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LETTER TO THE EDITOR

Spin dynamics in the spin–Peierls compound $CuGeO_3$

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Abstract. The spin dynamics of the spin–Peierls compound $CuGeO_3$ has been studied by polarized and unpolarized inelastic neutron scattering techniques. The presence of a continuum of excitations and a pseudogap is discussed in the light of the dimensionality of the magnetic interactions and the current theories involving competing magnetic exchange interactions along the chain axis.

Among the tests that one can apply to elucidate whether a given theory is relevant to the understanding of the physical properties of a certain compound, the study of the correlation functions and related scattering cross-sections is probably one of the most rigorous. The answer provided by these tests is in most cases clear, and helps to orient and further advance the theories. In this article we present a polarized and unpolarized inelastic neutron scattering (INS) study on the spin dynamics in the quantum spin-$\frac{1}{2}$ Heisenberg antiferromagnetic chain (QHAFC) compound $CuGeO_3$, with special attention paid to the line-shape of the magnetic excitations. $CuGeO_3$ (space group $Pbmm$, with c as the chain axis) is the first known inorganic compound to exhibit a spin–Peierls phase transition. The magnetic sublattice (formed by $S = \frac{1}{2}$ Cu^{2+} ions) lacks long-range order [1], and the magnetic response arises from triply degenerate excited states, well separated from the non-magnetic singlet ground state by a gap. X-ray [2] and neutron diffraction [3] experiments have confirmed the presence of a very weak lattice superstructure which develops at a temperature $T_{SP} \sim 14$ K. At the same temperature the spin-triplet gap opens, with a modulation wavevector $\boldsymbol{k}_{SP} = (\frac{1}{2}\,0\,\frac{1}{2})$. This magnetoelastic coupling in quantum chains has been reported for other spin-$\frac{1}{2}$ compounds and is a signature of the spin–Peierls state. Nishi *et al* [4] and Regnault *et al* [5] have measured the dispersion curve of the magnetic excitations along the main crystallographic directions and have shown that the zone centre of the magnetic sublattice is located at $(0\,1\,\frac{1}{2})$ and equivalent reciprocal-lattice points. However, the values of the spin-exchange constants raise some fundamental questions: for example, the exchange constant along the chain direction, J_c, determined by INS is relatively small ($2J_c \approx 120$ K) compared to that reported for other Cu chain compounds like Sr_2CuO_3 (of the order of 1000 K, reference [6]). In the light of this result, Castilla *et al* [7] and

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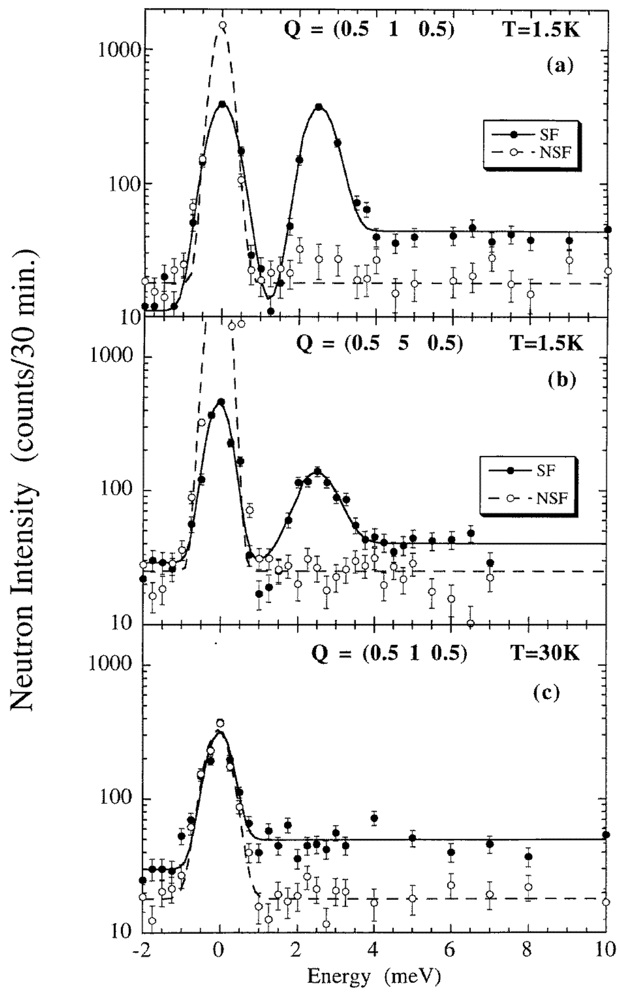

