Excitations of the field-induced soliton lattice in CuGeO$_3$

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Here we report the first inelastic neutron scattering study of the magnetic excitations in the incommensurate high-field phase of a spin-Peierls material. The results on CuGeO$_3$ provide direct evidence for a finite excitation gap, two sharp magnetic excitation branches and a very low-lying excitation which is identified as a phason mode, the Goldstone mode of the incommensurate soliton lattice.

A one-dimensional (1D) spin $\frac{1}{2}$ Heisenberg antiferromagnet is unstable with respect to dimerization as well as long-range antiferromagnetic order. Coupled to a three-dimensional (3D) phonon field, it can undergo a second-order phase transition at a finite temperature into a dimerized (spin-Peierls) ground state with total spin $S_{\text{tot}} = \sum_i S_i = 0$ (D-phase). The dimerization is supported by antiferromagnetic next-nearest-neighbor exchange in the 1D chain direction. Antiferromagnetic (AF) interchain couplings prefer a Néel-type ground state and compete with dimerization.

In the D-phase of a spin-Peierls material, the lowest magnetic excitation is an isolated triplet branch ($S_{\text{tot}} = 1$). This excitation is a bound pair of domain walls with respect to the dimer order parameter. The two domain walls, or solitons, are created by breaking and delocalizing one dimer bond. The binding energy depends on the magnetic and elastic interchain interactions. The energy of the triplet is finite over the entire Brillouin zone and should have an energy $g\mu_B H_{\delta}$. A longitudinal branch \( \Delta_0 \) should also be present with minima at $k = 0$ and $k = \pi$, where $m$ is the magnetization per spin in units of $\mu_B$. At $k = \frac{\pi}{2}$ this branch should have an energy $g\mu_B H_{\delta}$. The precise value and field dependences of the modes \( \Delta_1 \) and \( \Delta_0 \) depend on the details of the assumptions used in the models $\mathbb{1}$ $\mathbb{2}$ $\mathbb{3}$.

CuGeO$_3$ is the first spin-Peierls compound where large single crystals are available, thus allowing the complete phonon and magnetic excitation spectra to be measured using neutron scattering techniques. The IC phase is also accessible, since magnetic fields up to 14.5 T have become available for neutron experiments, well in excess of the critical field in CuGeO$_3$ of $\mu_0 H_c \approx 12.5$ T. Our recent neutron scattering study of the magnetic soliton lattice in the IC-phase $\mathbb{1}$ reveals a static magnetic modulation with the same period as the distortive modulation, and in particular the superlattice Bragg peaks at $(1,0,0)$ were found to be almost entirely magnetic in origin. Outside the critical field region, the magnetic soliton width, and the amplitudes of the staggered and uniform magnetic modulation are in reasonable agreement with the predictions of field theory.

In this letter we report on the magnetic excitation spectrum in the IC phase, measured both close to the superlattice peak $(\frac{1}{2},1,\frac{1}{2} \pm \delta k_{sp})$, and also at the AF zone center $(0,\frac{1}{2},1)$, where the dispersion of the magnetic excitations in the D-phase has its minimum. The experiments were performed at the cold triple axis spectrometer FLEX at BENSC, Berlin, using the vertical cryomagnet VM-1. Single crystals of CuGeO$_3$ of 0.34 cm$^3$ and 0.49 cm$^3$ were aligned in the $(0,k,\ell)$ and $(h,2h,\ell)$ scat-
tering planes, respectively. The collimation was guide-60°-60°-60° with either \( k_f = 1.3\) Å fixed and a nitrogencooled Be-filter in \( k_i \), or \( k_f = 1.54\) Å and the Be-filter in \( k_f \). The critical fields at (0, 1, ½) and (½, 1, ½) differ (12.58 T and 12.31 T) because of the different field directions and hence \( g \)-factors (2.152 and 2.199) in the respective scattering geometry.

