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Spin-Peierls transition in CuGeO$_3$: Electron paramagnetic resonance study

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Measurements of electron paramagnetic resonance (EPR) at 9 and 35 GHz between 2 and 300 K in single crystals and powder samples of CuGeO$_3$ are presented. Below 14 K a large decrease in the intensity of the Cu^{2+} EPR signal is observed. The data can be interpreted as due to a spin-Peierls transition. However, an alternative interpretation in terms of a simple structural transition cannot be ruled out. An opening of an energy gap of ~25 K is calculated from the analysis.

It is now well established that, as the temperature is reduced, a one-dimensional (1D) metallic lattice of uniformly spaced atoms with a half-filled conduction band can exhibit a Peierls transition.[1] Such a transition results from a distortion of the lattice in which alternate atoms are displaced in opposite directions. A splitting of the conduction band and a reduction in the energy of the electrons occupying the lower band is observed. There is a magnetic analog to the electronic Peierls instability, the so-called spin-Peierls (SP) transition.[2] A uniform antiferromagnetic (AF) quantum chain becomes unstable with respect to an underlying lattice distortion which dimerizes into AF chains.[2,3] It has been argued that for the SP transition to occur, the 3D lattice, where the 1D magnetic chains are embedded, needs first to undergo a strong softening. A softening of the phonons at high temperature in the undimerized state has been found in the few 1D organic materials where, at much lower temperature, a SP transition has been observed.[4]

The AF chains are characterized below the SP transition by an energy gap between a nondegenerate singlet ground state and a band of triple excited states. The energy gap is dependent on the degree of alternation and goes to zero in the uniform chain limit. In zero magnetic field the transition is second order and the degree of alternation increases as the temperature, T, is lowered, reaching its maximum at $T=0$ K.[2-4] The first experimental evidence confirming the existence of such compounds followed the discovery of the 1D organic materials TTF-CuBDT, TTF-AuBDT, and MUM(TCNQ)$_2$. Their properties can be satisfactorily explained within the framework of the theory of a SP transition.[5] In many instances the spin-Peierls nature has been disputed, questioning if the doubling of the period of the 1D unit cell is due to a SP instability. The observed alternation of the AF coupling between the spins can be just a consequence of a simple structural transition which results in the doubling of the lattice period. It is then important to find whether or not the AF interaction is essential to the phase transition.

Recently the presence of a SP transition has been reported in an inorganic compound, CuGeO$_3$.[6] That study showed that the susceptibility, χ, in all the directions of the crystal rapidly decreases to zero below 14 K. Besides, the magnetic field dependence of the transition temperature, T_{sp}, agrees well with the theoretical predictions and experimental results reported previously for the organic SP systems. Electron paramagnetic resonance (EPR) is an ideal technique to study CuGeO$_3$, as Cu^{2+} is one of the easiest ions to detect by EPR. This technique has been shown to be extremely sensitive for studying the dynamics of low-dimensional spin systems, which includes the already well characterized SP systems.[5,7,8] If an energy gap opens in this compound, with a nonmagnetic singlet ground state, a rapid decrease of the intensity of the Cu^{2+} ($S=1/2$) EPR signal is expected.

In this paper we present measurements of EPR at 9 and 35 GHz between 2 and 300 K on single crystals and powder samples of CuGeO$_3$. Single crystals of about $0.1\times0.5\times3$ mm^3 parallel to the $\bar{a}$, $\bar{b}$, and $\bar{c}$ axes, respectively, were obtained. Powder samples were prepared by the usual sintering method. X-ray studies shows no trace of impurity phases and the data are in good agreement with previous reports on this compound.[9] Previous EPR has been reported in CuGeO$_3$.[10] However, the authors did not observe a decrease in the intensity of the EPR signal or at least did not report it. Instead, they observed for $T\leq7$ K an increase of the magnetization and a broadening of the EPR linewidth which they attributed to long-range magnetic ordering.

Magnetization data on our samples are similar to the data reported by Hase *et al.*[6] That is, a rapid decrease of the susceptibility is observed below 14 K, with no significant increase below 7 K, contrary to the measurements reported by Petrakovskii *et al.*[10] A strong EPR signal of Cu^{2+} was measured for the single crystal as for the powder samples for $T\geq14$ K. The intensity, I, of the signal diminishes rapidly below this temperature. In Fig. 1 we show the linewidth, ΔH, as a function of T for a single crystal measured at 35 GHz. Similar data for ΔH are obtained at 9 GHz. The inten-
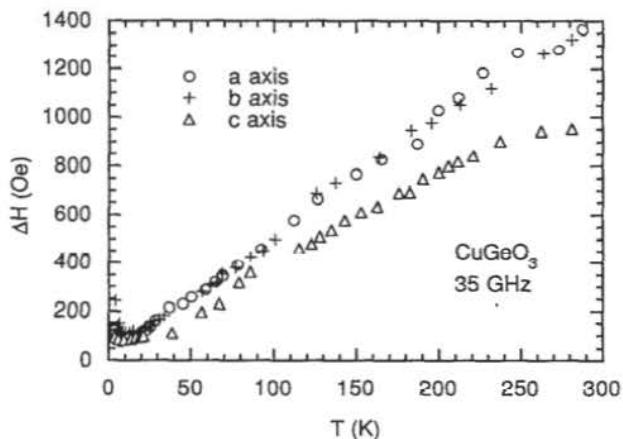
FIG. 1. EPR linewidth as a function of T for a CuGeO$_3$ single crystal measured at 35 GHz.