Figure 1. Neutron scattering data with spin-polarization analysis taken at constant final energy (14.7 meV or 2.662 Å^{-1}) at different temperatures and $\boldsymbol{Q}$-positions. Full circles represent the spin-flip (SF) channel and open circles the non-spin-flip (NSF) channel plotted on logarithmic scales. The continuous and dashed lines are guides to the eye.

Haas and Dagotto [8] have emphasized the role played by the second-neighbour intrachain interactions in the understanding of the magnetic properties of such systems. In addition, the interchain coupling constant J_b is only ten times smaller than J_c, which means that this compound cannot be regarded as a *very* good realization of a QHAFC. This ratio is several orders of magnitude larger than those for previously studied quantum chain compounds like NENP (reference [9]) and $KCuF_3$ (reference [10]).

The goal of our letter is threefold. First, we will show that there is a continuum of triplet excitations, as in other $S = \frac{1}{2}$ prototypical quantum chain compounds. Second, we will show that the spectral weight associated with this continuum is greatly reduced and that the line-shapes cannot be reproduced by the standard theory developed for *strictly* 1D quantum chains. Finally, we will prove that the spin gap does not vanish at T_{SP}, but remains finite over a narrow range of temperatures above T_{SP}.

Our polarized INS experiments were performed on the IN20 triple-axis spectrometer (TAS) located on a thermal beam at the Institute Laue–Langevin. The incident and final neutron energies were selected from a vertically focused Heusler Cu_2MnAl monochromator and analyser, respectively. The spectrometer was set in the constant-k_f mode, with $k_f = 2.662$ Å^{-1} and collimation of 60′–60′–60′–60′. Guide fields between 20 and 30 G were used to maintain the polarization along the neutron trajectory. The polarization direction at the sample position was controlled by means of a system of coils allowing a field of the order of 30 G to be applied, either vertically or horizontally. In both magnetic field configurations, the flipping ratio was typically measured to be 18. In addition, high-resolution INS experiments were performed on the cold-neutron IN14 TAS working with a fixed final wavevector of $k_f = 1.55$ Å^{-1}. In this case, the incident energy was selected from the (002) reflection of a pyrolitic graphite monochromator. We have used a Si(111) analyser and 40′–40′–40′–40′ collimation to improve the resolution in energy ($\Delta_\omega \approx 0.11$ meV).

