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Dynamics in the dimerized and the high-field incommensurate phase of $CuGeO_3$

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Temperature ($2.3<T<40$ K) and magnetic-field ($0<B<17$ T) dependent far-infrared-absorption spectroscopy on the spin-Peierls coumpound $CuGeO_3$ has revealed several interesting absorption processes in both the dimerized and high-field phase of $CuGeO_3$. These results are discussed in terms of the modulation of the $CuGeO_3$ structure. At low fields this is the well-known spin-Peierls dimerization. At high fields the data strongly suggest a field-dependent incommensurate modulation of the lattice as well as of the spin structure. [S0163-1829(96)52030-8]

The discovery of the spin-Peierls (SP) transition in $CuGeO_3$ about two years ago[1] has sparked an intense effort to characterize and understand the properties of this magnetoelastic quasi-one-dimensional $S=1/2$ Heisenberg antiferromagnet.[2–7] As a result, the magnetic chains in $CuGeO_3$ [space group *Pbmm* (Ref. 8)] are known to be made of $S=1/2$ Cu^{2+} ions running along the c axis of the crystal. The magnetic interaction can be described by the isotropic Heisenberg Hamiltonian with an intrachain exchange coupling $J=J_c\approx 120$ K. In the dimerized phase [space group *Bbcm* (Ref. 9)] small interchain couplings $J_b\approx 0.1J_c$ and $J_a\approx -0.01J_c$ have been found.[3].

As in most SP compounds,[10] the (B,T)-phase diagram of $CuGeO_3$ exhibits three phases.[2] At high temperatures the crystal is in the uniform (U) phase. In magnetic fields $B<13$ T $CuGeO_3$ undergoes a second-order phase transition (the SP transition) to a nonmagnetic dimerized (D) phase around 14 K. For fields $B>13$ T a second-order phase transition to a magnetic phase occurs at about 9 K.

Recently x-ray diffraction experiments have shown that in the high-field phase the lattice is incommensurately modulated.[6] If this is indeed the case, one expects a definite influence of the field-dependent modulation on the lattice and spin dynamics in $CuGeO_3$. The present paper, therefore, is concerned with the dynamics in the low-temperature dimerized and incommensurate (IC) phases of $CuGeO_3$, using temperature ($2.3<T<40$ K) and field- ($0<B<17$ T) dependent far-infrared-absorption (FIR) spectroscopy. Several absorption features have been observed in the D and IC phases which are assigned to phonon and spin resonances activated by the modulation. The results for the IC phase are found to be in good agreement with a field-dependent incommensurate modulation of the lattice as well as of the magnetic structure.

Single crystals used in this study, grown by a floating zone technique,[11] have been cleaved along the (100) planes. The obtained platelets (thickness $d=0.6$ mm) have been mounted in a variable temperature transmission insert. The magnetic field has been provided by a superconducting coil ($B<17$ T). Transmission spectra have been recorded in a Faraday geometry using a Bruker ifs-113v spectrometer (0.1 or 0.5 cm^{-1} resolution) equipped with a composite Ge bolometer as detector.

A convenient and sensitive method to study the FIR absorption as a function of temperature or magnetic field is to compare the transmission Tr of a sample at two different temperatures or fields by considering the absorbance difference defined by $\Delta\alpha=-\log_{10}(Tr_1/Tr_2)/d$.

Figure 1 shows difference spectra $\alpha(T)-\alpha(15.5\text{ K})$ at $B=0$ T for several temperatures in the D phase (upper six curves). The lower spectrum shows a difference spectrum $\alpha(15.5\text{ K})-\alpha(40\text{ K})$ between two temperatures in the U phase. Three prominent features are observed in these spectra around 10, 44.3, and 48.5 cm^{-1}, respectively.

From the transmission spectra (see inset of Fig. 1), it is clear that there is a strong absorption peak at 48.5 cm^{-1}. This peak can be assigned to a B_{2u} phonon, in agreement with a $\mathbf{k}=\mathbf{0}$ phonon observed in inelastic-neutron-scattering (INS) experiments.[12] The observation of this mode completes previous FIR experiments at higher frequencies[5] which reported on four out of the five expected B_{2u} phonons.

