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SPIN GAP AND SPIN-PHONON INTERACTION IN $CuGeO_3$

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We study the spin-Peierls transition in $CuGeO_3$ by means of Raman spectroscopy. Improved measurements directly show the opening of the spin-Peierls energy gap below the transition temperature T_{SP}. A continuous excitation between 30 and 230 cm^{-1}, including two well-known low-temperature peaks, is shown to originate from two-magnon excitations with magnons propagating one-dimensionally along the Cu-chains. Spin-phonon interaction inherent to the spin-Peierls state manifests in form of a pronounced Fano lineshape of the low-temperature peak at 107 cm^{-1} as well as newly observed magnon-phonon coupled modes. Additional novel spectral features inherent to the low-temperature phase are reported. Copyright ©1996 Published by Elsevier Science Ltd

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The compound $CuGeO_3$ has generated a lot of interest lately due its one-dimensional magnetic character and a spin-Peierls transition near 14 K [1,2]. Neutron and Raman scattering studies have analyzed the lattice and magnetic structural changes across the phase transition [3–6]. It is found that in the low-temperature phase the unit cell quadruples by doubling the axis in both **a** and **c** direction [7].

Raman scattering aside from yielding precise structural information about the low-temperature phase, is well-known to be capable of giving information about the density of magnetic excitations in the Brillouin-zone. This is normally manifested in the Raman spectra by two-magnon scattering with a corresponding peak near twice the Brillouin-zone boundary energy of the magnon. Due to magnon-magnon-interaction the maximum in the spectrum actually occurs at $\omega_{max} \approx 2.7J$ where J is the exchange coupling constant. Well-studied examples of this behavior are found in two-dimensional compounds such as K_2MnF_4 and Rb_2MnF_4 [8,9].

In this paper we demonstrate the appearance of such a continuous density of magnetic excitations in the Raman spectra of $CuGeO_3$, show directly the spin-Peierls gap in this continuum and show, as a novel feature, that the shape of the continuum is consistent with one-dimensionally propagating magnons. The energies of both the one and two-magnon excitations (including magnon–magnon interaction) at the center of the Brillouin zone are determined with high accuracy (better than 75 μeV). Spin–phonon interaction is known to be the driving force of the spin-Peierls transition. We demonstrate that in Raman spectra it manifests itself in form of a pronounced Fano lineshape of the low-temperature peak at 107 cm^{-1} as well as newly reported magnon–phonon coupled modes. Finally, we investigated a number of additional new spectral features.

The experiments were carried out in quasi-backscattering geometry using a triple grating spectrometer [10] with a liquid-nitrogen-cooled CCD detector for signal detection. An Argon/Krypton-ion laser [11] was used for excitation at 514.5 nm at a power level of about 8 mW. Focusing of the beam down to a spot diameter of $\sim$ 10 μm and collection of the scattered light was done by a $f/1.67$ objective. Great care was taken to avoid and remove any unwanted reflections and stray light in order to record spectra close to the exciting laser line (6 – 650 cm^{-1}). Well-crystallized needle-shaped single crystals were grown as described previously [12, 13]. In some of the crystals ^{65}Cu (enrichment > 99%) was substituted for the natural iso-

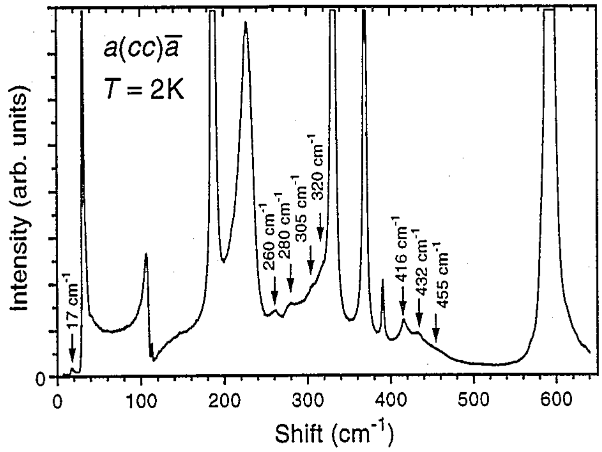

Fig. 1. Chain-polarized low-temperature spectrum of $^{65}CuGeO_3$. Several low-temperature peaks that have not been reported before are indicated by arrows along with their energy.

