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LETTER TO THE EDITOR

The temperature dependence of the spin–Peierls energy gap in $CuGeO_3$

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Abstract. We have studied the temperature dependence of the spin–Peierls (SP) energy gap in a single crystal of $CuGeO_3$ using cold neutrons. Our measurements enable us to examine the scaling relationship between the magnitude of the SP gap and the intensity of the structural superlattice peak in the vicinity of the transition temperature (T_{SP}). We also discuss our data in the context of recent numerical calculations for which different scaling laws are obtained depending on the magnitude of the intrachain next-nearest-neighbour interaction in a Heisenberg spin-chain Hamiltonian. The consequence of two-dimensional correlations and the possible existence above T_{SP} of a second low-lying energy gap due to frustration are considered.

The recent observation of a spin–Peierls (SP) transition at $T_{SP} = 14$ K in $CuGeO_3$ [1] has attracted much attention and many studies have been initiated to investigate the creation of such a state in an inorganic compound. In general, SP transitions occur when the antiferromagnetic one-dimensional (1D) correlations couple with a phonon to induce a dimerization of the atoms along the spin chains [2]. As the coupling between the neighbouring spins is asymmetric and regroups the oppositely aligned spins into dimers, the SP ground state is a non-magnetic singlet separated from the triplet excited state by an energy gap known as the SP gap. In $CuGeO_3$ ($Pbmm$ crystal structure with lattice constants $a = 4.81$ Å, $b = 8.47$ Å and $c = 2.94$ Å), the 1D character develops along the c-axis where the Cu^{2+}–Cu^{2+} ($S = \frac{1}{2}$) distance is the shortest. However, a comparison of the coupling constants along the three crystallographic axes ($J_c \sim 10.4$ meV, $J_b \sim 0.1\ J_c$ and $J_a \sim -0.01\ J_c$) and in particular the large value for J_b indicates that the 1D character in $CuGeO_3$ is not as pronounced as in organic SP systems. It is also found that the high-temperature part of the magnetic susceptibility deviates from the Bonner–Fisher nearest-neighbour Heisenberg model for an $S = \frac{1}{2}$ chain [1]. Although it is possible to improve the fit above 150 K [3], the agreement at low temperature is poor, and recent numerical models which include an intrachain next-nearest-neighbour interaction in the Heisenberg spin-chain Hamiltonian have recently been considered [4, 5].

Many neutron scattering studies have been performed to examine the properties of the SP ground state in $CuGeO_3$. After the initial work of Nishi and coworkers [6], who identified the formation of a ∼2 meV gap at the $(0,\ 1,\ \frac{1}{2})$ wave vector, the singlet nature of the ground state was demonstrated [7]. Structural studies have shown the existence of the dimerization at a wave vector of $(h + \frac{1}{2},\ k,\ l + \frac{1}{2})$ (h, l, all odd; k, integer) [8, 9] and subsequent efforts were directed at the identification of a soft phonon which would come as a precursor of the dimerization [10]. Although some anomalies were found in $CuGeO_3$, in particular the existence of a soft longitudinal mode along the b-axis, this softening has yet to be related to

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the SP transition. Another mechanism has recently been proposed where fluctuations near $\omega = 0$ at the structural superlattice peak are suspected to drive the transition [11].

One interesting problem in $CuGeO_3$ is the relationship between the antiferromagnetic correlations and the structural fluctuations as revealed by the temperature dependence of the SP gap. Until recently, this temperature dependence had only been studied with thermal neutrons [6]. In that energy range (14 meV) the energy resolution is $\sim$1 meV and, because of the intrinsic broadening of the excitations, such measurements cannot give accurate information near T_{SP}. In this letter, we report the results of experiments that have exploited the higher energy resolution offered by cold neutrons ($\sim$0.25 meV) to obtain the temperature dependence of the magnitude of the SP gap in $CuGeO_3$ in the vicinity of T_{SP}. We compare our results with some proposed scaling laws which relate the SP gap (Δ) to the lattice distortion (δ) that accompanies the dimerization of the spins.

