Soft longitudinal modes in spin-singlet $CuGeO_3$

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We present results from a neutron-scattering study of lattice anomalies associated with the transition to the gapped spin-singlet state observed in the spin-$\frac{1}{2}$ linear-chain compound $CuGeO_3$. Instead of the lattice dimerization along the chain direction (c axis) expected for a spin-Peierls system, we observe a remarkable softening of the longitudinal acoustic phonons in a direction (along the b axis) perpendicular to the chains. A spontaneous strain appears in the same direction below the magnetic transition temperature of 14 K.

Hase, Terasaki, and Uchinokura[1] recently reported the discovery of an unusual magnetic transition in $CuGeO_3$, an inorganic compound containing linear spin-$\frac{1}{2}$ Cu-O chains. Below the transition temperature T_c of 14 K, the magnetic susceptibility drops isotropically toward zero, indicating the development of an energy gap for spin excitations. Inelastic neutron-scattering experiments by Nishi, Fujita, and Akimitsu[2] have confirmed the existence of a gap, which reaches a value of 2.1 meV well below T_c. The singlet nature of the ground state has been directly demonstrated by Nishi *et al.*,[3] who have shown that the minimum-energy excitation splits into three when a magnetic field is applied, as expected for single-triplet excitations. Measurements of the magnetic-field dependence of T_c,[4] when scaled appropriately, agree quite well with both theoretical predictions[5] and experimental results[6] for organic spin-Peierls systems.

It appears that $CuGeO_3$ might be an example of an inorganic spin-Peierls system.[1] However, in a proper spin-Peierls transition, the pairing of spins in singlets occurs in the presence of a concomitant structural dimerization of the chains. Nishi, Fujita, and Akimitsu have found no evidence for such a chain distortion, which would double the unit cell along the c axis (parallel to the chains). They have also discovered a significant interchain exchange interaction, with a magnitude of approximately 10% of the intrachain coupling. The coupling between chains may be responsible for the very rapid growth of the gap below T_c.

We present here the results of a neutron-scattering study on a high-quality $CuGeO_3$ single crystal. Contrary to expectations, we observe lattice anomalies along the b direction, *perpendicular* to the chain direction. In particular, the longitudinal-acoustic (LA) mode in this direction is found, quite surprisingly, to be softer than a transverse-acoustic (TA) mode propagating in the same direction. Furthermore, a spontaneous strain along the b axis appears at the magnetic transition. Whether the distortion is coupled to a modulation of the exchange along the chains or between them is not yet clear.

Measurements were performed on the triple-axis spectrometer H8 located in the High-Flux Beam Reactor at Brookhaven National Laboratory. The single crystal used for the experiment was grown by the floating zone method and has dimensions $4\times3\times2$ mm^3. Although it is rather small for inelastic neutron studies, it is an exceptionally high-quality crystal, with a mosaic of less than 3 min. The lattice parameters at room temperature are $a=4.81$ Å, $b=8.47$ Å, and $c=2.941$ Å,[7,8] with c the chain axis. The sample was mounted inside an aluminum can with the crystallographic $(0kl)$ zone in the scattering plane of the spectrometer. The sample can, filled with He to favor thermal exchange, was attached to the cold finger of a two-stage He displex. The lowest attainable temperature with this setup is 3.3 K. The incident energy was selected by the (0 0 2) reflection of a pyrolitic graphite (PG) monochromator.

We first characterized the phase transition by measuring the temperature dependence of the intensity at 1 meV, repeating the measurements of Nishi, Fujita, and Akimitsu.[2] Measurements were done at constant final neutron energy ($E_f=14.7$ meV) with a PG filter after the sample and horizontal collimations of 40′-40′-80′-80′, as seen from reactor to sample. The results are shown in Fig. 1. The energy gap, its temperature dependence, and the phase transition temperature are identical to those reported by Nishi, Fujita, and Akimitsu.[2] Extensive elastic studies below T_c were carried out along directions (0, 0.5, l) and $(0,k,l+0.5)$ to investigate the existence of new superlattice reflections. We did not find any new peaks, in complete agreement with previous results.[2] Measurements of TA and LA phonons propagating along c^* indicated a normal behavior. In particular, we did not find any anomalies in the energy widths of the longitudinal

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phonons, contrary to the results in Ref. 2.