Above the U-D phase transition, the linewidth of the B_{2u} mode is strongly temperature dependent, leading to the asymmetric double structure around 48.5 cm^{-1} in the lower curve of Fig. 1. Once in the D phase, the linewidth becomes independent on temperature. These observations strongly suggest that the observed broadening in the U phase is due to higher order processes involving the 48.5 cm^{-1} phonon, and some low frequency-excitations in the U phase. A good candidate for these low-energy excitations are the spin excitations at $k=0$ and/or π (lattice constants are taken unity), which in the U phase are degenerate with the ground state. In the D phase these spin excitations are transferred to higher energy due to the opening of the SP gap. The structure around 48.5 cm^{-1} is found to be magnetic-field independent. The actual process responsible for the broadening is, therefore, most likely a one phonon, two spin process. For such a process one expects a new absorption peak in the D phase at higher energies (phonon plus twice the gap energy).

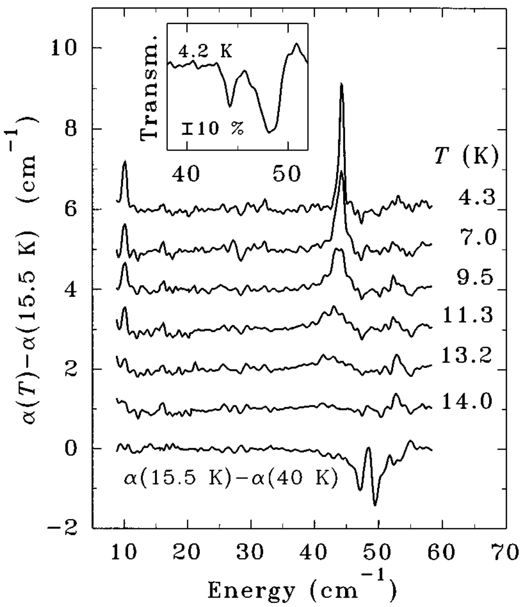

FIG. 1. Absorbance difference spectra $\alpha(T)-\alpha(15.5\ \mathrm{K})$ for $\mathrm{CuGeO_3}$ (at $B=0$ T) in the vicinity of the spin-Peierls phase transition (top 6 curves, spectra are shifted for clarity). The lower curve shows the absorbance difference $\alpha(15.5\ \mathrm{K})-\alpha(40\ \mathrm{K})$. The inset shows the transmission spectrum in the vicinity of the $B=0$ spin gap at $T=4.2$ K.

However, due to strong phonon absorption processes it is not possible to measure the transmission for this energy range. In Raman-scattering experiments similar processes have been observed, showing indeed additional structure at the phonon energy plus twice the $\mathbf{k=0}$ spin-gap energy in the D phase.[13]

The feature appearing around 44.3 $\mathrm{cm^{-1}}$ in the D phase can be assigned to the $\mathbf{k}=\mathbf{0}$ spin gap of $\mathrm{CuGeO_3}$, in agreement with previous electron paramagnetic resonance (EPR) results[4] and with the magnetic-field dependence presented below. The structure here appears somewhat asymmetric, and high-resolution experimental runs have show that in fact there is a second absorbance peak, about 0.8 $\mathrm{cm^{-1}}$ lower in energy. In contrast to the zone boundary spin gap at 16 $\mathrm{cm^{-1}}$,[3] the 44.3 $\mathrm{cm^{-1}}$ gap does not shift or broaden with increasing temperature up to 12 K. The appearent shift below 12 K observed in Fig. 1 is merely due to a change in the relative strength of the two features, the 44.3 $\mathrm{cm^{-1}}$ absorbance peak rapidly losing its intensity upon increasing temperature, whereas the 43.5 $\mathrm{cm^{-1}}$ peak is nearly temperature independent below 12 K. Above 12 K the observed structure broadens rapidly towards lower energy, and has completely vanished at 15.5 K.

Another feature at 10 $\mathrm{cm^{-1}}$ is found to be field independent and, furthermore, is observed in both the D and the IC phase. This leads us to assign this feature to a phonon mode which is activated in both the D and IC phase.