Quantum field theories and numerical calculations in QHAFC have shown that the dynamical correlation function is completely different to that of classical antiferromagnetic chains. Instead of being described by a δ-function in energy, the magnetic response is believed to display a continuum of magnetic excitations [11], limited on the low- and high-energy sides by two threshold values: $\omega_n(q) = n\pi J_c \sin(qc/n)$ ($n = 1, 2$ with $J_c \approx 5$ meV in our notation). Recent INS experiments on $KCuF_3$ have clearly demonstrated the existence of such a continuum in the purely isotropic case [10]. In order to verify its existence in $CuGeO_3$, we have measured the magnetic response using polarized neutrons and conventional polarization analysis. The measurements were performed at scattering vectors $\boldsymbol{Q} = (\frac{1}{2}\,k\,\frac{1}{2})$, with k odd, which correspond to superlattice peaks associated with the dimerization and with the zone boundary of the magnetic Brillouin zone along $\boldsymbol{a}^*$. In the various scans, the polarization field was maintained parallel to $\boldsymbol{Q}$. This allowed an unambiguous separation of lattice and magnetic contributions to be achieved, the former being detected in the non-spin-flip (NSF) channel and the latter in the spin-flip (SF) channel. In all cases, the raw data were corrected for the finite flipping ratio. Figures 1 show the resulting data, which demonstrate unambiguously for the first time the presence of a continuum of magnetic excitations in $CuGeO_3$. Figure 1(a) depicts the results obtained at 1.5 K and at the scattering vector $\boldsymbol{Q} = (\frac{1}{2}\,1\,\frac{1}{2})$, for which the lattice contribution is expected to be small and the magnetic contribution strong. Due to the configuration used, the SF channel contains part of the nuclear spin incoherent scattering (centred at zero energy) and the contribution from the magnetic excitations (solid line). The NSF channel contains the superlattice Bragg peak contribution, the isotopic incoherent scattering, part of the nuclear spin incoherent scattering (all three centred at zero energy), and all other lattice contributions. Within the experimental error, no additional *lattice* contribution was detected between 1 and 12 meV. In fact, the NSF contribution above 1 meV was used in the analysis as a good estimate of the background contribution. The SF contribution above 1 meV shows a well defined peak centred at 2.5 meV (maximum intensity of the order of 400 neutrons/30 min), with a very slowly decreasing tail extending at least up to 12 meV (maximum intensity of the order of 35 neutrons/30 min). Similar results were obtained at the higher scattering vector $\boldsymbol{Q} = (\frac{1}{2}\,5\,\frac{1}{2})$, which is associated with a strong superlattice Bragg peak. These data are shown in figure 1(b). Consistent with the previous measurements at $\boldsymbol{Q} = (\frac{1}{2}\,1\,\frac{1}{2})$, no additional lattice excitations could be observed at this position, whereas a clear magnetic signal remains, although the amplitude is smaller. The peak at 2.5 meV has been associated with the spin-gap previously observed [4, 5] and shifted slightly in energy by the interchain couplings along the $\boldsymbol{a}$-axis. By analogy with the case for the pure QHAFC, we have attributed the extra intensity observed above the gap to the existence of a continuum of triplet excited states. Figure 1(c) shows the evolution of the dynamic response at the point $\boldsymbol{Q} = (\frac{1}{2}\,1\,\frac{1}{2})$, and $T = 30$ K, a temperature well above T_{SP}. In comparison with the scans in figure 1(a), the latter scans are characterized by the disappearance of both the superlattice Bragg peak (the NSF channel) and the gap mode (the SF channel). Consequently, above T_{SP}, the magnetic response is mainly governed by the continuum. Qualitatively, one estimates that the spectral weights associated with the gap mode and the continuum are roughly equivalent. In agreement with unpolarized INS experiments by Hennion and Aïn [12], we have not found any additional phonon mode in the energy range 0–12 meV. This result is important and questions the standard model, which predicts the structural distortion as arising from the condensation of a soft phonon. We will return to this point below.

