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Low-energy magnetic excitations in the dimerized and incommensurate phase of $CuGeO_3$

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Abstract

Low-energy magnetic excitations in the dimerized (D) and incommensurate (I) phase of $CuGeO_3$ were studied by Raman spectroscopy. Based on temperature and magnetic field dependent experiments on pure and Si-doped samples the Raman peak at 17 cm^{-1} for $T = 2$ K in the D-phase is attributed to a soliton-assisted one-magnon excitation. We further present a Raman-study of the low-energy spin dynamics of a spin-Peierls system in the incommensurate phase. The magnetic field induced transition between D- and I-phase of $CuGeO_3$ ($B_c \gtrsim 12.5$ T) is characterized by the appearance of an intense new low-energy mode. For the incommensurate phase a finite zone-center excitation gap of $\Delta = 2.3 \pm 0.2$ cm^{-1} is deduced. © 1999 Published by Elsevier Science Ltd. All rights reserved.

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Being the first inorganic spin-Peierls (SP) compound, $CuGeO_3$ has attracted much theoretical and experimental attention for the last few years [1,2]. The interest was triggered partly by the applicability of a number of experimental methods to a SP system for the first time and partly by the fact that significant deviations from the expected behavior became evident. One of the topics still under investigation concerns the details of intrachain Cu–Cu next nearest neighbor exchange interaction as well as interchain coupling.

Most of the experimental studies address the high-temperature uniform (paramagnetic) and the low-temperature dimerized (nonmagnetic) phase at zero magnetic field. Because of a high critical magnetic field of ~12.5 T the field-induced incommensurate phase at low temperature was so far accessible for only a few investigations. Notably, the early magnetic susceptibility measurements by Hase et al. [3] evidenced the third phase at magnetic fields in excess of 12.5 T and thus confirmed $CuGeO_3$ as a true spin-Peierls system where the lattice distortion is driven by a gain in magnetic energy. Kiryukhin and Keimer determined the nature of the lattice distortion in the high-field state by means of X-ray diffraction [4,5]. Their experiments indicate a soliton lattice where dimerized regions are separated by domain walls, which is also consistent with NMR studies by Fagot-Revurat et al. [6]. First information on the spin dynamics of the high-field phase was obtained from infrared spectroscopy by van Loosdrecht et al. [7]. Nonetheless, little is known about the magnetic excitation spectrum in the incommensurate phase since inelastic neutron scattering experiments have not yet been possible.

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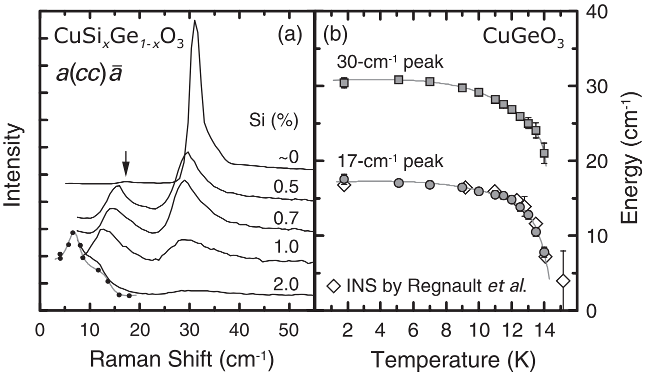

Fig. 1. (a) Chain-polarized Raman spectra of the low-frequency excitations near 17 and 30 cm^{-1} in pure and Si-doped CuGeO$_3$ at $T = 2$ K. (b) Temperature dependence of the peak energies for the undoped sample. For comparison, the T-dependence of the spin-Peierls gap as determined by inelastic neutron scattering is marked by ◇ (data after Ref. [19]).

The present communication addresses low-energy magnetic excitations in both the dimerized and the incommensurate phase of CuGeO$_3$. First, we will clarify the origin of a Raman mode observed near 17 cm^{-1} at $T = 2$ K in nominally undoped samples [8]. Second, we present the first Raman-study of the low-energy spin-dynamics in the incommensurate phase of a spin-Peierls system and analyze the behavior of a so far unknown magnetic field and temperature dependent excitation in the high-field phase of CuGeO$_3$.