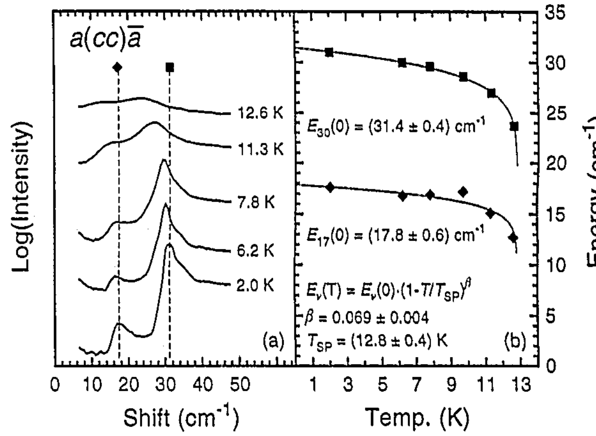

Fig. 2. Temperature dependence of the low-frequency excitations at 17 and 30 cm^{-1}. a) Raman spectra in the temperature range 2–12.6 K. Note the logarithmic intensity scale in order to enhance the weak peak at 17 cm^{-1}. b) Temperature dependence of the peak energies. The dotted curves show the results of fitting the experimental data with Eq. (1) using the parameters noted for both data sets.

tope mixture of 69% ^{63}Cu and 31% ^{65}Cu in order to investigate the significance of Cu-vibrations for the low-temperature modes whose origin is still not resolved. The crystals were mounted in a cryostat which could be used both as He-bath and continuous-flow cryostat allowing temperatures between 2 and 55 K.

Figure 1 shows the chain-polarized $[a(cc)\bar{a}]$ Raman spectrum of $CuGeO_3$ taken at $T = 2$ K. There is a continuous background below ~ 500 cm^{-1} with a sharp cut-off at 30 cm^{-1}. Below, there are no continuous excitations and there is no background at all in the perpendicular $[a(bc)\bar{a}]$ polarization. Given that the continuous background is due to magnetic excitations we thus directly observe the opening of the spin gap below T_{SP}. Its temperature dependence—shown in Fig. 2a)—proves this depression a property of the spin-Peierls state. Within the gap, a weak peak at 17 cm^{-1} is observed. We assign this peak to a one-magnon excitation and that at 30 cm^{-1} to a two-magnon exitation, both at the center or near the center of the Brillouin-zone, i.e. excitations directly marking the spin gap.

First, we investigate the temperature dependence for both peaks between 2 and 13 K (Fig. 2a). Both peaks clearly shift to lower energy upon raising the temperature. Following Nishi *et al.* [3] the line positions are fitted by

$$E_\nu(T) = E_\nu(0)(1 - T/T_{SP})^\beta \qquad (1)$$

yielding $E_{30}(0) = 31.4 \pm 0.4$ cm^{-1}, $\beta = 0.069 \pm 0.004$, and $T_{SP} = 12.8 \pm 0.4$ K for the 30-cm^{-1} peak and $E_{17}(0) = 17..8 \pm 0.6$ cm^{-1} for the 17-cm^{-1} peak with β and T_{SP} fixed at the above values. Due to a larger uncertainty in determining the position of the 17-cm^{-1} peak the fit is less stable than in the case of the 30-cm^{-1} peak. Fitting all three parameters simultaneously does not significantly change the results. The resulting curves are shown in Fig. 2b). We cannot fit our data with $E(0) = 16.9$ cm^{-1} and $T_{SP} = 14$ K as was done in [3]. Actually, fitting the data from Fig. 4 of Ref. [3] to (1) with $E(0)$, T_{SP} and β as free parameters results in $E(0) = 16.8$ cm^{-1} $= 2.1$ meV, $\beta = 0.063$, and $T_{SP} = 13.1$ K which is in good agreement with our data and also with similar Raman data in Ref. [4]. It should be noted that for both the Raman as well as the inelastic neutron scattering measurements fitting of the temperature dependence of the spin gap consistently results in $T_{SP} \approx 13$ K whereas specific heat measurements indicate $T_{SP} = 14.2$ K [13]. This discrepancy suggests that (1) is not adequate to properly describe the temperature dependence near T_{SP} but can be used at lower temperatures to describe the data and compare results of different measurements.

The energy of the 17-cm^{-1} peak ($E_{17}(0) = (17.8 \pm 0.6)$ cm^{-1}) is slightly larger than the spin-Peierls energy gap of 16.9 cm^{-1} as determined by inelastic neutron scattering [3], magnetic susceptibility [2], and specific heat [13, 14] measurements. This deviation can be explained by the assumption that the peak is the result of a combination of simple one-magnon and domain-wall excitations [15] which causes a shift towards higher energy. On the other hand, the energy of the 30-cm^{-1} peak is lower than twice the gap energy (34 cm^{-1}) which is attributed to magnon–magnon interaction known to shift two-magnon Raman peaks to lower energies [8, 9, 16].

