High-Energy Magnetic Excitation in $CuGeO_3$

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The high-energy magnetic excitation continuum in $CuGeO_3$ has been studied by inelastic neutron scattering. At low temperatures, the upper part of the continuum expected for an ideal Heisenberg chain is replaced by a well-defined magnonlike excitation. This branch exhibits a sinusoidal dispersion with frequencies below the positions where the upper boundary of the continuum would be expected. In contrast to the triplet excitation, this high-energy magnonlike branch is not affected by the spin-Peierls transition, but disappears near 150 K. The high-energy feature seems to be a signature of a strong frustration induced by spin phonon coupling.

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The magnetic excitation spectrum of ideal Heisenberg spin one-half antiferromagnetic chains (HAFC) has been studied by a combination of exact Bethe-Ansatz and finite chain calculations [1]. From these studies, a continuum of excitations is expected between upper and lower energy boundaries [2] of the form $\epsilon_l(q) = \frac{\pi}{2}J|\sin(q2\pi)|$, $\epsilon_u(q) = \pi J|\sin(q\pi)|$, where q is the wave-vector transfer in reciprocal lattice units (rlu). The structure factor for inelastic neutron scattering $S(q,\omega)$ exhibits a divergence at the lower boundary and levels off with increasing energy as $S(q,\omega) = A[\omega^2 - \epsilon_l^2(q)]^{-1/2}$ for $\epsilon_l(q) < \omega < \epsilon_u(q)$ [1]. Recent numerical calculations for finite chains by Karbach *et al.* [3] have qualitatively confirmed this result, and are themselves in good agreement with experiments on the $KCuF_3$ [4].

Magnetic excitation spectra of the inorganic spin-Peierls (SP) compound $CuGeO_3$ (CGO) [5] were analyzed with an emphasis on the triplet excitation below T_{SP} [6–8]. In spite of the fact that rather different approaches seem to describe the dispersion reasonably well [6,7,9,10], it is generally assumed that the triplet dispersion is flattened due to the frustrating next nearest neighbor (nnn) interaction. Arai *et al.* observed the entire continuum by inelastic neutron scattering (INS) using the time-of-flight technique [11] and showed that the observed structure factor is inconsistent with the HAFC theories. In this paper we present further INS results with improved statistics and q resolution. We find that, at low temperature, there is a well-defined excitation near the expected upper boundary of the continuum which remains unaffected by the SP transition.

The single crystal of about 600 mm^3 volume (used for our previous experiments [12]) was studied in the [101]/[010] and [010]/[001] scattering geometries. The experiments were performed on the 1 T and 2 T thermal triple axis spectrometers of the Laboratoire Léon Brillouin using a Cu-(111) monochromator and a PG-(002) analyzer with constant final energies of 3.55 or 7.37 THz, respectively. The high resolution enabled us to distinguish between the magnetic and phonon contributions up to high Q values, where phonon cross section is dominant. (We use Q for the neutron scattering vector and q for the propagation vector in the first Brillouin zone: $Q = \tau + q$ with τ a reciprocal lattice vector.)

The first indication of an anomalous magnetic excitation near the top of the two-spinon continuum was obtained in scans aiming at the dimerization phonon mode at 6.7 THz [12]. Figure 1a compares the constant-Q scans obtained at 1.5 and 160 K at (0.5 4 0.5), showing that additional intensity appears at low temperature with a width slightly larger than the experimental resolution [13]. Apart from the fact that the absolute intensity depends on the Q value, similar results were obtained for many other Brillouin zones. For comparison, Fig. 1b shows a low temperature scan at $Q = (1.5\ 1\ 1.5)$ in which the phonons, and, in particular, the dimerization mode, contribute to a similar degree to that seen in the $Q = (0.5\ 4\ 0.5)$ scan. A comparable feature—with regards to its intensity, position, and width—was also observed at $Q = (0\ 4\ 0.5)$, where the magnetic signal is extracted from the difference of low and high temperature scans. Around the (0 2 0) lattice point, however, the phonon contribution is reduced due to significantly smaller structure factors and the lower absolute Q value, which also gives rise to an increase of the magnetic intensity through the form factor. Unfortunately, kinematical conditions compelled us to use a higher final neutron energy (7.37 THz), which resulted in significantly poorer resolution and reduced incident flux. Nevertheless, the scans at $Q = (0\ 2\ 0.5)$ and at $Q = (0.5\ 2\ 0.5)$ yield essentially the same feature, thereby excluding a mainly phononic origin; see Figs. 1c and 1d.