The single crystal used for the neutron scattering measurement is the same one as used in our previous study [12]. As only a few per cent of impurities can trigger 3D antiferromagnetic order at low temperature, we checked that our sample did not show any sign of magnetic order down to the lowest temperature available ($\sim$1.5 K). Based on studies of the doped material, and from spectroscopic measurements, we can infer that the impurity content of this nominally pure sample is very low (<1 ppm). The neutron scattering data were collected at the TASVII and TASVI spectrometers situated at the cold source of the DR3 reactor Risø National Laboratory, Denmark. At both spectrometers, the (002) reflection of pyrolytic graphite was used to select the energy of the incident and of the scattered neutrons. All the constant-$\boldsymbol{Q}$ scans were performed with a fixed monochromator (TASVII) or analyser (TASVI) energy held at $\sim$5 meV. The measurements were also made with a Be filter to limit higher-order contributions at the elastic wave vector. At TASVII, the reactor-to-detector collimation was 28′–open–60′–120′ (vanadium width, 0.2meV) while at TASVI collimations were kept at 30′–52′–81′–104′ (vanadium width, 0.26 meV). The sample was cooled using a ^{4}He flow cryostat with a base temperature of 1.5 K.

To measure the temperature dependence of the SP gap, we aligned the sample in the $(0, k, l)$ scattering plane and performed a series of constant-$\boldsymbol{Q}$ scans at the $(0, 1, \frac{1}{2})$ wave vector for several temperatures. The measurements are summarized in figure 1(a) where a subset of the raw data is shown for temperatures ranging from 1.5 K to 20 K. The neutron intensity was modelled using a Lorentzian lineshape [13]:

$$I(\omega) \propto A\omega\langle n+1\rangle\left[\left(1+((\omega-\Delta)/\Gamma)^2\right)^{-1}+\left(1+((\omega+\Delta)/\Gamma)^2\right)^{-1}\right]$$

where $A = k_f^3 \cot(\theta_A)$ for fixed monochromator, and $A = 1$ for fixed analyser energy scans, and $1/\langle n+1\rangle = (1 - \mathrm{e}^{-\hbar\omega/k_B T})$, the temperature factor. Δ and Γ are respectively the magnitude of the SP gap and the width of the excitation. Figure 1(b) and (c) shows in more detail the fits at 12 K and 20 K, respectively. In figure 2(a), we plot the temperature dependence of the magnitude of the gap Δ against temperature. At low temperature, the gap is 1.93 ± 0.01 meV (22.5 K) and is in agreement with previous measurements [7, 11, 13]. As the temperature increases, the gap remains relatively constant below $\sim$8 K until it softens and broadens in the vicinity of T_{SP} as expected for a phase transition (see figure 2(b)). The previous measurement by Nishi *et al* obtained by a thermal neutron measurement is also shown in that figure. It is apparent from figure 2(a) that the use of cold neutrons has allowed us to measure the gap closer to T_{SP} than in earlier studies. In figure 2(a) and (b), the vertical dashed line indicates the T_{SP} for the sample we used: 13.9 K $\pm$ 0.01 K as estimated from the onset of the structural superlattice reflection at $(\frac{1}{2}, 3, \frac{1}{2})$.

In the theory of Cross and Fisher for the SP transition [14], the magnitude of the SP gap (Δ) is related to the generalized atomic distortion (δ) such that $\Delta \sim \delta^{2/3}$. In $CuGeO_3$,

