Temperature dependence of the spin-Peierls energy gap and anomalous line shapes in CuGeO$_3$

Michael C. Martin and G. Shirane
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973-5000

Y. Fujii and M. Nishi
Neutron Scattering Laboratory, Institute for Solid State Physics, University of Tokyo, Shirakata, Tokai, Ibaraki 319-11, Japan

O. Fujita and J. Akimitsu
Department of Physics, Aoyama Gakuin University, Chitosedai, Setagaya-ku, Tokyo 157, Japan

M. Hase
Institute of Physical and Chemical Research (RIKEN), Wako 351-01, Japan
and Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

K. Uchinokura
Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan
(Received 12 February 1996)

Neutron-scattering measurements on a large single crystal of CuGeO$_3$ have been used to determine the temperature dependence of the spin-Peierls energy gap. While the power-law behavior of the intensity of structural superlattice peaks is well fit by $I(T) \propto (T_c - T)^{2\beta}$ with an exponent of $\beta = 0.33$, the exponent for the temperature dependence of the energy gap is significantly smaller than expected for conventional spin-Peierls materials. Usual scaling relations relate the energy gap to the superlattice reflection intensity as $\Delta(T) \propto I^a$ with $a = 1/3$; the present results suggest an exponent of $a \approx 1/6$ for CuGeO$_3$. An additional scattering cross section is observed in constant-$q$ and constant-$E$ scans creating a long tail extending to higher energies relating to a proposed scattering continuum. [S0163-1829(96)50422-4]

A spin-Peierls transition in the inorganic compound CuGeO$_3$ was first reported in 1993$^1$ and has since been the subject of many studies. This compound has chains of Cu$^{2+}$ ($S = 1/2$) along its $c$ axis and was therefore expected to be fairly one dimensional (1D) in nature. When the spin-Peierls transition occurs, the Cu$^{2+}$ chains distort into dimers$^2$ yielding a singlet ground state, and a triplet excited state at an energy $\Delta_{SP}$ (the spin-Peierls energy gap).$^3$ Neutron studies by Nishi et al.$^4$ demonstrated the existence of this gap at about 2 meV at $q = (0, 1, 0.5)$ in reciprocal space.

Evidence is beginning to mount that CuGeO$_3$ is not a typical one-dimensional spin-Peierls system. Nishi et al.$^4$ reported spin-wave-like energy dispersions from which the nearest-neighbor exchange parameters were obtained. These resulted in a ratio of the interchain coupling $J'$ to the intra-chain coupling $J$ of $J'/J = 0.1$. This is significantly larger than other one-dimensional systems $[J'/J \sim 1.7 \times 10^{-2}$ for CsNiCl$_3$ (Ref. 5) and $J'/J \sim 4 \times 10^{-4}$ for the Haldane Ni(C$_2$H$_5$N$_2$)$_2$NO$_2$ClO$_4$ system$^6$] which implies that CuGeO$_3$ is not as one-dimensional as was initially thought. Recent high-pressure neutron-scattering measurements$^7,8$ have shown that the dimerizing lattice distortion does not follow the spin-Peierls transition temperature and energy gap implying that an additional mechanism, such as a spin-only effect, is at play. Furthermore, susceptibility measurements above the spin-Peierls transition temperature$^9$ are substantially different from the theoretical calculation of Bonner and Fisher$^9$ which works well for other one-dimensional $S = 1/2$ organic spin-Peierls systems.

Since the spin-Peierls ordering is related to a dimerizing lattice distortion, $\delta$, it is of interest to understand the relationship between this distortion and the onset of various features of the spin-Peierls phase. For example the intensity of a superlattice Bragg peak is proportional to $\delta^2$. So by fitting the temperature-dependent peak intensity data to a power law, one can discover the exponent of the power law for $\delta$ as a function of temperature. Scaling rules have been developed by Cross and Fisher$^10$ to relate the temperature dependence of the spin-Peierls energy gap ($\Delta_{SP}$) to $\delta$ as well. This relates the energy gap and the superlattice intensity such that $\Delta \propto \delta^a$; in Cross-Fisher scaling $a = 1/3$. Alternatively a ground state that is dimerized without a lattice distortion was theoretically predicted by Majumdar and Gosh$^{11}$ for a 1D $\Delta = 1/2$ antiferromagnet having a nearest-neighbor interaction $J$ and a next-nearest-neighbor interaction $J_2$ related by $J_1 = 2J_2$. Indeed Castilla et al.$^{12}$ showed that a second-nearest interaction can explain the measured susceptibility and dispersion curves. It is possible that the dimerization in CuGeO$_3$ has origins in both the spin-Peierls spin-phonon mechanism and the latter spin-only mechanism. We will present the fits we obtain for the energy gap as a function of temperature and show that this copper germanate system does not behave as a typical spin-Peierls system.