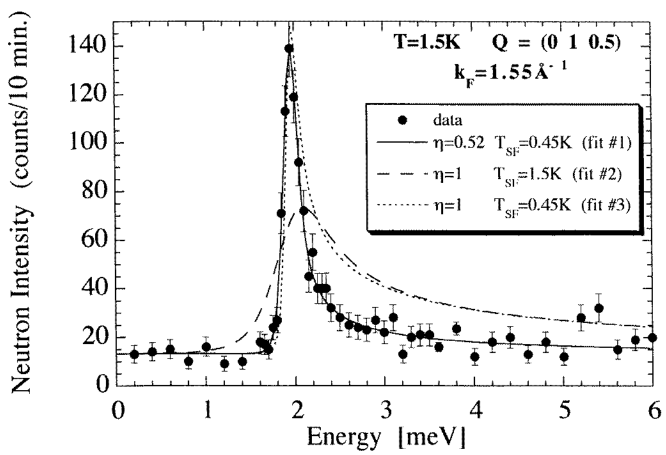

Figure 2. High-resolution inelastic neutron (non-polarized) scans at the zone centre of the magnetic Brillouin zone, $\boldsymbol{Q} = (0\,1\,\frac{1}{2})$, at 1.5 K. The continuous line is the fit to equation (1) with all parameters free; the dashed line is the calculation with $\eta = 1$ and $T_{SF} = 0.45$ K; finally the dotted line is the calculation with the values of η and T_{SF} expected for a pure quantum spin-$\frac{1}{2}$ antiferromagnetic chain compound. The energy of the gap at $T = 1.5$ K is $\Delta = 1.93 \pm 0.03$ meV.

A central question regarding $CuGeO_3$ concerns the existence of a spin gap in the magnetic excitation spectrum above T_{SP}. Our polarized INS data have shown the absence of such a feature at 30 K (figure 1(c)). However, the presence of a spin gap could explain the anomalous shape of $\chi(T)$ (reference [1]) and the structural correlations observed well above T_{SP} (reference [2]). In order to check its existence, a high-resolution INS study on the temperature dependence of the magnetic response was performed on the IN14 TAS. Figures 2 and 3 show typical constant-$\boldsymbol{Q}$ scans performed at the scattering vector $\boldsymbol{Q} = (0\,1\,\frac{1}{2})$ and at various temperatures below and above T_{SP}. In these experiments, the instrument resolution conditions ($\Delta_q \approx 0.008$ Å^{-1} and $\Delta_\omega \approx 0.11$ meV) were such that the line-shapes are almost free from dispersion curve integrations, and hence one can compare them straightforwardly with predicted theoretical calculations. Qualitatively, the magnetic response at $T = 1.5$ K and $\boldsymbol{Q} = (0\,1\,\frac{1}{2})$ appears clearly peaked at an energy of about 2 meV (i.e. the energy of the gap) and displays a tail extending at least up to 6 meV. The latter feature is a trace of the continuum, reduced in intensity with respect to the previous polarized INS measurements

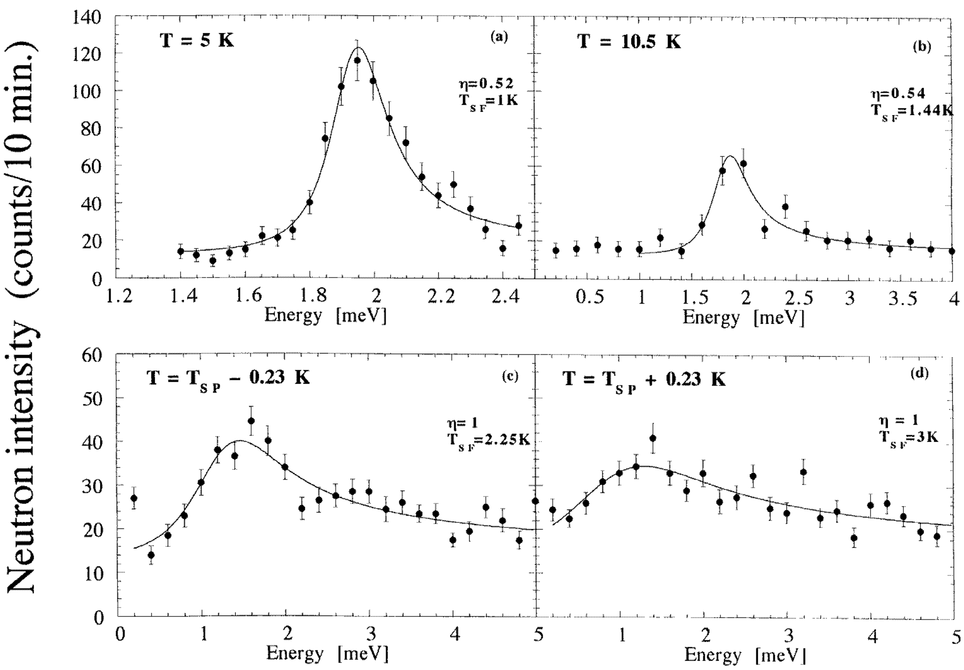

Figure 3. As figure 2, but for different temperatures. Continuous lines are fits to equation (1) with η, T_{SF}, and Δ the fitted parameters.

due to the smaller volume of the resolution ellipsoid. Our measurements show qualitatively that, when the temperature increases, the gap energy decreases slightly whereas the damping increases strongly.