The experiments were carried out in back-scattering geometry using a triple-grating spectrometer with a liquid-nitrogen-cooled CCD detector. An Ar$^+$/Kr$^+$ laser was used for excitation at 514.5 nm at power levels of 5–10 mW. Focusing of the beam down to a spot diameter of ~5 μm and collection of the scattered light was achieved by a *f*/1.7 objective. Great care was taken to avoid and remove any unwanted reflections and laser stray light in order to record spectra close to the exciting laser line down to 6 cm^{-1}. The needle-shaped single crystals [9–11] were mounted in a magnet with a variable temperature inset which could be operated at 2–55 K and magnetic fields up to 15 T. All spectra were recorded in Faraday configuration with the magnetic field parallel to the crystal *a*-axis (space group Pbmm).

Fig. 1(a) displays chain-polarized [$a(cc)\bar{a}$] low-frequency Raman spectra of an undoped CuGeO$_3$ crystal and of samples with Si contents in the range 0.5–2.0% at a temperature of 2 K with zero magnetic field. The intense peak near 30 cm^{-1} has been studied in some detail before [8,12–18] and can most consistently be attributed to a spin-singlet two-magnon bound state. Here, we concentrate on the low-energy mode of the pure sample which decreases in energy with increasing temperature (Fig. 1(b)) and which cannot be observed for temperatures higher than the spin-Peierls transition temperature of $T_{SP} = 14.3$ K. For comparison, Fig. 1(b) also shows the temperature dependence of the spin gap as determined by inelastic neutron scattering [19]. Clearly, the temperature dependence of the 17 cm^{-1} mode observed by Raman spectroscopy coincides with that of the spin-Peierls gap. The mode cannot be attributed, however, to a direct excitation across this gap, i.e. from the singlet ground state to the triplet band of excited states. First of all, such a transition is not allowed in first-order Raman scattering due to total spin conservation. Second, we have performed corresponding experiments with magnetic fields up to 15 T. The low-energy peak does not split nor does it shift significantly below the critical field of ~ 12.5 T, although the splitting of the triplet state was observed by inelastic neutron scattering as expected [19–21].

Experiments on Si-doped samples provide the crucial information for an assignment of the low-frequency mode [18]. Obviously, the 17 cm^{-1} peak is much enhanced in the doped samples, and the peak intensity increases with increasing silicon concentration (Fig. 1(a)). Silicon substitutes germanium which plays a crucial role for the antiferromagnetic

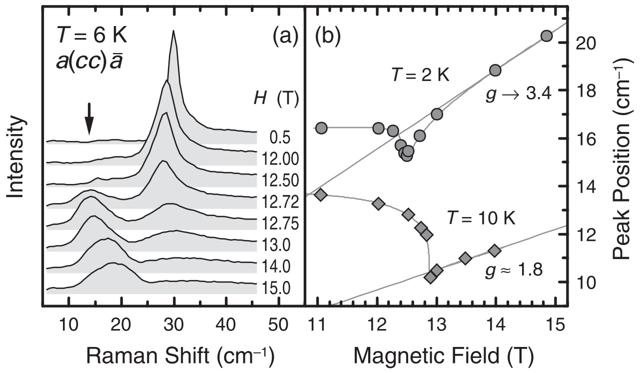

Fig. 2. (a) Low-frequency Raman spectra of $CuGeO_3$ for magnetic fields up to 15 T. (b) Center frequency of the 17 cm^{-1} peak versus magnetic field at 2 and 10 K.

exchange interaction in the Cu chains [22,23]. Doping $CuGeO_3$ with Si leads to a dissection of the spin chains into segments of finite length [22]. In segments with an odd number of spins one of them remains unpaired and the ground state contains a soliton. Other kinds of defects will affect the spin chains in a similar fashion, and we must anticipate the "pure" samples also to have some defects. In the strong-dimerization limit, which is a simple but adequate description of the ground state [24], the vicinity of the soliton may be sketched as

$$\underset{\sigma_{12}}{\uparrow_1\downarrow_2} \quad \uparrow_3 \quad \underset{\sigma_{45}}{\downarrow_4\uparrow_5},$$

where the arrows denote "up" and "down" spins and $\sigma = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ is the spin-singlet pair state. The soliton is represented by the unpaired spin "$\uparrow_3$".