We assign the continuum beginning at 30 cm^{-1} including both peaks at the edges (30 cm^{-1} and

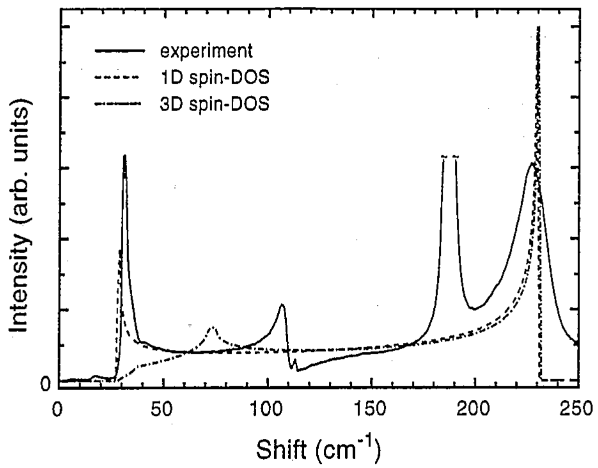

Fig. 3. Comparison of the low-frequency Raman spectrum ($T = 2$ K) with calculated one- and three-dimensional spin densities of states (DOS).

228 cm^{-1}) to two-magnon excitations thus reflecting the spin density of states. The shape of the background gives further evidence for the one-dimensional character of the magnetic properties of $CuGeO_3$ as it is well explained by an excitation of two magnons propagating along the Cu-chains; we will show this in the following.

Figure 3 depicts the Raman spectrum from 6 to 250 cm^{-1} together with the calculated 1D-spin density of states (magnons propagating along **c**-axis only) and the full 3D-density of states. The spin densities are calculated from the magnon dispersion relation measured by means of inelastic-neutron scattering [3]:

$$(\hbar\omega_{\mathbf{q}})^2 = \left(\frac{\pi}{2}J_c + J_b + E_A - J_a(1 - \cos 2\pi h)\right)^2 - \left(\frac{\pi}{2}J_c \cos 2\pi l + J_b \cos \pi k\right)^2 \quad , \qquad (2)$$

with

$$\mathbf{q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad . \qquad (3)$$

$\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ denote the reciprocal lattice vectors of the room-temperature phase, J_a, J_b, and J_c the exchange constants along the principal axes, and E_A was introduced to replace the spin-Peierls energy gap. We adopt the numerical values determined by Kuroe *et al.* [4]: $J_a = -0.044$ meV, $J_b = 0.35$ meV, $J_c = 10.4$ meV, and $E_A = 0.13$ meV.

In first approximation, the shift of two-magnon Raman peaks is proportional to the magnon energy itself [16]. Therefore it can be accounted for by scaling the energy axis with a constant factor. We estimate this factor R from the measured energy of the 228 cm^{-1}-peak and twice the magnon energy (271 cm^{-1}) given by the dispersion relation (2) at ($h = 0$, $k = 1$, $l = 0.75$): $R = 0.84$. The resulting curves for the density of states $D(R \cdot \omega/2)$ are plotted in Fig. 3 along with the measured Raman spectrum.

Apparently, the 3D-density of states does not explain the measured intensity distribution as was proposed in Ref. [4]. It does not account for the peak at 30 cm^{-1} and the predicted peak at $\sim$ 75 cm^{-1} cannot be seen experimentally. In contrast, the 1D-DOS explains both the position of the two peaks and the plateau inbetween. The peak at 30 cm^{-1} thus is due to a singularity caused by a 1D dispersion curve, the peak at 228 cm^{-1} is due to a singularity corresponding to the maximum of the dispersion curve smeared out experimentally as the density of state calculation did not take into account magnon-magnon interaction. Note, that in the long-wave limit ($\mathbf{q} \approx 0$, $2\omega \approx 30$ cm^{-1}) the theoretical density of states describes the experimental lineshape rather well. It also explains the tails on the high and low-energy side of the peaks at 30 and 228 cm^{-1}, respectively.

The peak at 228 cm^{-1} persists up to temperatures well *above* T_{SP} and vanishes around 30 K, i.e. about $2\times T_{SP}$. Such behavior is familiar from two-magnon excitations at the zone boundary indicating short-range magnetic ordering even above the transition temperature. In contrast, the long-wave excitations at the zone center vanish at T_{SP} as expected (Fig. 2). This interpretation in terms of two-magnon excitations gains further support by the fact that the scattering cross section is largest in A_g symmetry with both incident and scattered waves being polarized parallel to the spin chains as expected for a 1D-spin system.

To summarize, based on symmetry properties, lineshape, peak position, and temperature dependence of the measured Raman spectra we assign the continuous excitation between 30 and $\sim$ 230 cm^{-1} including both peaks at the edges to two-magnon excitations with magnons propagating one-dimensionally along the Cu-chains. The background at higher energies is ascribed to higher-order magnetic processes.