The additional intensity can be followed along b^*, whereby no shift in position was found in contrast with the pronounced dispersion of the triplet branch in the dimerized phase [6,7]. However, at the top of the magnon branch along c^*, i.e., at $q_c = 0.25$, the theory of Uhrig predicts a flat dispersion in the b direction [10] as well, i.e.,

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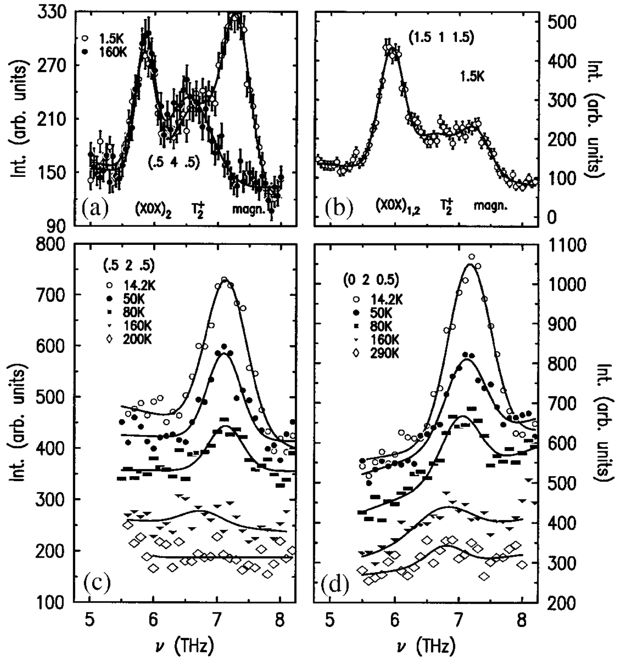

FIG. 1. Several scans through the magnetic excitation at 7.25 THz taken at different temperatures. The lines correspond to fits with one or more Gaussian peaks and a sloping background. Upper panels: (a) Comparison between constant-Q scans at (0.5 4 0.5) at 1.5 K (open circles) and 160 K (closed circles); $E_f = 3.55$ THz. (b) Low temperature scan at (1.5 1 1.5), where the dimerization phonon mode contributes to a similar degree as at (0.5 4 0.5); $E_f = 3.55$ THz. $(X0X)_1$ and $(X0X)_{1,2}$ designate the positions of phonon modes, T_2^+ that of the dimerization mode, and magn., the magnetic intensity. Lower Panels: Constant-Q scan through (0 2 0.5) (d) and (0.5 2 0.5) (c) at different temperatures $E_f = 7.37$ THz; the 14.2 K scans correspond to the y-axis scale, which were shifted successively by 50 counts.