In considering possible structural distortions associated with the magnetic phase transition, we came to appreciate the fact that the b axis is unique in that there are two Cu atoms per unit cell in that direction, but only one along a and c. The presence of the b glide plane in the space group *Pbmm* establishes some reflection conditions and, as a result, the $(0k0)$ and $(0kl)$ reflections with k odd are extinct. Thus, a distortion causing pairing of the chains along b could occur without causing a doubling of the unit cell [space group *P2mm* (Ref. 8)]. A check of the $(0k0)$ reflections with k odd, under conditions that minimized the multiple scattering, indicated that their intensity remains negligible below T_c. Nevertheless, we decided to study the dispersion of acoustic phonons along b^*, working in the Brillouin zones corresponding to the (0 6 0) and (0 0 2) Bragg reflections. Quite surprisingly,

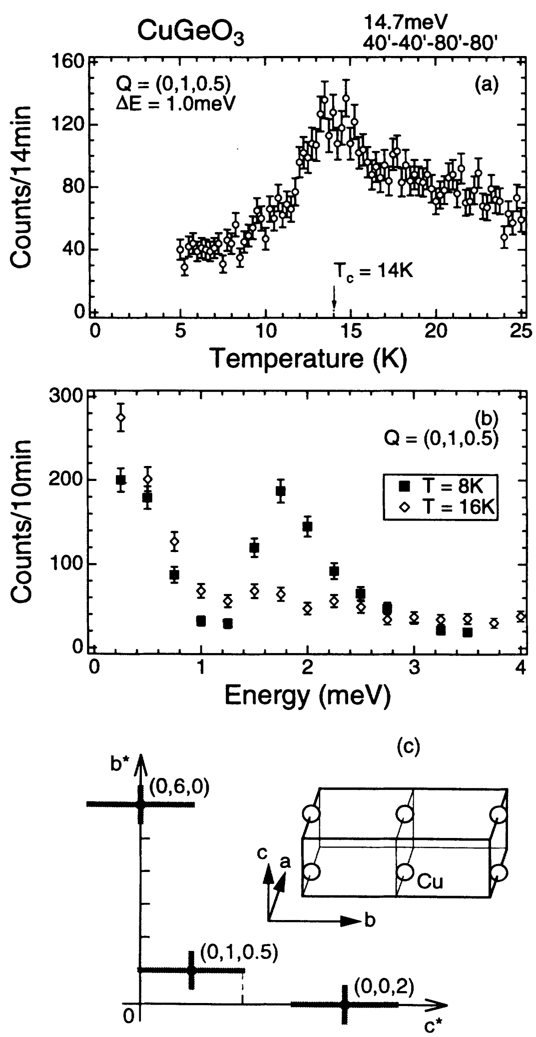

FIG. 1. (Top) Temperature dependence of the neutron intensity at $\Delta E = 1$ meV. (Center) Energy scans at $\mathbf{Q} = (0,1,0.5)$ above and below the phase transition temperature. The gap disappears above T_c. (Bottom) Sketch of reciprocal space in the $(0kl)$ plane. The shadowed regions represent the positions explored in our inelastic neutron-scattering measurements. The inset shows the unit cell with the atomic positions for Cu.

we discovered that the energy of the LA mode along b^* is so low that it lies *below* that of the measured TA branch propagating in the same direction (see Figs. 2 and 3).

These measurements are particularly difficult due to the small size of the crystal, and it is not easy to follow the dispersion curve down to small q. Nevertheless, we have found an experimental window (40′-40′-20′-80′ and $E_i = 14.7$ meV) that allows us to measure down to $\mathbf{q} = (0, 0.15, 0)$. In order to prove that the observed longitudinal mode is actually the acoustic branch and not a low-lying optical mode, we have carried out a careful search at the conventional location of the longitudinal-acoustic mode, namely, above the TA branch. The constant-E ($\Delta E = 2$ and 4 meV) scans, displayed in Fig. 3(c), demonstrate that there is no acousticlike mode lying above the TA branch. This type of scan is more effective than the conventional constant-Q scan when the dispersion is steep, and the broad peaks observed in Fig. 3(c) are completely consistent with the dispersion shown in Fig. 2. Because of the trade-off between phonon intensity and instrumental resolution we have not succeeded in observing the temperature dependence of the LA mode. Similar scans along c^* show a normal LA mode above the corresponding TA.