Soliton-assisted one-magnon excitation was recently proposed as the origin of the 17 cm^{-1} peak in the dimerized phase [18] and was studied independently in some theoretical detail by Els et al. for Zn-doped $CuGeO_3$ [25]. Consider the Fleury–Loudon type operator for inelastic light scattering based on the exchange scattering mechanism [26,27]

$$\mathscr{H}_R = \sum_i (1 + \gamma(-1)^i)\mathbf{S}_i\cdot\mathbf{S}_{i+1}, \qquad (1)$$

where $\mathbf{S}_i$ denotes the spin-1/2 operator at site i, and γ is an empirical parameter to take into account the alternation of the exchange coupling along the spin chains. Application of $\mathbf{S}_2\cdot\mathbf{S}_3$ to a spin singlet adjacent to the unpaired spin gives

$$\mathbf{S}_2\cdot\mathbf{S}_3|\sigma\uparrow\rangle = \tfrac{1}{4}[-|\tau_0\uparrow\rangle + \sqrt{2}|\tau_{+1}\downarrow\rangle], \qquad (2)$$

where $\tau_{0,\pm1}$ denote triplet states with S^z spin components of 0, ± 1, respectively. Eq. (2) thus describes the excitation of a single magnon. Interaction with the adjacent isolated spin, i.e. the soliton, hence allows a one-magnon excitation without changing the total spin $S = 1/2$ and keeping $S^z = 1/2$ as in the ground state such that no magnetic field effect occurs. Note that the $S^z = +1$ of the magnon in the second term is compensated for by flipping the spin of the soliton. The weak peak observed at 17 cm^{-1} in the dimerized phase of $CuGeO_3$ is therefore assigned to a soliton-assisted one-magnon excitation. It fully accounts for the observed properties, in particular the Si-doping, temperature, and (lack of) magnetic field dependence.

The magnetic field induced transition from the dimerized to the incommensurate phase of $CuGeO_3$ is characterized by the appearance of an intense Raman mode at ~17 cm^{-1}. This is illustrated in Fig. 2(a) showing a series of Raman spectra at $T = 6$ K and magnetic fields up to 15 T. Near the critical field of 12.7 T, the spectra change drastically within a narrow range of applied field. The magnetic field dependence of the frequency of the low-energy peaks in both the dimerized and the incommensurate phase is shown in Fig. 2(b). For $T = 2$ K only a minor change of the peak position of the soliton-assisted excitation is observed for fields up to 12.2 T. The energy then drops, reaching a minimum at 12.5 T. At this point, the new peak gains in intensity and shifts towards higher energy.

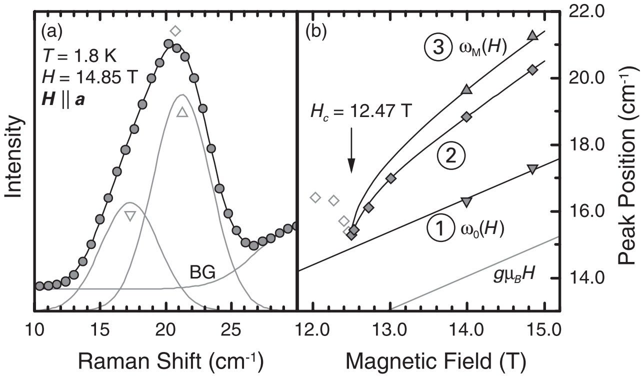

Fig. 3. (a) High-field splitting of the one-magnon peak at $B = 14.85$ T and $T = 2$ K. Circles denote the experimental data, grey lines the underlying Gaussian peaks and background (BG); the resulting fit is shown by a black line. (b) Magnetic field dependence of the low-energy magnetic excitations in the incommensurate phase. (▼) low-energy component, (▲) high-energy component, (◆) peak center. Solid lines are discussed in the text.