Figure 2(a) presents the field dependence of the absorbance difference $\alpha(B)-\alpha(12\ \mathrm{T})$ at 2.3 K. In the D phase one expects the $\mathbf{k}=\mathbf{0}$ spin gap (a triplet state) to split into three components. However, due to the selection rules for magnetic dipole transitions from the singlet ground state $(\Delta m_s=\pm 1)$, only the two components with $m_s=\pm 1$ are observed in the spectra. The energy positions of the observed splitting is plotted in Fig. 2(b) (closed symbols), and from this a spectroscopic splitting factor $g_a^D=2.13$ is derived. Around $B=12.6$ T the $\mathbf{k}=\mathbf{0}$ spin gap structures disappear, showing the phase transition to the IC phase. The first-order nature of this transition is evidenced by a small hysteresis and coexistence region of about 0.3 T. In the IC phase an absorbance peak appears at low energies in the spectra, with a linearly increasing energy upon increasing field. The field dependence of this mode is also plotted in Fig. 2(b) (open symbols), yielding $g_a^{\mathrm{IC}}=2.03$, a value slightly, but significantly, different from the result in the D phase. In addition to this absorption process, three other absorbance peaks are clearly observed. One mode with a field-independent energy of 44.7 $\mathrm{cm^{-1}}$ appearing only below around 15 T, and two other features with field-dependent energies ending at 39.3 and 42.4 $\mathrm{cm^{-1}}$ in the 17 T spectrum. The detailed field dependence of these modes is shown in Fig. 2(c).

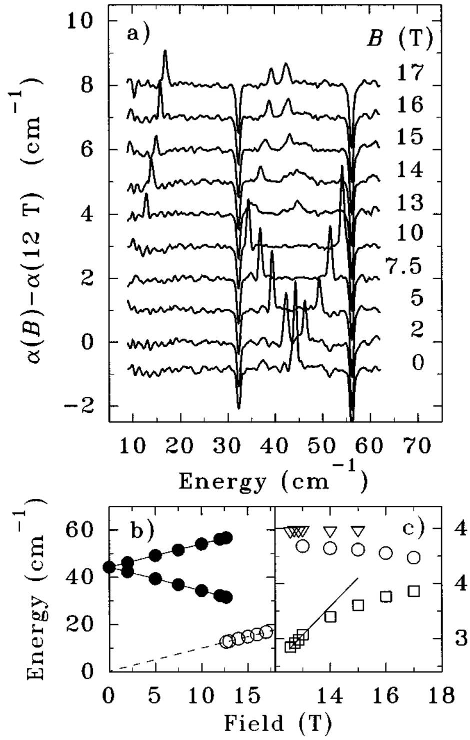

FIG. 2. (a) Absorbance difference spectra $\alpha(B)-\alpha(12\ \mathrm{T})$ at $T=2.3$ K. (b) Field dependence of the gap energy in the D (closed symbols) and IC phases (open symbols). (c) Field dependence of the 33.3 (squares), 43.5 (circles), and 44.7 $\mathrm{cm^{-1}}$ (triangles) features in the IC phase.

In order to understand the results presented above, we propose the following qualitative picture of the phase diagram and excitation spectrum for a spin-Peierls compound. As discussed in Ref. 14, the magnetic excitation spectrum for an $S=1/2$ antiferromagnetic Heisenberg chain has a rich and complicated appearance as a function of an applied magnetic field. In zero field and temperature the ground state has a singlet nature. The magnetic excitations are triplet states and fall into a two parameter spin-wave continuum (SWC) bounded at $\omega_1=(\pi J/2)\sin(k)$ and $\omega_2=\pi J\sin(k/2)$. The structure factor $S(k,\omega)$ has a divergence at the lower boundary. One of the most important features of the SWC is that it is degenerate with the ground state at $k=0$ and $k=\pi$, leading to the possibility of a dimerization (i.e., a modulation with $k=\pi$), and the opening of a gap in the spin excitation spectrum, in the presence of magnetoelastic couplings.[15]

Application of a magnetic field to the chain leads to a magnetic ground state, with a gradually increasing multiplicity (triplet, quintet, ...).[14] In the magnetic excitation spectrum a spin gap $g\mu_BH$ opens at $k=0,\pi$, and the degeneracy with the ground state moves away from $k=0,\pi$.[14] For small fields these shifts are given by $\Delta k(H)=g\mu_BH/J$. Again this degeneracy may lead to a modulation and a gap in the presence of magnetoelastic couplings, but now with a wave vector which is generally incommensurate with the structure and depends on the magnetic field. For low fields, however, the presence of umklapp processes will prevent the modulation wave vector to move away from $k=\pi$, and up to a critical field H_c the modulation will remain a simple dimerization of the lattice, and the magnetic ground state will remain of singlet nature.