The soft longitudinal mode naturally suggests a very strong temperature dependence of the lattice constant along the b direction. To test the lattice expansion, we have improved on the relatively poor Q resolution typical of neutron scattering by tightening the collimation to

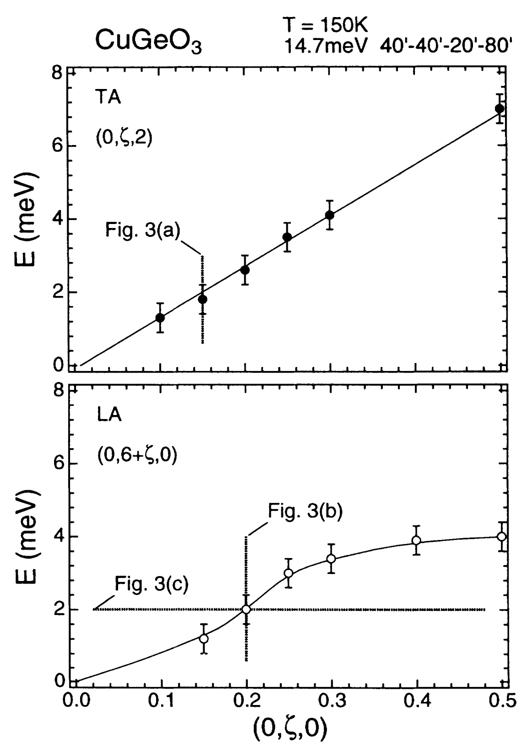

FIG. 2. Phonon-dispersion curves of the c-polarized transverse-acoustic branch along b^* direction (top) and of the longitudinal-acoustic mode along b^* (bottom). The dotted lines correspond to the scans presented in Fig. 3.

10′-10′-10′-10′. Then we selected the (2 2 0) reflection of a perfect Ge crystal as analyzer, as it has a nearly perfect matching with the (0 4 0) reflection from $CuGeO_3$. The narrow mosaic of our high-quality crystal is crucial to achieving good Q resolution. Finally, we have lowered the incident energy to the limit of our spectrometer, 7.48 meV ($k_i = 1.9$ Å^{-1}). The resulting full width at half maximum (FWHM) at (0 4 0) is 0.002 Å^{-1}. Our measurements of the b lattice constant, shown in Fig. 4, confirm the expected large contraction. In addition, they show clear evidence for the development of a spontaneous srain, Δb, below T_c. The solid line in Fig. 4 is a simple model calculation to represent the normal thermal contraction. Even though the error bars are still relatively large, the deviation Δb from the solid line is reproducible and well established. The dotted line represents a fit to the spontaneous strain below T_c. We speculate that Δb, and not the gap, is the order parameter of the phase transition.

The soft longitudinal-acoustic mode above T_c and the appearance of a spontaneous strain Δb support a model of phonon instability at the zone center. Phase transitions involving acoustic-mode condensation are known in a number of systems, such as Nb_3Sn (Ref. 9) and V_3Si (Ref. 10). A LA mode falling below the TA has been observed in $Sm_{0.75}Y_{0.25}S$ and TmSe;[11] however, this is the first case, to our knowledge, where it appears that the longitudinal-acoustic mode actually condenses.

High-resolution powder neutron experiments are under way to check the space group both above and below T_c.[12] Preliminary results indicate no change. We note that Raman-scattering studies[13] observed a sharp soft mode at 34 cm^{-1} (4.2 meV) at 5 K. This peak, together with other features of the Raman spectrum, can be quantitatively explained by the magnetic excitations (not phonons) appearing below T_c and reported in Ref. 2. The energy gap of 2.1 meV produces a peak at 4.2 meV by a two-magnon-scattering process.

Summarizing, the key characteristics established for the 14-K phase transition in $CuGeO_3$ are (a) A spin gap opens up at T_c and the magnetic excitations correspond to a singlet-triplet transition.[1–3] (b) A specific-heat anomaly at T_c has been observed.[14] (c) Our current study establishes that Δb shows the temperature dependence of an order parameter. (d) No new peaks are observed below T_c.