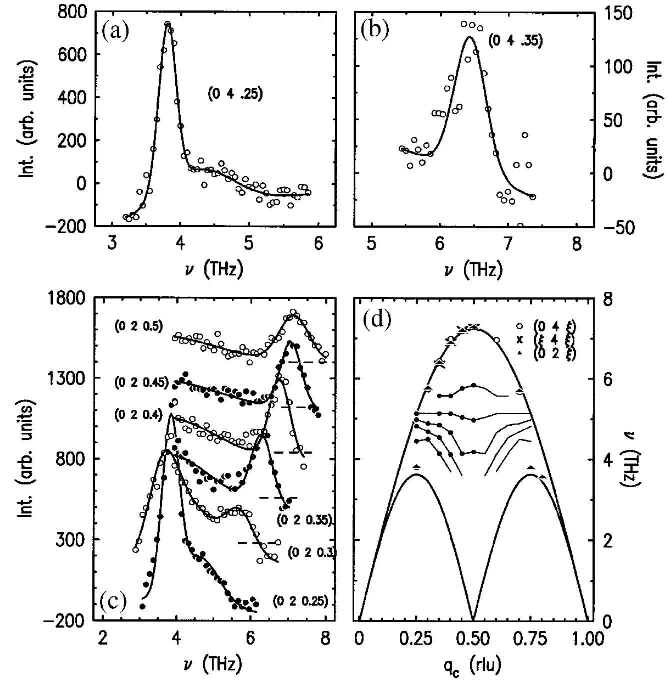

FIG. 2. [(a)–(c)] Intensity differences of the constant-Q scans at (0 4 q_c) at 12 and 120 K for $q_c = 0.25$, 0.35, and at (0 2 q_c) at 10 and 120 K. The lines correspond to fits with Gaussians. In (c) the y-axis scale was shifted for the successive scans; the zero line is indicated by the broken line. (d) Positions of the sharp high-energy excitations at low temperatures as a function of ξ corresponding to (ξ 0 ξ) and (0 0 ξ). The thick solid lines represent $7.25\sin(\xi\pi)$ and $0.5 \times 7.25|\sin(2\pi\xi)|$. The small closed circles and the thin lines represent the lines of equal continuum scattering as obtained from the difference scans shown in panel (c).

along (0 q_b 0.25), which was experimentally confirmed [14,15]. Also, the additional intensity at 7.25 THz is found at a maximum of the spectrum, which might, by analogy, explain the absence of dispersion along b^*. The scattering intensity of the high-energy excitation was found to depend on Q_b and can be well described by the product of the square of the Cu^{2+} magnetic form factor [16] and the sinusoidal relation $\sqrt{0.3 + 0.7\cos^2[Q_b(\pi/2)]}$ in which Q_b is expressed in rlu. The increased intensity at even Q_b values indicates an in-phase coupling of neighboring chains (along b). The orientation of Q with respect to the chains does not have an essential influence, since at $Q = (0.5\ 5\ 0.5)$ and at $Q = (1.5\ 1\ 1.5)$ comparable excitation intensities have been observed. This finding points to a mainly isotropic character of the high-energy excitation.

A pronounced dispersion of the high-energy mode is observed along c^*, as can be seen in the intensity differences of scans performed at $T = 12\ K$ and $T = 120$ K; see Figs. 2b and 2c. At $Q = (0\ 4\ 0.25)$ we find the triplet excitation near 3.8 THz, with a broad shoulder which has to be attributed to the continuum. An isolated mode near the upper boundary of the continuum would result in a rather sharp peak in these scans due to an efficient focusing. A similar situation was observed in scans collected at (0 2 0.75) and (0 2 0.25). However, slightly away from $q_c = 0.25$, a sharp peak appears in the temperature differences, comparable to that found at $q_c = 0.5$. The series of scans across (0 2 q_c) shown in Fig. 2c allows one to follow this well-defined excitation, which becomes sharper still at intermediate q_c values due to focusing effects [17]. The energies of the high-energy modes are given in Fig. 2d as a function of q_c. The branch exhibits a sinusoidal dispersion similar to $\epsilon_u(q)$, as indicated by the solid line. However, the scaling factor of 7.25 THz is much smaller than the $\pi J = 10.7$ THz describing the upper continuum boundary of an ideal chain with $J \sim 160$ K. One may also note that the high-energy excitation energies do not correspond to twice those of the triplet branch at half q_c, as can be deduced from the line $0.5 \times 7.25|\sin(2\pi q)|$ added in Fig. 2d.