The second intriguing feature of the low-temperature spectrum in Fig. 1 is the pronounced Fano-type lineshape of the 107-cm^{-1} peak. Its temperature dependence is displayed in Fig. 4. There is only little broadening upon increasing the temperature and no shift of the peak position ($\omega = 109 \pm 1$ cm^{-1}, $\Gamma = 2.7 \pm 0.1$ cm^{-1}, $q = -1.5 \pm 0.1$). A faint reminescence of the peak can still be seen up to 16.5 K. The small peaks at 113 cm^{-1} and 115 cm^{-1} are phonons of the high-temperature phase which appear only weakly because they are forbidden for these polarizations. We cannot correlate the energy of this peak with two- or four-magnon excitations at critical points of the Brillouin-zone. The Fano-lineshape suggests an inter-

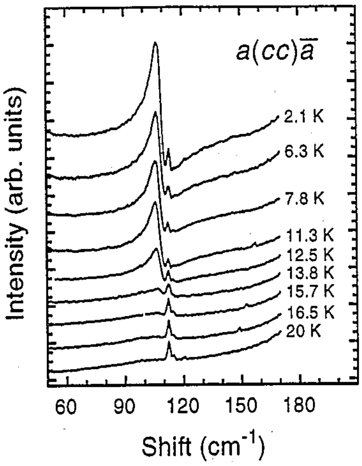

Fig. 4. The 107-cm^{-1} peak shows a pronounced Fano-type lineshape attributed to spin-phonon interaction. There is no temperature-dependent broadening or shift of the peak position.

ference between a discrete and a continuous excitation. As we have shown before, there is a quasi-continuous two-magnon excitation and spin-phonon interaction is an essential ingredient for spin-Peierls systems. We therefore tentatively assign this feature to a phonon interacting with the continuous two-magnon background. From the comparison of the frequency in our isotope-pure sample with the samples with the natural $^{63}Cu/^{65}Cu$-abundance we conclude that the eigenvector of this mode does not contain an appreciable amount of Cu displacement ($\Delta\omega_{exp} < 0.2$ cm^{-1} *versus* the expected $\Delta\omega_{max} = 1.2$ cm^{-1} for a pure Cu-mode).

Finally, our measurements reveal additional peaks correlated with the low-temperature phase that—to the best of our knowledge—have not been reported before. The only new mode apparent in $a(bc)\bar{a}$ geometry was found at 569 cm^{-1} and its linewidth is limited by the spectrometer's resolution of 2 cm^{-1}. It does not exhibit a temperature induced lineshift but vanishes around 14 K.

Eight more structures observed in $a(cc)\bar{a}$ geometry are indicated in Fig. 1 by arrows along with their frequency. First, there is a set of four peaks between 260 and 320 cm^{-1}. Due to the large number of peaks and the lack of detailed knowledge about their lineshape it is not possible to determine the peak positions accurately enough to decide whether or not the peak positions are temperature sensisitive. Again, they vanish at around 14 K.

We have analyzed the structures at 416, 432 and 455 cm^{-1} in detail. Surprisingly, the temperature dependence of the peaks may be fitted also by

$$E(T) = E_0 + \Delta E(1 - T/T_{SP})^{\beta} \quad . \qquad (4)$$

The experimental data does not accurately define the parameters, but the important result is that $T_{SP} \approx 12.8$ K, $\Delta E \approx 18$ cm^{-1}, $\beta \approx 0.07$ for the 416-cm^{-1} peak and $\beta \approx 0.10$ in case of the 455-cm^{-1} peak. What follows is that, quite remarkably, these peaks show the same temperature dependent-energy shift as was observed for the spin gap. The physical origin of these excitations is yet unclear, but their temperature dependence suggests a combination of two elementary excitations, one of them being a zone-center magnon, e.g. such as magnon-assisted phonon creation. These new modes would then be a second manifestation of the spin–phonon interaction inherent to the spin-Peierls state. Further analysis of these new excitations will be necessary to assertain their physical origin.

In conclusion, we have demonstrated that Raman spectroscopy allows one to directly observe the opening of the spin-Peierls energy gap below T_{SP}. A novel continuous excitation between 30 and 230 cm^{-1}, including the two peaks at the edges, has been explained by two-magnon excitations with magnons propagating one-dimensionally along the Cu-chains. The well-known low-temperature peak at 107 cm^{-1} exhibits a pronounced Fano-type lineshape which we attributed to spin–phonon coupling. A number of novel spectral features have been reported, at least two of them showing a temperature-dependent energy shift below T_{SP} which matches that of the spin energy gap.

Note added in press—After completion of the manuscript a paper was published by van Loosdrecht *et al.* [17] which confirms part of our results.

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