptibilities in the three principal orientations rapidly decrease below 14 K, which definitely shows the occurrence of the spin-Peierls transition. We also observed the magnetic-field dependence of the transition temperature. This behavior can be quantitatively explained by the theories of BBK or Cross. As far as we know, $CuGeO_3$ is the first inorganic compound that exhibits the existence of this transition.

We would like to thank H. Obara of Electrotechnical Laboratory and T. Sekine and H. Kuroe of Sophia University for collaborations.

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