FIG. 3. Intensity vs T for a single crystal measured at 9 GHz. The solid curve corresponds to the best fitting to Eq. (2) with $m = 40$ K.

sity was estimated by finding the area of the EPR signal. We present I vs T for a single crystal measured at 35 and 9 GHz, and susceptibility data in Figs. 2–4, respectively.

The angular dependence of the Cu^{2+} line can be described by the spin-Hamiltonian:

$$H = \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H}, \qquad (1)$$

where $S = 1/2$, $\mathbf{g}$ is the gyromagnetic tensor, μ_B is the Bohr magneton, and $\mathbf{H}$ the external magnetic field. In Fig. 5 the angular variation of the gyromagnetic factor measured at 35 GHz for the three principal lattice planes is given. The g values for the principal axes, obtained from the best fit of the data, are listed in Table I for three temperatures.

The first question to ask is if CuGeO$_3$ is well described by 1D Heisenberg AF. If anisotropic components would be present in the coupling between the Cu spins, shifts in the g values as a function of T would be observed. As seen in Table I these shifts are small, so the principal exchange mechanism may be assumed to be isotropic.

In Fig. 1 we see that ΔH increases with T between ~ 40 and 300 K. It has been suggested that at high temperatures

the long wavelength modes, $q \sim 0$, constitute the dominant contribution to ΔH for a 1D AF chain, with ΔH predicted to be proportional to χT.[11,12] In our case the agreement is good. The increase in ΔH observed in single crystals for $T \leq T_{sp}$ shown in Fig. 1 can be explained as follows: The number of nonmagnetic singlet pairs increases as we lower the temperature. Then, the exchange narrowing becomes less effective and ΔH broadens. However, no broadening below T_{sp} has been found in powder samples. We do not have an explanation for this behavior. Other mechanisms such as the interaction between chains, short-range ordering, etc., may also contribute to ΔH at lower temperatures. Finally, the broadening observed in our single crystals may be due to the presence of impurities or defects in them.

For $T \leq T_{sp}$ we have fitted the intensity of the electron spin resonance (ESR) line to

$$I(T) = \frac{A}{T} \exp\left(\frac{-m}{T}\right), \qquad (2)$$

this expression was obtained by Bulaesvkii for an alternating chain of spins in the Hartree–Fock approximation.[13] This approximation is expected to be accurate for temperatures
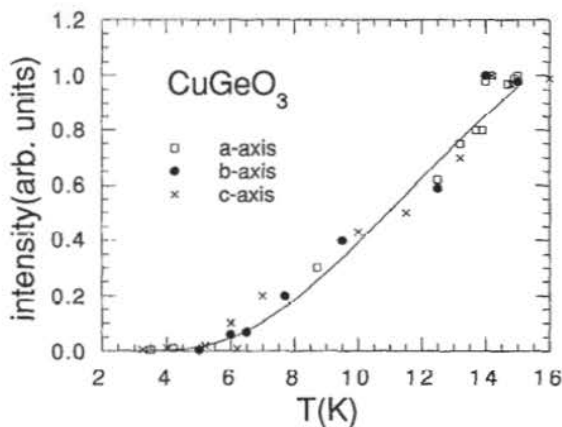