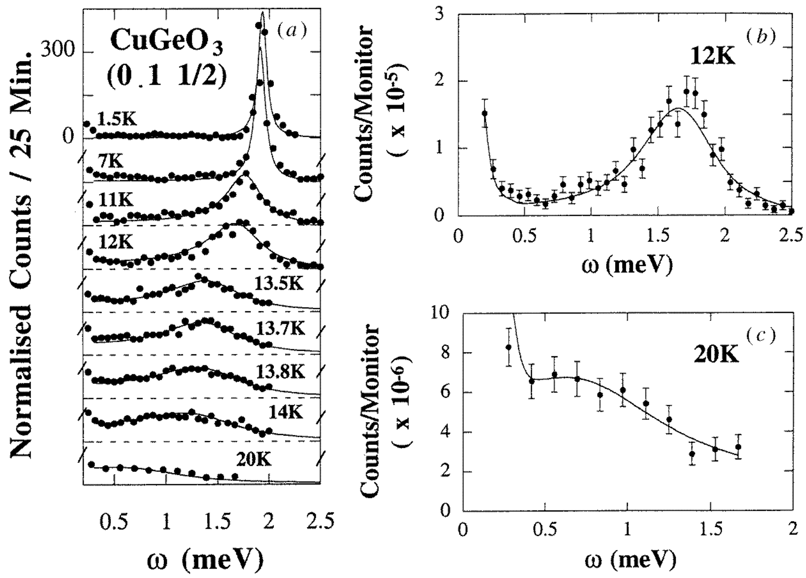
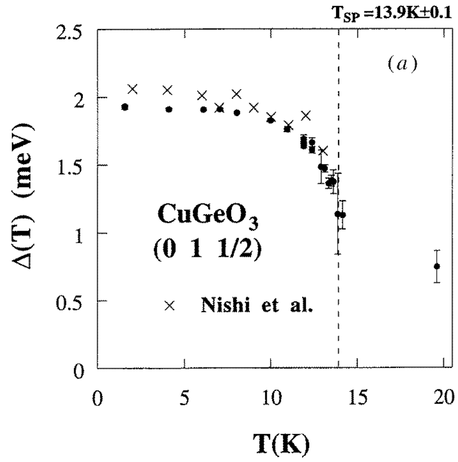


Figure 1. (a) The scattered neutron intensity is observed in constant-$\boldsymbol{Q}$ scans at $(0, 1, \frac{1}{2})$ for several temperatures. The continuous lines are guides to the eye using the lineshape described in the text and the horizontal dashed line represents the background. (b, c) The details of the real fit for two temperatures: 12 K and 20 K respectively.

spontaneous strains develop along all the crystallographic axes at T_{SP} [15, 16] and, as Harris *et al* pointed out, since the intensity of the structural superlattice peak would follow $I \sim \delta^2$ in a Landau theory, the magnitude of the SP gap should scale as $\Delta \sim I^{1/3}$ in the vicinity of T_{SP}. More recently, numerical calculations [4, 5] have focused on the fact that the coupling between the Cu^{2+} atoms along the chain is mediated through two oxygen atoms in $CuGeO_3$ and higher-order interaction terms, such as next-nearest-neighbour (NNN) intrachain interactions, may come into play. This approach helps restore a certain level of agreement with the high-temperature part of the magnetic susceptibility but the value of the parameter α, the ratio between NN and NNN coupling constants, necessary to obtain this agreement is rather controversial. When the value of α is set below a critical value of $\alpha_c \sim 0.24$, the fit to the high-temperature part of the susceptibility is poor [5], but in that regime Cross–Fisher scaling is believed to hold with $\Delta \sim I^{1/3}$. However, as pointed out in an earlier study by Riera and Dobry, a much better fit to the susceptibility is obtained with $\alpha \sim 0.36$, a value above α_c. In that regime, the SP gap is expected to scale linearly with the distortion $\Delta \sim \delta \sim I^{1/2}$ and a second gap, resulting from frustration, is predicted to appear above T_{SP} at ~0.2 meV [4]. This gap should be observable at $q = \pi$ (along the chain) when referenced to the non-dimerized unit cell.