Above 13.0 T, the peak intensity remains constant. Apparently, the shift becomes linear at the highest fields, but it is distinctly nonlinear just above the critical field. Relating the linear shift ΔE to the magnetic field H in a Zeeman-like fashion ($\Delta E = g\mu_B \Delta H$, where μ_B is the Bohr magneton) gives $g = 3.4$ in the high-field limit. At higher temperatures, up to 10 K, a similar overall behavior was observed. The slope of the high-field shift, however, shows a pronounced temperature dependence: it decreases continuously with increasing temperature, reaching a value of $g \approx 1.8$ at $T = 10$ K. Thus, the observed effect cannot be explained by a simple Zeeman-type shift.

The crucial point for understanding the peculiar field and temperature dependence of the observed low-energy excitation is the field-dependent incommensurate lattice distortion of the high-field phase. After compiling some important theoretical and experimental results from the literature we will show for $T = 2$ K that the peak we observed above the critical field actually originates from two peaks with a small field-dependent separation. We will demonstrate that both peaks are related to spin-wave excitations.

The incommensurate phase is appropriately described by a soliton lattice as was first shown by X-ray [4,5] and nuclear magnetic resonance studies [6]. The magnetic structure is then given by an array of weakly interacting Heisenberg spin-1/2 chains with alternating exchange coupling. The degree of alternation varies from zero at the center of each soliton to some maximum value midway between adjacent solitons. For simplicity we discuss the experimental data in the framework of the limiting cases of the uniform and the uniformly alternating spin chain, respectively[†]. In either case a continuum of excited states is expected above a lower bound $\omega_l(q)$ with large spectral weight which corresponds to the classical magnon dispersion. Explicitly, we use

$$\omega_l^u(q) = \omega_{max}|\sin 2\pi q| \tag{3}$$

for the uniform case and

$$\omega_l^a(q) = \sqrt{\Delta^2 + (\omega_{max}^2 - \Delta^2)\sin^2(2\pi q)} \tag{4}$$

for the alternating case based on the XY-model. Δ denotes the excitation gap and $\omega_{max} = \pi J$ the maximum frequency of the dispersion. It should be noted that $\omega_l^a(q)$ was found to overestimate the magnon frequency at small but finite wave vectors q in the dimerized phase [19]. In the presence of an external magnetic field H an additional Zeeman energy $E_Z = g\mu_B H$ is required for the spin-wave excitation. Therefore, the field dependence of a zone-center magnon ($q = 0$) becomes

$$\omega_0(H) = \Delta + g\mu_B H, \tag{5}$$

with Δ vanishing in the uniform limit.

[†] A theoretical model for the magnetic properties of the incommensurate phase was recently published by Uhrig et al. [36].

The incommensurate lattice modulation in the high-field phase opens the possibility to observe additional excitations. Let Q_M denote the incommensurable wave vector, then magnons at $q = n \cdot Q_M$ with $n = 1,2,3,\ldots$ may be excited due to relaxed momentum conservation [28]. Excitations with $n > 1$ are expected only if the lattice modulation contains higher harmonic terms. For $CuGeO_3$ it was shown that the lattice distortion rapidly approaches a nearly sinusoidal one above the critical field [18] so that one should not expect higher-*n* modes to be observable. The field dependence of the incommensurability vector $Q_M(H)$ above the critical field H_c was studied theoretically based on the *XY* model [29]

$$Q_M(H) = \theta\left(\ln\frac{8H_c}{H - H_c}\right)^{-1}. \tag{6}$$

It is in reasonable agreement with the X-ray data for $CuGeO_3$ of Kiryukhin et al. [5] with $\theta \approx 0.058$ r.l.u. In the uniform limit, one can then calculate the field dependence of a one-magnon excitation at $q = Q_M(H)$