Cross and Fisher [13] proposed an analytical functional form for $S(q,\omega)$ for the Heisenberg spin–Peierls system based on the work of Luther and Peschel [14], where the spin–phonon coupling is treated in the mean-field approximation. Taking into account the general result obtained by Schulz [15] in the case of a QHAFC, the dynamical correlation function used in the analysis of our data for $CuGeO_3$ can be written as follows [14]:

$$S(q,\omega) \propto (n(\omega)+1)\,\mathrm{Im}\left\{T_{SF}^{\eta-2} B\left[\frac{\eta}{4} - \frac{\mathrm{i}}{2}\frac{\omega-\Delta+\nu q}{2\pi T_{SF}}, 1-\frac{\eta}{2}\right]\right.$$
$$\left.\times\ B\left[\frac{\eta}{4} - \frac{\mathrm{i}}{2}\frac{\omega+\Delta-\nu q}{2\pi T_{SF}}, 1-\frac{\eta}{2}\right]\right\} \qquad (1)$$

with $B(x,y) = \Gamma(x)\Gamma(y)/\Gamma(x+y)$, where Γ is the gamma function, $n(\omega)$ is the Bose factor, Δ the spin-triplet gap, T_{SF} a parameter characterizing the energy scale of magnetic fluctuations (related to the damping of the gapped mode), ν the spin-wave velocity, and η a characteristic exponent describing the decay of the spin–spin correlation function. For a HAF chain system this exponent is 1, whereas one has $\Delta = 0$ and $T_{SF} = T$. Tennant *et al* [10] have obtained excellent fits of their INS data on $KCuF_3$ using this functional form. From equation (1) it is easy to verify that the response function becomes progressively more peaked as $\eta \to 0$ (implying a correlation function that is less and less rapidly decaying). A quantitative analysis of our data has been undertaken using equation (1), with η and T_{SF} as adjustable parameters. Figure 2 shows different fits for data taken at 1.5 K. The fit corresponding to the model parameters ($\eta = 1$ and $T_{SF} = 1.5$ K) yields a very poor agreement, especially on the high-energy side (fit No 2). In addition, fit No 2 does not reproduce the sharp line-shape which was observed below the energy gap. The best fit (fit No 1) is obtained for the strongly renormalized parameters $\eta = 0.52$ and $T_{SF} = 0.45$ K. To better understand the origin of this discrepancy we have calculated the dynamical correlation function for the set of parameters $\eta = 1$ and $T_{SF} = 0.45$ K (fit No 3). Clearly, fits No 2 and No 3 both overestimate the continuum of excitations with respect to fit No 1. So, the sharpness of the resonance and the reduced continuum are both consequences of the small value of η obtained in the fitting procedure. On the basis of the similarity with classical phase transitions, we attribute the small value of η ($\sim\frac{1}{2}$) to the quasi-2D character of the magnetic interactions in $CuGeO_3$ (remember that $J_b/J_c \sim 0.1$ and $J_a/J_c \sim 0.01$).

The same analysis has been applied to the data which were obtained at higher temperatures. The solid lines in figures 3(a), 3(b), 3(c) and 3(d) are the best fits with the parameters η and T_{SF} which depend monotonically on the temperature. As $T \to T_{SP}$ the parameter η recovers a value consistent with theory ($\eta \sim 1$), whereas T_{SF} remains roughly a factor of four times smaller than T. Although Schulz [15] has discussed the phase diagram of the QHAFC, predicting different types of magnetic ground state depending on the value of the exponent η, we cannot explain, under this formalism, the temperature behaviour of both η and T_{SF}. The conclusion of our analysis is that the analytical expression of the dynamical correlation function obtained for 1D HAF systems does not satisfactorily describe our experimental results, though it accounts well for the observed line-shapes.