The primary CuGeO$_3$ single crystal (No. A12) used in the present studies was grown by the traveling floating zone method and checked with x-ray diffraction and magnetization measurements.$^4$ It is approximately $35 \times 10 \times 4$ mm$^3$ in volume, and has a good mosaic spread in the $b$ direction, but
The spin-Peierls energy gap measurements reported here were obtained using collimations of axis configuration. The spin-Peierls energy gap measured at Brookhaven National Laboratory in the standard triple-formed at the H7 beam line of the High Flux Beam Reactor for cooling. Neutron-scattering measurements were performed in an aluminum can, and placed in a 3-K Displex for cooling. The crystals were oriented in an \((hkh)\) or \((0kl)\) zone, mounted in an aluminum can, and placed in a 3-K Displex for cooling. Neutron-scattering measurements were performed at the H7 beam line of the High Flux Beam Reactor at Brookhaven National Laboratory in the standard triple-axis configuration. The spin-Peierls energy gap measurements reported here were obtained using collimations of \(40\)-\(20\)-\(5\)-\(20\)-\(40\), yielding approximately a 0.6 meV energy resolution. The incoming neutrons were monochromated using the \((002)\) reflection of pyrolytic graphite (PG) to select 13.7 meV fixed incoming energy neutrons, and two PG filters were placed before the sample to reduce higher energy contamination. PG \((002)\) was also used as an analyzer.

As reported by Hirota et al., \(^2\) structural superlattice peaks due to the spin-Peierls dimerization are observed at \((h/2,k,h/2)\), where \(h\) is odd and \(k\) is any integer. We plot the intensity of the \((0.5\ 3\ 0.5)\) reflection as a function of temperature in Fig. 1. The onset of this peak is well described by a power-law behavior in the region just below \(T_c\). The solid line in Fig. 1 is a fit of the data from 12–16 K, to a power law, \(I(T)\propto(T_c-T)^\beta\). \(\beta\) is the exponent from the temperature dependence of the atomic displacement \(\delta\) since \(I\propto\delta^2\). The fit demonstrates that the three-dimensional Ising model result of \(\beta=0.33\) is a good description of the intensity data. This value of \(\beta\) is somewhat higher than was originally reported by Harris et al., \(^14\ 0.24\), which had made Cross-Fisher scaling appear to hold. However, this report was revised with more accurate measurements to be 0.36 by neutrons \(^13\) and 0.33 by x-rays, \(^15\) both consistent with the present results, which we will show leads to a significant deviation from the Cross-Fisher scaling rule. The \(T_c\) is also obtained for this sample from the fit in Fig. 1 to be \(14.21\pm0.02\) K, in good agreement with previously reported values for CuGeO \(_3\).

We studied the spin-Peierls energy gap in the two 
\(\text{CuGeO}_3\) crystals. Figure 2 presents the temperature-dependent data on the larger No. A12 sample, which was aligned in the \((hkh)\) zone, at \(q = (0.5, 1, 0.5)\). While this is not at the zone center, we do not expect a significant change in the energy-gap behavior since the dispersion in the \(a\) direction is small. Indeed we will show that the energy-gap data measured on sample No. 10 at the zone center, \(q = (0, 1, 0.5)\), has the identical temperature dependence. The data points of Fig. 2 are the uncorrected data with each successive temperature’s data set being shifted vertically by 50 counts for clarity. The solid lines are fits to two Gaussians, one at zero energy (Bragg) and one for the energy gap. Arrows denote the fitted center positions of the energy gap at each temperature. We can clearly observe an energy-gap peak for temperatures up to 14.0 K, after which we can no longer accurately fit a peak. During the course of this experiment we became aware of works claiming that a “psuedogap” feature persists to a few degrees above \(T_c\). \(^16\) As seen in Fig. 2, our data for temperatures above 14 K do not have any clearly identifiable peak positions.

We summarize the energies of the gap peaks at all temperatures measured in Fig. 3. According to the Cross-Fisher scaling theory\(^10\) the onset of the energy gap can be related to

\[
er_T = 
\]
the atomic dimerization displacement such that $\Delta_{SP} \propto \delta^{2a}$ with $a = 1/3$. This theory has been used to successfully fit data of other organic spin-Peierls materials and one would expect that if CuGeO$_3$ is a typical spin-Peierls system this Cross-Fisher scaling would again fit the observed temperature dependence. From the data in Fig. 1 we found that near $T_c$ the exponent $\beta = 0.33$ works well. Using the Cross-Fisher result, we fit the energy-gap data in Fig. 3 to $\Delta_{SP} \propto (T_c - T)^{2a}$ with $a = 1/3$, and obtain the solid line labeled $a = 1/3$. This clearly does not describe the energy-gap data, even in the vicinity of $T_c$.