![Figure 1](image1)

**FIG. 1.** Field dependence of the triplet excitation in CuGeO₃ at (0, 1, ½), 2 K. Solid lines: triplet splitting \( g \mu_B H \delta \mu \), \( \mu = 2.152 \). The critical field is \( \mu = 12.58 \) T. The inset shows the high-field region in more detail.

Figure 1 shows the magnetic field dependence of the excitations at the AF zone center (0, 1, ½). With increasing field, the lowest triplet branch decreases to about 0.4 meV but never becomes completely soft. At the critical field, two new sharp excitations appear at ~1 meV and ~0.5 meV. The 1 meV mode shows barely any field dependence between 12.5 T and 14.5 T, while the energy of the lower mode increases towards the higher mode.

The excitations at (½, 1, ½), close to the magnetic Bragg peaks at (½, 1, ½ ± \( \delta k_{sp} \)), display the same field dependence as those at (0, 1, ½), apart from an overall shift towards higher energies (1.2 meV and 1.6 meV) which is entirely accounted for by the ferromagnetic interchain interaction along \( \alpha^* \).

In Fig. 2 we show high-resolution scans of the low-energy region at a wave vector of (½, 1, ½) for selected magnetic fields. At 12 T, the widths of the middle and the lowest triplet excitation are resolution limited. Both broaden significantly at the critical field (about 12.3 T) and then disappear. In a small field region, the new sharp IC-phase excitations at 1.2 meV and 1.6 meV coexist with the broadened D-phase modes (see scan at 12.5 T), confirming the first-order character of the transition which has also been observed with other methods. No evidence was found for a third excitation at an energy of \( g \mu_B H \delta \mu \) at any of the fields investigated.

The spectral weight of the two new modes in the IC-phase is concentrated in a very small region extending from the commensurate position \( \ell = ½ \) to the incommensurate one at \( \ell = ½ ± \delta k_{sp} \). The upper part of Fig. 3 shows the dispersion of the lowest two excitations at (½, 1, ½) along the chain direction \( \alpha^* \), at \( T = 2 \) K and \( B = 14.5 \) T, where \( \delta k_{sp} = 0.015 \). The dispersion (solid lines) appears significantly flatter than the dispersion calculated from the zero field spin-wave velocity (dashed lines). Neither at (0, 1, ½) nor at (½, 1, ½) do the dispersions of the two sharp modes exhibit minima at the IC positions \( \ell = ½ ± \delta k_{sp} \).

![Figure 2](image2)

**FIG. 2.** Energy scans at (½, 1, ½), \( T = 2 \) K. Solid lines: fits to Lorentzian-type profiles including the Bose factor. The critical field is \( \mu = 12.31 \) T.

A search was also made for excitations emanating from the magnetic IC Bragg peaks at (½, 1, ½ ± \( \delta k_{sp} \)). This revealed a mode at ~0.29 meV (Fig. 4), at \( T = 2 \) K and \( B = 14.5 \) T. The energy of this mode (at the respective IC wave vector) changes only little between 13 T (\( \delta k_{sp} = 0.011 \)) and 14.5 T (\( \delta k_{sp} = 0.015 \)). The dispersion of this mode was studied at \( B = 14.5 \) T and is plotted in the bottom part of Fig. 3. Its spectral weight is concentrated at the IC wave vector (½, 1, ½ ± \( \delta k_{sp} \)), the minimum of its dispersion.