At the lowest temperatures, we found almost no signature of a continuum of magnetic excitations below or above the high-energy excitation. The scans performed with higher resolution allowed us to estimate the value of the scattering function in the continuum to be lower than 15% of that of the high-energy mode. We mapped the magnetic scattering contributions at (0 2 q_c), as shown in Fig. 2c, by subtracting the 120 K intensities from those at low temperature. The constant intensity lines obtained from these curves were transferred to the map in Fig. 2d, corresponding to 50 (highest line), 100, 150, 200, 250, and 300 counts. These intensities should be compared with those of the sharp excitations, which amount to ~1200 for the triplet excitation maximum and to ~300 counts for the high-energy excitation maximum. We note that the ratios between the intensities of the well-defined modes and the continuum are higher in the data shown in Fig. 2d than discussed above, because these data were obtained with lower resolution. Taking, furthermore, the temperature dependence of the background into account, we estimate that the 50 counts line corresponds to roughly 15% of the high-energy excitation structure factor. The intensity map demonstrates that, immediately below the sharp excitation and down to rather low energies, there is relatively little intensity in the continuum at $q_c = 0.5$. *It therefore appears that the structure factor of the magnetic continuum expected for an ideal HAFC is largely transferred into the high-energy magnonlike branch in the case of CGO.*

The temperature dependence of the high-energy mode intensity is shown in Fig. 3, from which it can be seen that this feature seems to disappear around 150 K. It is of interest to note that anomalous changes in structural parameters [18] and dimerization-related phonon frequencies [12] have been observed in the same temperature region. In contrast to the low-energy scattering [7], the high-energy excitation does not follow a $\frac{1}{T^2}$ relation. Concerning the position and the width of the excitation, no variation with temperature was detected below 100 K, although the continuum gains some weight at the expense of the sharp excitation at intermediate temperatures. Above 100 K, the weakness of the excitation prevents reliable determination of line shape parameters. However, even at 160 K, there is evidence to suggest that some magnetic intensity persists beyond the energy of the well-defined excitation observed at low temperature.

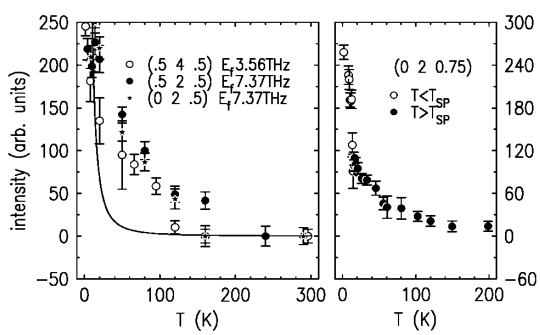

FIG. 3. Left: Temperature dependence of the peak height at 7.25 THz {corrected for the Bose factor: $n(\nu) = [\exp(h\nu/kT) - 1]^{-1}$ with ν the frequency of the excitation} observed at (0.5 4 0.5), (0.5 2 0.5), and (0 2 0.5) scaled to each other at low temperature; the solid line designates a $\frac{1}{T^2}$ relation. Right: Temperature dependence of the peak height (corrected for the Bose factor) observed at (0 2 0.75); below T_{SP}, the raw data were fitted by three Gaussian peaks corresponding to the triplet excitation (open circles), the weak continuum, and a temperature-independent phonon scattering with fixed parameters (after correction for the Bose factor). Above the transition, only two Gaussians were fitted to the data corresponding to the continuum contribution (closed circles) and to the constant phonon contribution.

The absence of any apparent influence of the SP transition on the high-energy excitation contrasts not only with the behavior of the triplet branch at its minimum energy [6–8], but also at its maximum energy, which we have studied with relaxed resolution at $Q = (0\ 2\ 0.75)$. The temperature dependence of the peak height observed at the triplet branch maximum is shown in the right panel of Fig. 3. At the SP transition, the sharp peak disappears, leaving in its place a broad signal resulting from the continuum, which decreases monotonically upon further increasing the temperature. At this q value, only the temperature dependence of the magnetic scattering above T_{SP} resembles that of the high-energy excitation.

Our observations agree qualitatively with the work of Arai *et al.* [11], who reported a ridge of scattering surrounding a valley in the continuum. However, there are several reasons why the well-defined excitation observed here has escaped detection in the previous study. First, in contrast to the experiment of Ref. [11], we had no need to average over Q_b but analyzed the even values, where the sharp feature is stronger; second, the intensity maps in Ref. [11] involve some inevitable degree of smoothing and q_c averaging, and third, the separation of phonon contributions in the earlier experiment seems to be less than perfect [19]. Finally, our study benefits from a higher statistics than the experiment performed in Ref. [11] and the more recent work reported by the same group [20]. Another important difference with Ref. [11] concerns the pronounced reduction of the scattered intensity in the continuum directly below the sharp excitation at low temperature.

