Temperature Dependence of the Spin-Peierls Energy Gap and Anomalous Line Shapes in CuGeO₃.

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(12 February 1996, revised 27 March 1996.)

Abstract

Neutron scattering measurements on a large single crystal of CuGeO₃ 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 CuGeO₃. 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.

PACS: 64.70.Kb, 61.12.-q, 64.60.Fr
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 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 intrachain 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$_3$ [3] and $J'/J \sim 4 \times 10^{-4}$ for the Haldane NENP system [3]) 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 [1] 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 $\Delta \propto \delta^{2a}$; 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 $S = 1/2$ antiferromagnet having a nearest neighbor interaction $J_1$ and a next nearest neighbor interaction $J_2$ related by $J_1 = 2J_2$. Indeed Castilla et al. [12] showed that a second neighbor interaction can explain the measured susceptibility and dispersion curves. It’s 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 (#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 a poorer mosaic along $c$. A second, previously studied sample (#10) was also used [13]. It has a smaller volume, $27 \times 3 \times 2$ mm$^3$, and a slightly reduced transition temperature, however its mosaic and low background rate are excellent. The crystals were oriented in an $(h \ k \ h)$ or $(0 \ k \ l)$ zone, mounted in an aluminum can, and placed in a 3K 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'-Sample-20'-40', yielding approximately a 0.6 meV energy resolution. The incoming neutrons were monochromated using the (0 0 2) 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 (0 0 2) 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 Figure 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 12K - 16K, to a power-law: $I(T) \propto (T_c - T)^{2\beta}$. $\beta$ is the exponent from the temperature dependence of the atomic displacement $\delta$ since $I \propto \delta^2$. The
fit demonstrates that the 3 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 \([10]\) 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 Figure 1 to be $14.21 \pm 0.02K$, in good agreement with previously reported values for CuGeO$_3$.

We studied the spin-Peierls energy gap in the two CuGeO$_3$ crystals. Figure 2 presents the temperature dependent data on the larger #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 #10 at the zone center, $q = (0, 1, 0.5)$, has the identical temperature dependence. The data points of Figure 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 14.0K, 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 Figure 2, our data for temperatures above 14K do not have any clearly identifiable peak positions.

We summarize the energetics of the gap peaks at all temperatures measured in Figure 3. According to the Cross-Fisher scaling theory \([10]\) the onset of the energy gap can be related to 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 \([10]\) 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 Figure 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 (#10). This sample’s slightly depressed $T_c$ is evident in the top panel of Figure 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 [1] 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 Figure 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 (FWHM $\times$ intensity) is monotonically decreasing with increasing $h$ in support of the results of a calculation by Haas and Dagotto [10], the peak
shows a dramatic narrowing near \( q = (0.7, \bar{1}, 0.7) \). 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 \((0.5, \bar{1}, 0.5)\) and goes up to 15.2 meV Å at \((0.7, \bar{1}, 0.7)\). 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 wavevectors originates from focusing effects and is not intrinsic to the sample.

A constant-energy scan, such as the one shown in Figure 6, demonstrates that the extra scattering intensity discussed is centered around \( h = 0.5 \); instead of two peaks symmetrical around \( q = (0.5, \bar{1}, 0.5) \), 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 from polarized Raman scattering measurements [20], and similar to what has recently been observed in KCuF\(_3\) [21]. The inset to Fig. 6 shows a sketch of this continuum (in the case of a uniform chain) and the solid horizontal line indicates where the constant-energy scan shown in the main portion of the figure was obtained. A full analysis and understanding of these observations is yet to be completed, and larger and higher quality crystals are required for still better counting rates enabling a further exploration of this continuum. Recently we have been made aware that just such a magnetic continuum is clearly observed by Arai et al. [22] from pulsed neutron measurements.

Note After this work was completed we became aware of the results of Lussier et al. [23] which presents very similar data to that of our Figure 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.

ACKNOWLEDGMENTS

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. OF and JA were supported by NEDO and by the 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.
REFERENCES

[1] M. Hase et al., Phys. Rev. Lett. 70, 3651 (1993).

[2] K. Hirota et al., Phys. Rev. Lett. 73, 736 (1994).

[3] O. Fujita et al., Phys. Rev. Lett. 74, 1677 (1995).

[4] M. Nishi et al., Phys. Rev. B 50, 6508 (1994).

[5] W.J.L. Buyers et al., Phys. Rev. Lett. 56, 371 (1986).

[6] J.P. Renard et al., Europhys. Lett. 3, 945 (1987).