In interpreting the data the first thing to establish is whether the three modes shown in Fig. 3 are magnetic or nuclear in origin. It is known from our earlier study that the satellites at (½, 1, ½ ± \( \delta k_{sp} \)) are predominantly magnetic (by a factor of ~40) and it follows that the low-lying mode emanating from the satellites must also have a predominantly magnetic character. For the higher-lying modes it was observed that their intensity decreased at equivalent \( k \) but larger total wave vector transfer. They too can therefore be ascribed to be mainly magnetic in origin. It should be noted, however, that a
Calculations of the excitations in the IC-phase are reported for three cases, with dimerization parameters \( \epsilon = \frac{J_{\text{nn}} - J_{\text{nnn}}}{2J_{\text{nn}}} = 0.014 \) \([4]\), \( \epsilon = 0.14 \) \([4]\), and \( \epsilon = 0.4 \) \([2]\). Poilblanc et al. \([8]\) and Schönfeld et al. \([8]\) also included frustrating next-nearest-neighbor intrachain exchange \( \alpha = \frac{J_{\text{nnn}}}{2J_{\text{nn}} + J_{\text{nnn}}} = 0.24 \) and \( \alpha = 0.36 \), while in the calculations of Yu et al. \([2]\) only nearest-neighbor intrachain exchange was considered. Irrespective of this large spread of the parameters \( \epsilon \) and \( \alpha \) the spectral weight is concentrated at the commensurate position \( \ell = \frac{1}{2} \) \([4]\), where \( \Delta_{\pm} \) have minimum excitation energy \([1]\). This agrees with the observed upper two modes at 1.3 meV and 1.7 meV (14.5 T, Fig.3), which we therefore identify with the modes \( \Delta_{\pm} \). The longitudinal mode \( \Delta_0 \) should have its minimum at \( q_c = \frac{1}{2} \pm \delta k_{sp} \) with \( \Delta_{\min} \gtrsim \frac{1}{2}(\Delta_{\min}^{\text{nn}} + \Delta_{\min}^{\text{nnn}}) \) \([2]\) and \( g\mu_B H \) at \( q_c = \frac{1}{2} \) \([1]\). Therefore the 0.29 meV excitation cannot be identified with \( \Delta_0 \). A weak longitudinal contribution at higher energies could be hidden by the transverse excitations. However, the weakness or absence of the longitudinal mode is probably related to the significant interchain interaction in CuGeO_3. Calculations \([8]\) which imply significant spectral weight of the longitudinal mode do not include interchain interaction, and it is known that longitudinal modes usually become stronger with increasing one dimensionality of the exchange \([8][10]\).

While the field dependences of the modes \( \Delta_{\pm} \) could in principle be used to place further constraints on the values of the coupling parameters, this turns out to be difficult in practice. This is mainly due to two reasons, to the fact that the values of \( \epsilon \) used in the calculations \([4]\) lead to gaps much larger than reported here, and to the fact that the magnetization range studied starts at larger values than the maximum magnetization \( m = 0.015 \mu_B \) in our experiment. It is, however, perhaps worth noting that the calculation with a finite and large value of \( \alpha \) \([4]\) predicts that \( \Delta_+ \) should increase with increasing field, while \( \Delta_- \) should be field independent, in qualitative agreement with the data shown in Fig. 1. In this sense our data are consistent with the large value of \( \alpha \) needed to explain various experimental facts \([4][14]\), and with the notion that the spin-Peierls transition in CuGeO_3 is driven by hard phonons \([13][17]\).

We now address the origin of the observed excitation at 0.29 meV. Its field dependence is too small for an optic mode arising from a folding back of the Brillouin zone. Such an optic mode should shift with \( \delta k_{sp} \) by about 0.1 meV from 13 T to 14.5 T. A fit to a Lorentzian line-shape including the Bose factor for \( T = 2 \) K yields the finite energies shown in Fig. 3. The same gap energy (2.3±0.2 cm\(^{-1}\) ≈ 0.29 meV) was observed in a Raman experiment \([13]\), which mainly probes the structural excitations, pointing to a magneto-structural origin for this excitation. We attribute the mode at 0.29 meV to phase oscillations of the soliton lattice, so-called phasons. The IC long-range order in the high-field phase breaks the quasi-continuous translation symmetry of the soliton lattice with respect to simultaneous shifts of the soliton centers along the chain axis. The Goldstone modes corresponding to this symmetry breaking are phase oscillations of the magnetic and distortive soliton structure. The corresponding eigenvectors carry magnetic and clas-
tic amplitudes. Their dispersion close to the IC superlattice Bragg peak is expected to be given by the spin-wave velocities of the dimerized phase, except close to the critical field \[20\]. Indeed the experimentally observed dispersion along \(\ell\) is of the same order of magnitude as that of the transverse magnetic excitations (Fig. 3), and is flatter by a factor of 3 than the zero-field spin-wave velocity.