What is the significance of these results? While the nature of the magnetic phase diagram[4] provides strong circumstantial evidence for a spin-Peierls transition in

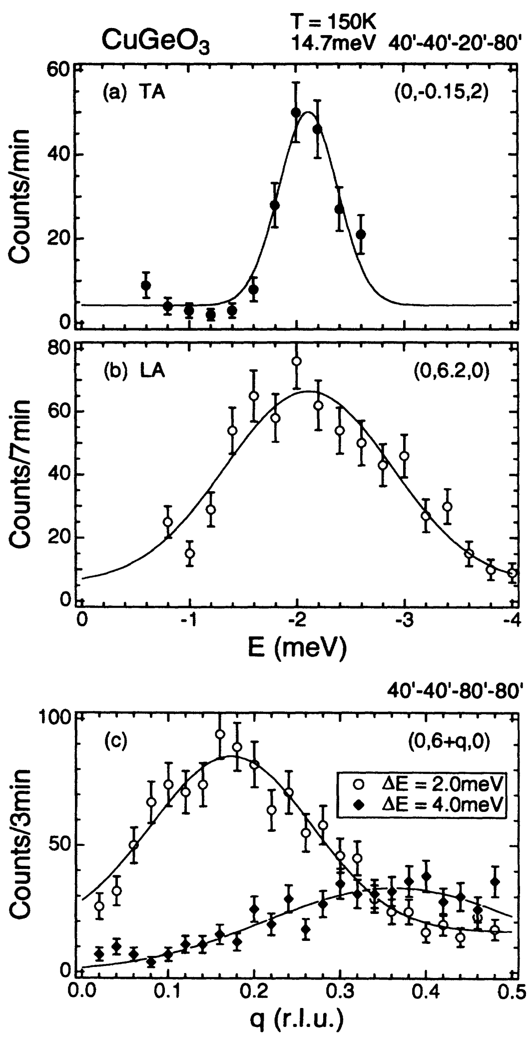

FIG. 3. Typical energy scans at constant Q. (a) Transverse phonon at $\mathbf{q} = (0, 0.15, 0)$ and (b) longitudinal phonon at $\mathbf{q} = (0, 0.2, 0)$. Note that the FWHM of the longitudinal phonon is twice the instrumental resolution (1 meV). (c) q scans looking for longitudinally polarized excitations at $\Delta E = 2$ and 4 meV. There are no extra modes above the TA branch.

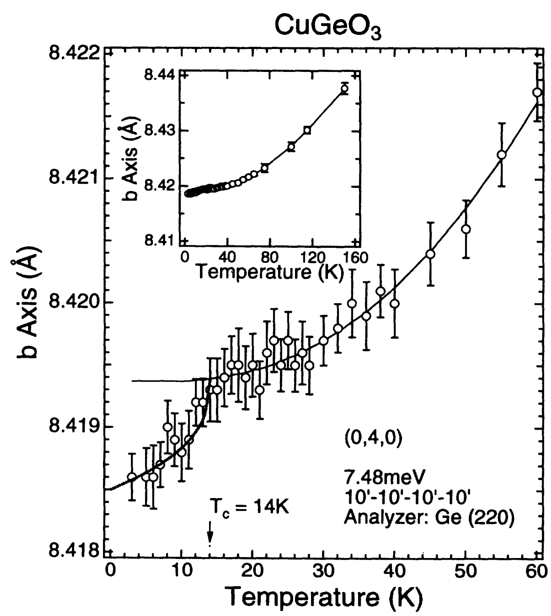

FIG. 4. Temperature dependence of the b lattice constant measured at $\mathbf{Q} = (0, 4, 0)$. At $T_c = 14$ K the lattice undergoes a contraction. The solid line is a model calculation and the dotted line is a fit to the spontaneous strain, Δb. The inset shows the measurements over a wider temperature range.

$CuGeO_3$, the lack of evidence for structural dimerization along the chain direction argues against it. Another mechanism for generating a singlet state with an energy gap in an antiferromagnetic spin-$\frac{1}{2}$ Heisenberg chain involves frustration caused by an antiferromagnetic second-neighbor coupling, as discussed by Majumdar and Ghosh.[15] Such a mechanism gains some credibility when one considers the superexchange paths in the Cu-O chains. The coupling between nearest-neighbor Cu atoms is relatively weak because the Cu-O-Cu superexchange path is bent at an angle of nearly 90°. A significant second-neighbor coupling through the Cu-O-O-Cu exchange path seems quite likely. The relative strengths of the superexchange energies should depend sensitively on the bond angles, which would allow a possible coupling to displacements of the oxygen atoms perpendicular to the chains. Alternatively, the elastic anomaly might couple to the exchange interaction between chains. In any case, the magnetic-elastic transition in $CuGeO_3$ is quite fascinating and deserves further study.

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