[7] S. Katano et al., Phys. Rev. B 52, 15364 (1995).

[8] M. Nishi et al., Phys. Rev. B 52, R6959 (1995).

[9] J.C. Bonner and M.E. Fisher, Phys. Rev. 135, A640 (1964).

[10] M.C. Cross and D.S. Fisher, Phys. Rev. B 19, 402 (1979).

[11] C.K. Majumdar and D.K. Gosh, J. Math. Phys. 10, 1399 (1969).

[12] G. Castilla et al., Phys. Rev. Lett. 75, 1823 (1995).

[13] K. Hirota et al., Phys. Rev. B 52, 15412 (1995).

[14] Q.J. Harris et al., Phys. Rev. B 50, 12606 (1994).

[15] Q.J. Harris et al., Phys. Rev. B 52, 15420 (1995).

[16] J.E. Lorenzo et al., preprint.

[17] J. Riera and A. Dobry, Phys. Rev. B 51, 16098 (1995).

[18] L.P. Regnault et al., preprint.

[19] Stephan Haas and Elbio Dagotto, Phys. Rev. B 52, 14396 (1995).

[20] P.H.M. van Loosdrecht et al., Phys. Rev. Lett. 76, 311 (1996).
[21] D.A. Tennant et al., Phys. Rev. B 52, 13381 (1995); D.A. Tennant et al., Phys. Rev. B 52, 13368 (1995).

[22] M. Arai, M. Fujita, M. Motokawa and J. Akimitsu, private communication.

[23] J.-G. Lussier et al., J. Phys. Condens. Matter 8, L59 (1996).
FIGURES

FIG. 1. Superlattice peak intensity as a function of temperature showing the onset of the spin-Peierls state. The solid line is a power-law fit with the parameters shown.

FIG. 2. Constant $q = (0.5, 1, 0.5)$ scans at various temperatures near the spin-Peierls transition. The energy gap is clearly observed up to 14.0K. Solid lines are fits to Gaussian line shapes.

FIG. 3. The spin-Peierls energy gap, obtained from scans as in Fig. 2, plotted as a function of temperature. The two solid lines show the (poor) fit if Cross-Fisher scaling is applicable ($a = 1/3$), and the best fit having an exponent over twice as small.

FIG. 4. $q = (0.5, 6, 0.5)$ intensity and $q = (0, 1, 0.5)$ energy gap as a function of temperature for sample #10. Inset demonstrates a constant-$q$ scan of the energy gap at T=12.2K.

FIG. 5. Constant $q = (0.5, \bar{1}, 0.5)$ scan at T=4.0K showing the spin-Peierls energy gap and its non-Gaussian line shape. The solid line is a guide to the eye while the dashed line is a fit to a Gaussian line shape.

FIG. 6. A constant-energy scan at $E = 6.0$ meV around $q = (h, \bar{1}, h)$ at T=4.0K. The inset sketches a proposed scattering continuum (for a uniform spin-$\frac{1}{2}$ chain) and its relation to where the scan was obtained.
CuGeO$_3$ #A12

Fit to $(T_C - T)^{2\beta}$, $\beta = 0.33$

$T_C = 14.21 \pm 0.02$ K

$q = (0.5, 3, 0.5)$

$E_i = 13.7$ meV
CuGeO$_3$ #A12
H7 40'-20'-S-20'-40'
q = (0.5, 1, 0.5)
Energy Gap (meV) vs Temperature (K) graph

Best Fit: $a = 0.147 \pm 0.012$
Fit to $(T_C - T)^{2\beta a}$, $\beta = 0.33$

CuGeO$_3$ #A12
$q = (0.5, 1, 0.5)$

$a = 1/3$
CuGeO$_3$ #10

$q = (0.5, 6, 0.5)$

$E_i = 13.7$ meV

40'-40'-S-40'-80'

Fit to $(T_C - T)^{2\beta}$, $\beta = 0.33$

$T_C = 13.29 \pm 0.02$ K

$q = (0, 1, 0.5)$

Best fit: $a = 0.154 \pm 0.027$
CuGeO$_3$ #A12
T=4.0K

$H_8 \ E_1 = 14.7 \text{meV}$

$q=(0.5, -1, 0.5)$

$20'-40'-S-20'-80'$
$q = (h, -1, h)$ (r.l.u.)

$E = 6.0 \text{meV}$

$\text{CuGeO}_3$

Data scan

Continuum

Counts / 10,000 Mon. (6-7 min.)

Energy

$q = (h, -1, h)$ (r.l.u.)

$E = 6.0 \text{meV}$