If the mode at 0.29 meV is indeed a phason, it remains to be explained why it has a gap. For a spin-Peierls system with soft phonons, a first-order transition into the high-field phase could proceed via a series of lock-in transitions, which implies a finite phason gap \[20\] \[21\]. No soft phonons have been found in CuGeO\(_3\), and a number of other possible mechanisms need to be explored, including: impurities, discreteness of the lattice, and \(k\)-dependent spin-phonon coupling. A pinning to impurities would create a disordered soliton lattice, in contradiction to our earlier structural study \[22\]. The discreteness of the lattice leads to a phason pinning energy of the order 0.003 meV \[20\], which is much too small. However, this estimate neglects interchain couplings, and does not into account the non-sinusoidal magnetic modulation \[22\], both of which may enhance the phason gap in CuGeO\(_3\). In the absence of soft-phonons, lock-in phenomena in CuGeO\(_3\) could be produced by a \(k\)-dependent spin-phonon coupling. Schönfeld et al. \[22\] introduce a \(k\)-dependent effective elastic constant \(K(k) = \sum k \Omega(k)/g(k)\), where \(\Omega(k)\) are the dimerization phonons and \(g(k)\) the respective coupling constants. The relevant phonons in CuGeO\(_3\) do not display a softening in the dispersion at the commensurate wave vector \(k_{\text{sp}}\) \[22\], but the spin-phonon coupling increases towards \(k_{\text{sp}}\) \(K(k_{\text{sp}}) \approx 4K(0)\) \[23\]. This preference for a commensurate structure enhances the influence of the discreteness of the lattice, and may lead to a finite phason energy and a commensurate wave vector, instead of gapless phasons and a truly IC modulation.

The hysteresis observed in ESR experiments in the whole IC-phase \[24\] supports the picture of a lock-in of the soliton centers to the discrete lattice. Nevertheless, in the past, several experimental results were taken as evidence for gapless phasons: i) an increase of the \(T^3\)-contribution of the specific heat capacity in the IC-phase \[22\]; ii) the absence of discrete lines in the NMR-lineshape; iii) the reduced ratio \(m_s/m_u\) of the staggered and uniform magnetic modulation amplitude \((m_s, m_u)\) derived from NMR experiments. At closer inspection i) could be explained by an altered elastic constant in the IC-phase rather than by gapless phasons. Phasons with a dispersion similar to magnons yield \(T^\alpha\)-contributions with \(\alpha' = 1\) or \(2\) corresponding to their 1D or at least 2D density of states. ii) The NMR lineshape could equally well be explained by an unresolved assembly of the expected \(\sim 150\) (discrete) lines within 0.5 T and hence is still consistent with the presence of lock-in phenomena. iii) Zero-point fluctuations of gapless phasons should lead to the same reduced \(m_s/m_u\) in a neutron experiment where no such reduction was observed. The neutron result agrees within 20\% with field theory where phasons are neglected. This shows that zero-point phason oscillations are suppressed and hence indicates independently a finite energy gap of the phasons.

In summary, we have observed the predicted transverse magnetic excitations \(\Delta_\pm\) in the IC phase of a spin-Peierls material which correspond to the creation or destruction of a domain-wall pair. The longitudinal magnetic excitation \(\Delta_0\) was not found, probably due to the 3D interactions. The phason mode of the IC modulated structure has also been observed, and is gapped with a maximum spectral weight at the position of the IC satellites, \(\left(\frac{1}{2}, \frac{1}{2}, \pm \delta_{\text{sp}}\right)\). We argue that the finite energy of the phason mode is consistent with all of the experimental data available to date. We hope that our data will stimulate and guide the development of a microscopic model of CuGeO\(_3\) which will ultimately provide a consistent description over the entire temperature-field phase diagram of this unconventional spin-Peierls system.

We thank G. Uhrig, R.A. Cowley, W.J.L. Buyers, and K. Knorr for helpful discussions, and TMR and BMBF for funding.

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