This failure may be attributed to the fact that interchain interactions are much more relevant in $CuGeO_3$ than, for example, in $KCuF_3$. The deviation from one dimensionality may explain the smaller weight of the continuum of excitations which was observed, and the relatively small values of the characteristic energy scale T_{SF}.

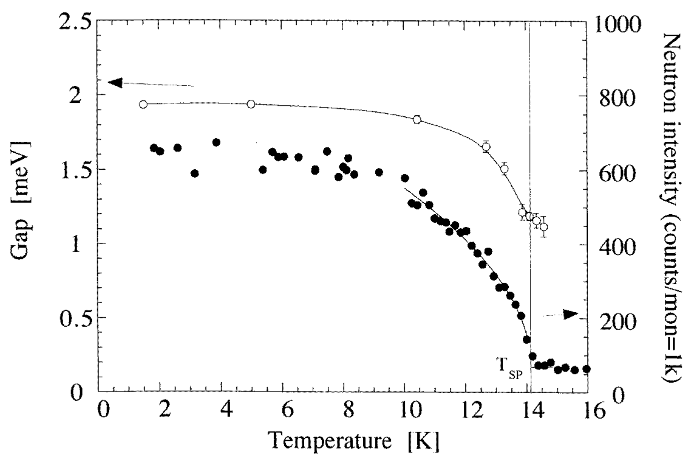

Figure 4. The temperature dependence of the gap (open circles), and of the intensity of the $(\frac{1}{2}\,3\,\frac{1}{2})$ superlattice reflection (full circles). The value of the gap is $\Delta = 1.2 \pm 0.05$ meV at $T_{SP} = 14.1$ K.

Despite this difficulty, we have used equation (1) to analyse quantitatively the data for temperatures close to T_{SP}. Typical results are shown in figures 3(c) and 3(d). The fits are satisfactory and provide us with a finite value for the spin gap right above T_{SP}. This result is in contrast with previous INS data [4] and questions the validity of the interpretation of the phase transition in $CuGeO_3$ as arising from a spin–phonon interaction. By analogy with the case for low-dimensional metals undergoing a Peierls transition we term the gap of the magnetic fluctuations a 'pseudogap' (reference [16]). In these measurements the central issue is that of accurately determining the phase transition temperature, as the range of temperatures where the line-shape of the spin-triplet excitations is well defined is very narrow, spanning only 1 K above T_{SP}. In figure 4 we show the temperature dependence of the gap Δ, T_{SF}, and of the intensity of the $(\frac{1}{2}\,3\,\frac{1}{2})$ superlattice reflection obtained for the same sample and the same sample environment conditions. From these measurements, one estimates $T_{SP} = 14.1 \pm 0.05$ K. Above 15 K, the magnetic excitations are clearly observed but we cannot obtain *reliable* values for the pseudogap. For example at $T = 15.05$ K, the best fit was achieved with a finite value of the pseudogap $\Delta \sim 0.6$ meV, which suggests a rapid vanishing of the pseudogap above T_{SP}.

In summary, we have shown in this letter that the continuum of excitations, the signature of the quantum character of the magnetism in $CuGeO_3$, is greatly suppressed with respect to the expected value for a QHAFC compound. In the light of the work of Castilla *et al* [7] this is a striking result, as the competing interactions that they propose in their model should enhance quantum fluctuations. We have found out that interchain interactions are important and that they *do* affect the critical behaviour close to T_{SP}. In fact this is not surprising, as all known antiferromagnetic chain-like compounds order three dimensionally at sufficiently low temperatures [17]. The presence of a pseudogap can be understood as a manifestation of the competing interactions above T_{SP}, and of the very-low-energy lattice fluctuations. The lack of a phonon soft mode, with a larger characteristic energy scale than the magnetic fluctuations, is also consistent with the presence of the pseudogap.

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