The singular excitation near the top of the two-spinon continuum remains completely unexplained within the HAFC theories. We conclude that additional coupling parameters have to be introduced for an explanation.

At present it seems generally accepted that the nnn interaction, αJ, is important in CGO, resulting in pronounced frustration [21,22]. The influence of frustration on the neutron scattering function has been studied numerically by finite chain calculations by Fabricius *et al.* [23] and by Yokoyama *et al.* [24]. Using different calculation techniques, both groups find an intensity maximum near the upper boundary of the two-spinon continuum, which seems to point in the direction of our observations. The numerical studies also obtain a maximum in the structure factor at ~2.15J (note the different definitions of J) [22,25] weakly dependent of the value of α. This result agrees very well with the frequency of the sharp high-energy excitation observed in our experiment and the commonly accepted value of $J = 3.4$ THz at $\sim$160 K [21,22,25]. However, both groups predict rather strong scattering from the continuum below the maximum. Hence, the agreement with our experiment is at most qualitative. Furthermore an extremely high frustration, $\alpha \sim 0.45$, was essential to obtain these results, which appears to be unrealistic in the case of CGO for which $\alpha = 0.35$ is frequently assumed [21,22,25]. Already the latter, smaller, α value yields a magnetic gap without dimerization [21] and does not agree very well with the antiferromagnetically ordered structure observed for minor substitutions [8,26].

We now turn our attention to the influence of the spin phonon coupling. Wellein *et al.* have recently shown that the coupling to a phonon branch is essential for the triplet branch dispersion [27]. Therefore this dynamic magnetoelastic coupling might be relevant for the high-energy part of the spectrum as well. The phonons involved in the magnetoelastic coupling and the SP transition possess energies of the order of $(1-2)J$ [12], i.e., there is no reason for an adiabatic approximation. On the contrary, the phonons should be considered as fast when compared to the magnetic excitations [27,28]. Within a nonadiabatic treatment of the spin phonon coupling, Uhrig has demonstrated the existence of an effective frustration induced by phonons which is temperature dependent [28]. Similar magnetoelastically induced coupling parameters might be responsible for the sharp high-energy excitation.

Following Ref. [28] we extend the original Hamiltonian of the HAFC, H_0, by the spin phonon coupling terms $H = H_0 + V$ with

$$V = \sum_q \frac{1}{\omega(q)} \sum_k g(q,k) S_k S_{-k-q} \sum_{k'} g(-q,k') S_{k'} S_{k'+q}\,, \tag{1}$$

where $\frac{1}{\omega(q)}$ denotes the phonon frequency and $g(q,k)$ denotes the modulation of the magnetic interaction through the phonon. The spin phonon coupling induces additional four-spin interactions which are, however, difficult to treat. Furthermore, we have to neglect the interchain coupling, though the experiment has demonstrated its relevance.

In order to get a qualitative picture one may use the RPA approximation and the Green-function formalism, which will be described in detail elsewhere [29]. The spin Green function G of the coupled system is related to that of the HAFC, G_0, by $G = \frac{G_0}{1-G_0V}$. Therefore, the imaginary part describing the neutron scattering function strongly increases when $(1 - \mathrm{Re}G_0V)$ is close to zero with $\mathrm{Im}G_0$ small, which corresponds to a resonance mode. This condition is fulfilled close to both boundaries of the two-spinon continuum of the HAFC [1,3] outside the continuum, in particular, near the upper boundary where the sharp high-energy excitation is observed. The fact that for the high-energy part of the spectrum magnetic excitations and the strongly coupled phonon modes possess similar energies should favor the effect.

In conclusion we suggest that the well-defined excitation near the frequencies where the upper boundary of the two-spinon continuum is expected may be explained by frustrationlike four-spin interactions induced by a dynamic magnetoelastic coupling.

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