In figure 3, we compare the temperature dependence of the SP gap with the intensity of the structural superlattice peak according to the expected scaling laws: $\Delta \sim I^{1/3}$ $(\alpha < \alpha_c)$ and $\Delta \sim I^{1/2}$ $(\alpha > \alpha_c)$. In figure 3(a), the structural superlattice intensity at $(\frac{1}{2}, 3, \frac{1}{2})$ was obtained from a neutron scattering measurement on the same sample. To normalize the curves, we scaled the superlattice intensity so that it matches the magnitude of the gap at low temperature. This scheme, already used by Harris *et al* [15], may neglect some logarithmic corrections which could be present [5] and assumes, in consequence, that the scaling law holds far from T_{SP}. To study better the scaling relationship in the vicinity of T_{SP}, we have



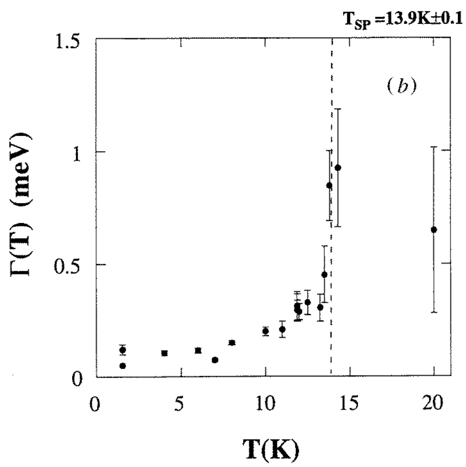
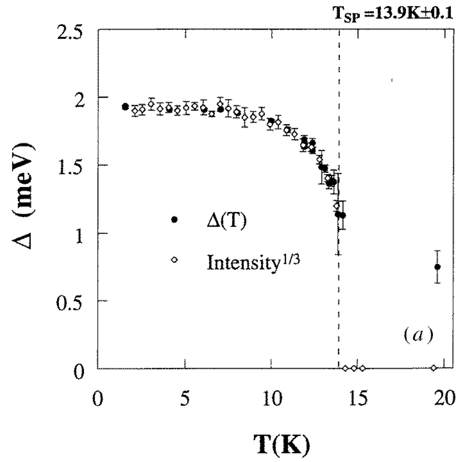


Figure 2. (a) ●, the magnitude of the SP gap at (0, 1, $\frac{1}{2}$) determined from the fit described in the text. ×, the thermal neutron data previously published by Nishi *et al* [6]. (b) The width of the excitation determined from the fit. In both parts, the vertical dashed line indicates the T_{SP} for the sample we used.



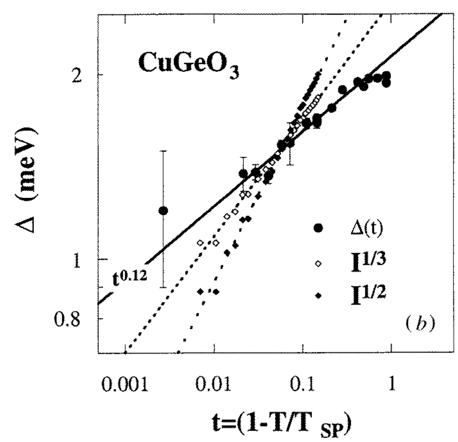


Figure 3. A comparison between the magnitude of the SP gap $\Delta(T)$ (●, as in figure 2) and the intensity of the structural superlattice reflection ($\frac{1}{2}$, 3, $\frac{1}{2}$) obtained by neutron scattering (◊). The intensity of the superlattice reflection was scaled to the power $\frac{1}{3}$ and renormalized to match the magnitude of the SP gap at low temperature. (b) A comparison between the magnitude of the SP gap $\Delta(t)$ (●, as in figure 2) and the intensity of the structural superlattice reflection ($\frac{7}{2}$, 1, $\frac{1}{2}$) obtained from a synchrotron measurement (◊, ♦) in the critical regime near T_{SP}. Note that the scales are logarithmic and the abscissae is expressed in terms of reduced temperature t. The intensity of the synchrotron measurement (I) was raised to $I^{1/3}$ (◊) and $I^{1/2}$ (♦) as indicated (see the text). The dashed lines represent a power law fit of the form $I \sim t^{\lambda}$. The same power law fit through selected points of the SP gap data (●) in the critical region gives $\lambda = 0.12$ (solid line).