$$\omega_M(H) = g\mu_B H + \pi J|\sin 2\pi Q_M(H)|. \tag{7}$$

A *g*-value of $g_a = 2.15 \pm 0.01$ for $\mathbf{H} \| \mathbf{a}$ was determined for both the dimerized and incommensurate phase in ESR studies [30,31]. The exchange constant J is known from numerous experiments yielding values of 4.9–5.3 meV [13,19,32,33]. The average value of $J = 5.1$ meV is found to be consistent with the energy of the two-magnon peak observed by Raman spectroscopy (at 228 $cm^{-1} \approx 2.75J$, a relation observed before for 2D antiferromagnets [34,35]) and will therefore be used here.

Fig. 3 displays a Raman spectrum taken at 15 T and 2 K. The low-energy mode is distinctly asymmetric and can be represented by two Gaussian peaks, separated by only 3.9 ± 0.1 cm^{-1}. A smaller splitting of 2.2 ± 0.1 cm^{-1} could still be determined at 14 T. Because of the half width (FWHM) of ~ 5 cm^{-1} such a double-peak structure cannot be resolved for lower fields with correspondingly smaller separations. Fig. 3(b) shows the field dependence of the two components at high fields (up and down triangles) as well as the center frequency of the asymmetric peak (diamonds). The latter corresponds to the data shown in Fig. 2(b).

The low-energy component can be attributed to a zone-center excitation according to Eq. (5) with a gap $\Delta = 2.3 \pm 0.2$ cm^{-1}. Curve (1) in Fig. 3(b) marks the field dependence where the slope is given by the *g*-value from the above-mentioned ESR experiments. The Zeeman term $g\mu_B H$ is shown for comparison. The higher-energy component cannot be attributed to an excitation at $q = Q_M(H)$ as outlined above, but to a magnon at $q = 1/2Q_M(H)$ according to Eq. (7). Without any free parameters, the field-dependent energy of this second component can be computed as is shown by curve (3). From the positions of the two peaks which can be calculated for any field $H > H_c$, we can now evaluate the expected field dependence of the center position of the asymmetric peak observed experimentally. The result is shown as curve (2) in Fig. 3(b). It is in good agreement with the experiment, also near the critical field, where the individual components could not be resolved. Especially, it reproduces very well the nonlinear behavior just above the critical field. We stress that besides the assignment of the higher-energy component to an excitation at $q = 1/2Q_M(H)$ no free parameters were used for the calculation of curve (2).

Qualitatively, the observations at higher temperatures can be understood on the basis of the second-order phase transition between incommensurate and uniform phase which occurs near 10 K. Magnon-like excitations are not possible in the uniform phase because of the lack of long-range magnetic order. In view of the second-order nature of the phase transition one may expect the magnon frequency to decrease continuously with increasing temperature, as in the case of the low-field dimerized-uniform transition. This notion is in agreement with the experimental data. A quantitative analysis of the finite-temperature effects, however, is beyond the scope of the work, while further study of this topic would certainly be of interest.

In conclusion, a soliton-assisted one-magnon excitation is proposed as the origin of the Raman peak near 17 cm^{-1} in the dimerized phase of $CuGeO_3$. The model explains the coincidence with the temperature dependence of the spin gap, the lack of magnetic field dependence, and the observed Raman selection rules. A detailed magnetic field and temperature-dependent analysis of a newly observed low-energy Raman peak in the incommensurate phase was given.

It was assigned to magnetic excitations at the Brillouin zone center and at a wave vector related to the incommensurability vector of the soliton lattice. The model is in good quantitative agreement with the experimental data and associates the peculiar nonlinear field dependence with the field dependence of the soliton lattice. It remains to be explained why this excitation appears to occur at $q = 1/2Q_M$ instead of $q = Q_M$. A finite excitation gap $\Delta = 2.3 \pm 0.2\ \mathrm{cm}^{-1}$ at the Brillouin zone center was determined for the incommensurate phase.

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