FIG. 2. Intensity of the Cu^{2+} EPR signal vs T, for a single crystal of CuGeO$_3$ measured at 35 GHz and $T \leq T_{sp}$. The solid curve corresponds to the fitting of Eq. (2) with $m = 42$ K.
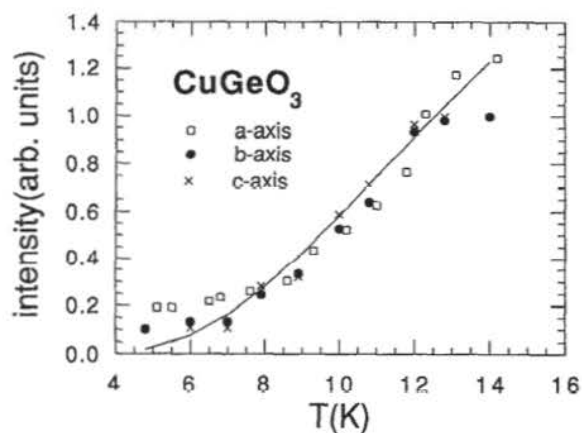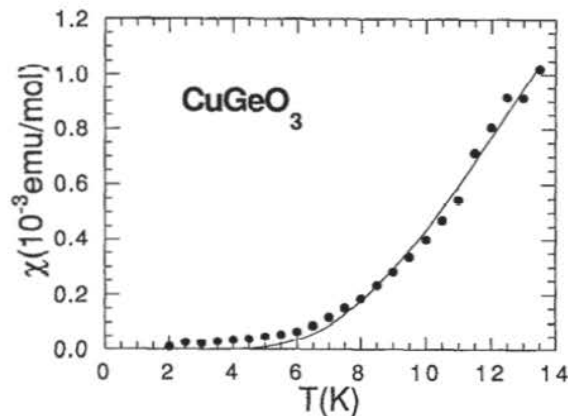

FIG. 4. Susceptibility data taken at 2 kOe in a powder sample. The solid curve is the best fitting to Eq. (2) with $m = 45$ K.
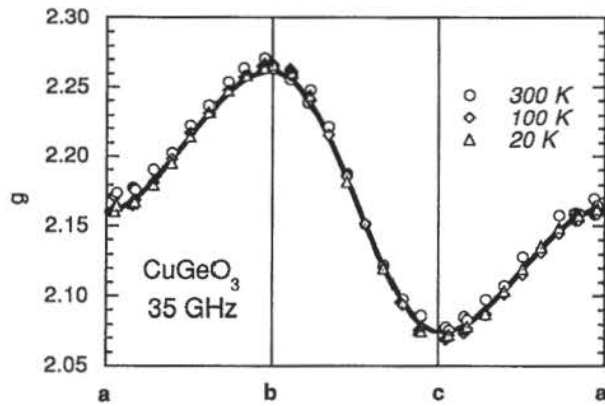
FIG. 5. Angular variation of the gyromagnetic factor at 300, 100, and 20 K. The solid curve corresponds to the best fitting to Eq. (1) for data taken at 20 K.

TABLE I. Gyromagnetic factors for the three principal axes. The data were taken at 35 GHz.

T(K)	g_a	g_b	g_c
300	2.170 ± 0.004	2.267 ± 0.005	2.078 ± 0.002
100	2.160 ± 0.002	2.266 ± 0.002	2.070 ± 0.002
20	2.162 ± 0.002	2.266 ± 0.002	2.070 ± 0.002

much smaller than the exchange interaction, $T \ll J$. As a value of $J \sim 90$ K is derived for CuGeO$_3$ from data,[6] Eq. (2) should be a good approximation for $T \leq T_{sp}$. The best fitting to the data taken in a single crystal measured at 9 and 35 GHz, on powder samples measured at 9 GHz, and susceptibility data give values of $m = 40$, 42, 46, and 45 K, respectively. In Figs. 2–4 the solid curve shows the fitting of the data to Eq. (2) for those values of m.

For $T \leq T_{sp}$ the Heisenberg Hamiltonian for a 1D chain may be written as[13]

$$H = \sum_{i=1}^{N/2} J_1 \mathbf{S}_{2i} \cdot \mathbf{S}_{2i-1} + J_2 \mathbf{S}_{2i} \cdot \mathbf{S}_{2i+1}, \tag{3}$$

where the relation between the two alternating J's of the chain are given by[5,14]

$$J_{1,2}(T) = J\{1 + \delta(T)\}, \tag{4}$$

according to mean-field theory the energy gap $\Delta(T)$ is given by

$$\Delta(T) = pJ \delta(T), \tag{5}$$

using values of $J = 90$ K,[6] $p = 1.637$,[3–5] and $m \approx 43$ K from our measurements, we obtained $J_2/J_1 \sim 0.7$, $\delta(0) \sim 0.17$, and $\Delta(0) \sim 25$ K in agreement with Hase et al.[6]

Preliminary specific heat measurements show a λ-shaped anomaly at ~ 14 K, similar to that observed in organic SP systems.[15] Measurements of the dc magnetization at high magnetic field, up to 26 T, show a rapid increase of M at ~ 12 T at low temperature.[16] In summary, our EPR results, preliminary specific heat and high-field dc magnetization could be interpreted as due to an SP transition in CuGeO$_3$. However, a careful analysis of the data is needed before we can rule out a structural transition with the doubling of the lattice period as the origin of the alternation of the exchange interaction in the spin chain.

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