used a synchrotron measurement performed at $(\frac{7}{2}, 1, \frac{1}{2})$ on a different crystal [17]. When fitted to a scaling law of the type $I \sim (1 - T/T_{SP})^{2\beta}$, we obtain $\beta = 0.33 \pm 0.02$ and $T_{SP} = 14.4$ K$\pm$0.1 K for this synchrotron measurement. This value for β is in agreement with the neutron data in figure 3(a). The comparison between the synchrotron measurement and the SP gap in the vicinity of T_{SP} is shown in figure 3(b). Note that both axes for this graph are logarithmic and the abscissa is expressed in terms of reduced temperature, which permits a satisfactory representation of the critical regime. Although none of the scaling relationship gives a satisfactory description of the data, we find that Cross–Fisher scaling ($\Delta \sim I^{1/3}$) describes the data better than $\Delta \sim I^{1/2}$/

To explain such a result, we recall that to fit the high-temperature part of the susceptibility, Riera and Dobry proposed that the NNN intrachain interaction term in the Heisenberg spin-chain Hamiltonian should be set at $\alpha = 0.36$ which is above the critical value $\alpha_c \sim 0.24$ [4, 5]. However, as mentioned by Riera and Dobry, the relatively large two-dimensional (2D) coupling along the crystallographic *b*-direction in $CuGeO_3$ may lead to a higher value of α_c. It is therefore possible that, even with a value of α as high as 0.36, the condition $\alpha < \alpha_c$ applied and that the validity of Cross–Fisher scaling is restored in $CuGeO_3$.

We also note that there is some residual inelasticity at and above T_{SP} which was neglected in the previous discussion. The existence of some 'overdamping' above T_{SP} has been observed by Nishi *et al* [6], Hirota *et al* [9] and particularly by Regnault *et al* [13] who claim the observation of an excitation at finite energy ($\sim$1 meV) at 15.6 K. In our data, this residual inelasticity is observed at 20 K in figure 1(c) and could be fitted as a small excitation peak at $\sim$0.75 meV. We are aware that a finite energy for this small excitation peak may be due to an artifact of the fitting and requires further studies. Nevertheless, the onset of a low-lying excitation directly at T_{SP} would certainly affect the analysis in the critical regime and complicate our final conclusion about the temperature dependence of the gap. Regnault *et al* ruled out the presence of a pseudogap which, according to them, would vanish at T_{SP}. It is therefore possible that the excitation at $\sim$0.75 meV is the signature of the low-lying energy gap due to frustration that is predicted by Riera and Dobry in the regime where $\alpha > \alpha_c$. The fact that this energy gap is larger than the proposed $\sim$0.2 meV may come from the failure to reproduce the correct energy scale for the SP gap ($\sim$2.8 meV) as well as the rather low $T_{SP} = 10.5$ K obtained from that study. It is possible that these discrepancies may be overcome by considering an appropriate interchain coupling which was neglected in the calculation.

We have shown that cold neutrons have allowed a more accurate measurement of the SP gap closer to T_{SP} than in earlier studies. We find that the SP gap is relatively constant for temperatures less than 8 K but collapses and broadens rapidly as the SP transition is approached from below. From a comparison between the two scaling relationships $\Delta \sim I^{1/3}$ ($\alpha < \alpha_c$) and $\Delta \sim I^{1/2}$ ($\alpha > \alpha_c$) obtained when the Heisenberg spin-chain Hamiltonian contains NNN intrachain interaction terms, we find that Cross–Fisher scaling ($\alpha < \alpha_c$) better describes the critical behaviour of the SP gap in $CuGeO_3$ in the vicinity of T_{SP}. This would contradict the condition that $\alpha > \alpha_c$ from a fit to the susceptibility data assuming that $\alpha_c = 0.24$. However, it is possible that all of these facts may be reconciled by the inclusion of a proper 2D interchain coupling in the Heisenberg spin-chain Hamiltonian, and we hope that this study helps stimulate further work in this direction.

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