Momentum conservation rules restrict single excitation absorption processes in an unmodulated structure to essentially $\mathbf{k}=\mathbf{0}$ excitations. In a modulated structure, however, the same rules lead to absorption processes involving excitations with $\mathbf{k}=\mathbf{0},\pm\nu\mathbf{q}$, where ν is an integer, and $\mathbf{q}$ is the modulation wave vector.[16] For example, modulation with $q=\pi$ leads to activation of excitations at the Brillouin zone boundary. The matrix elements for transitions involving $\nu\neq0$ generally decrease rapidly for increasing ν, which usually makes excitations with $\mathbf{k}=\pm\nu\mathbf{q}$, $\nu>1$ undetectable.

From the above, it is clear that one expects new phonon and spin absorption processes in IR absorption spectroscopy, not only in the D phase, but also in the IC phase. In addition to this one also expects a gap at the modulation wave vector in the spin excitation spectrum in the IC phase. It is interesting to note that the expected modulation in the IC phase is dependent on the magnetic field, hence by varying the magnetic field one can scan the modulation wave vector through part of the Brillouin zone, allowing for the observation of the k dependence of the optically active excitations with $k=\nu q$, which energies depends not only on the dispersion relation, but also on the gap induced by the spin-phonon interaction.

Now coming back to the experimental results again, and to facilitate the discussion, consider only the divergent lower bound of the SWC. This leads to a picture with magnonlike excitations with a dispersion $\omega(k_c)=(\pi J/2)|\sin(k_c)|$ for the low-temperature regime of the uniform phase. As shown previously, one can approximately describe the magnetic excitation spectrum in the D phase by magnonlike excitations with a dispersion $\omega^2(k_b,k_c)=\Delta^2+(\omega_c\sin(k_c))^2+(\omega_b\cos(k_b/2))^2$, where $\Delta=16\ \mathrm{cm}^{-1}$ is the spin-Peierls gap, $\omega_c=\pi J/2=130\ \mathrm{cm}^{-1}$ and $\omega_b=26\ \mathrm{cm}^{-1}$.[3] The dispersion in the k_b direction results from the nonnegligible interchain interaction. The dimerization in the D phase leads to activation of phonon excitations with $\mathbf{k}=\mathbf{0}$ or $\mathbf{q}=(\pi,0,\pi)$. For the spin system, however, there is no change in the magnetic periodicity and only $\mathbf{k}=\mathbf{0}$ excitations can be observed, leading to a single absorbance peak (at $44.3\ \mathrm{cm}^{-1}$ for $B=0$) as has been observed experimentally (Fig. 1).

For phonon absorption transitions at $\mathbf{k}=\mathbf{q}$ there are two candidates observed in the low-energy region in the D phase, at 10 and $43.5\ \mathrm{cm}^{-1}$, respectively. Knowing that INS experiments[12] have shown a TA phonon at the $\mathbf{a}^*$ zone boundary at $44\ \mathrm{cm}^{-1}$, the latter peak can be assigned to the corresponding folded mode in the D phase. These high-temperature experiments did not find, however, any phonon around $10\ \mathrm{cm}^{-1}$. It is therefore proposed here that this peak is due to the D phase counterpart of the soft mode of the U-D phase transition. From the proposed structure for the D phase[9] one expects an A_u symmetry for the soft mode. In the D phase this mode splits into $B_{2g}\oplus B_{3g}\oplus A_u\oplus B_{1u}$, where the latter is indeed IR active.