By allowing $a$ to be a free fitting parameter, we find that the best fit is obtained with $a = 0.147 \pm 0.012$. This value of $a$ is approximately a factor of two smaller than was expected from Cross-Fisher scaling ($1/3$). We therefore see that to relate the spin-Peierls energy gap in CuGeO$_3$ to the atomic displacement, the proportionality must be $\Delta_{SP} \propto \delta^{2a}$ with $a \approx 1/6$.

The gap as a function of temperature at the $q = (0, 1, 0.5)$ point in reciprocal space was measured on the second sample (No. 10). This sample’s slightly depressed $T_c$ is evident in the top panel of Fig. 4. A typical constant-$q$ scan is shown in the inset to the lower panel of Fig. 4, and the resultant temperature dependence is displayed in the main lower panel. A power-law fit results in a value of $a$ that, within errors, is the same as was found from Fig. 3, verifying our above analysis.

As we pointed out in the introduction, the susceptibility of CuGeO$_3$ above the transition temperature$^7$ was not well fit by the Cross-Fisher theory. A study by Riera et al.$^{17}$ pointed out that a much better fit to the susceptibility data could be obtained if the spin-Peierls energy gap scaled linearly with the atomic dimerization distortion $\Delta_{SP} \propto \delta^{2a}$ with $a = 1/2$.

However, our result that $a \approx 1/6$ heads in the opposite direction from that suggested by Riera et al.$^{17}$ A theoretical understanding of the temperature and pressure dependence of the energy-gap results, a challenging task, must be pursued.

When we extend the energy-gap scans to higher energies, we find that the peak has a tail with significant scattering intensity at higher energies. This is shown in Fig. 5 and is in agreement with other recent works.$^{16,18}$ The extra cross section observed at higher energies could be a signature of the theoretically predicted continuum above the well-defined dispersion.$^{19}$ The intensity and width of the energy-gap peak have an interesting $q$ dependence: while the integrated intensity (full width at half maximum $\times$ intensity) is monotonically.
cally decreasing with increasing $h$ in support of the results of a calculation by Haas and Dagotto,\textsuperscript{19} the peak shows a dramatic narrowing near $q = (0.7, 0.7)$. We have made preliminary calculations of the neutron-scattering resolution ellipse projected onto the relevant plane and find that its energy-$q$ slope is 14.7 meV Å at (0.5, 0.5) and goes up to 15.2 meV Å at (0.7, 0.7). This matches the dispersion near $h = 0.5$ and 0.75, whereas the dispersion is considerably steeper in between. Therefore, the narrowing observed near those wave vectors originates from focusing effects and is not intrinsic to the sample.

A constant-energy scan, such as the one shown in Fig. 6, demonstrates that the extra scattering intensity discussed is centered around $h = 0.5$; instead of two peaks symmetrical around $q = (0.5, 0.5)$, sizable intensity exists at $h = 0.5$. This indicates the presence of a continuum of scattering intensity, consistent with a Fano line shape recently reported to that of our Fig. 2. Although their best fit to a power law is with an exponent of $a = 0.12$, quite close to our present results, their interpretation differs somewhat.

We would like to thank R.J. Birgeneau, Guillermo Castilla, Vic Emery, Kazu Hirota, and Kazu Kakurai for informative discussions. We also thank J.E. Lorenzo and collaborators for communicating their results prior to publication. This work was supported in part by the U.S.-Japan Cooperative Research Program on Neutron Scattering operated by the U.S. Department of Energy and the Ministry of Education, Science, Sports, and Culture (MONBUSHO of Japan), and NEDO (New Energy and Industrial Technology Development Organization) International Joint Research Grant. O.F. and J.A. were supported by NEDO and by a Grant-in-Aid for Scientific Research from MONBUSHO of Japan. Research at Brookhaven National Laboratory was supported by the Division of Materials Research at the U.S. Department of Energy, under contract No. DE-AC02-76CH00016.

---

16 J.E. Lorenzo et al. (unpublished).
18 L.P. Regnault et al. (unpublished).
22 M. Arai, M. Fujita, M. Motokawa, and J. Akimitsu (private communication).