In the IC phase, two features are observed below $20\ \mathrm{cm}^{-1}$ (Fig. 2). Since one expects the magnetic ground state to have a triplet nature, the field-dependent peak (13–$17\ \mathrm{cm}^{-1}$) may be assigned to the $\mathbf{k=0}$ triplet-triplet transition ($m_s=-1\rightarrow0$, transitions to $m_s=1$ are magnetic dipole forbidden). For the $10\ \mathrm{cm}^{-1}$ feature it is clear that it should have the same origin as the one proposed above for the D phase.

In discussing the remaining $\mathbf{k}=\nu\mathbf{q}$ modes in the IC phase the magnetic excitations are considered first. Neglecting a possible interchain interaction, the energy of the magnetic excitations with wave vector $k=\pm(\pi-g\mu_BH/J)$ may be approximated by

$$E(H)=g\mu_bH+\sqrt{\Delta_{\mathrm{IC}}^2+(\pi J/2)^2\sin^2(g\mu_BH/J)},$$

or for small fields $(1+\pi/2)g\mu_bH+0.5(\Delta_{\mathrm{IC}}^2/g\mu_bH)$. At 13 T, the energy of the $k=\pm q$ excitation in the absence of a gap is thus about $33\ \mathrm{cm}^{-1}$. In the 13 T spectrum indeed a peak is observed at $35.3\ \mathrm{cm}^{-1}$ which, moreover, initially increases linearly with field with a slope $(1+\pi/2)g\mu_b$ [inset in Fig. 2(c), solid line]. From this, the gap at $k=q(H)$ is estimated to be about $\Delta_{\mathrm{IC}}=7\ \mathrm{cm}^{-1}$. Upon increasing field, the energy of this $m=0$ mode clearly shows a deviation from a linear behavior, strongly indicating interaction with another excitation, possibly the TA phonon near the zone boundary around $43.4\ \mathrm{cm}^{-1}$. When the lattice becomes incommensurate, one expects the energy of the TA phonon response to slowly decrease upon increasing field, i.e., upon decreasing modulation wave vector. This indeed corresponds to the observed behavior of the absorption peak at $43.4\ \mathrm{cm}^{-1}$ at 13 T, which moves to $42.4\ \mathrm{cm}^{-1}$ at 17 T. This strongly indicates a field-dependent incommensurate modulation of the lattice.

In addition to the $43.4\ \mathrm{cm}^{-1}$ peak, a second feature is observed at $44.7\ \mathrm{cm}^{-1}$ which exists only in a limited field range (12.6–15 T), and is not field dependent. A likely explanation for the appearance of this mode is that close to the IC-D phase transition, there exists discommensurations in which the modulation is pinned to a (nearly) commensurate value q_{comm}, leading to absorption processes involving excitations at $k=q_{\mathrm{comm}}$. The existence of such discommensurations is a quite general phenomenon in an incommensurate system close to a first-order lock in transition to a commensurately modulated structure.[17]

In conclusion, from the present experiments as well as from Raman experiments[7] it is clear that strong spin phonon couplings exist in $\mathrm{CuGeO_3}$. Though this is not surprising in a magnetoelastic compound, it remains to clarify the way it influences the SP transition.

The observation of newly activated phonon modes in the D and IC phase is consistent with a modulation of the crystal potential. Also in Raman experiments several newly activated modes have been reported in both the D and IC phases.[18,19] The origin of these activations may be the deformation of the lattice. However, only a few new modes have been observed in Raman and IR experiments and in addition the distortion of the lattice is quite small.[9] A more likely possibillity is that the phonons are in fact activated by spin phonon interactions which lead to a Bragg scattering of the phonons by the spin system. Similar effects have been observed for instance in the vanadium dihalides.[20]

The results presented for the high-field phase are in good agreement with a field-dependent incommensurately modulated phase, as evidenced by the observation of $\mathbf{k}=\nu\mathbf{q}$ modes. The field dependence of these modes can be understood in a simple model for the excitations in the IC phase. From this model, the $k=q$ spin gap in the IC phase is estimated to be about 7 cm^{-1}.

The structure observed at 10 cm^{-1} in the D and IC phase has been assigned here to the low-temperature counterpart of the soft mode of the SP transition. For a definite assignment, however, additional experiments are needed, for instance inelastic neutron scattering or Raman spectroscopy.

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