Temperature Evolution of the Quantum Gap in CsNiCl₃

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Neutron scattering measurements on the one-dimensional gapped S=1 antiferromagnet, CsNiCl₃, have shown that the excitation corresponding to the Haldane mass gap Δ at low temperatures persists as a resonant feature to high temperatures. We find that the strong upward renormalisation of the gap excitation, by a factor of three between 5 and 70 K, is more than enough to overcome its decreasing lifetime. We find that the gap lifetime is substantially shorter than that predicted by the scaling theory of Damle and Sachdev in its low temperature range of validity. The upward gap renormalisation agrees with the non-linear sigma model at low temperatures and even up to T of order 2Δ provided an upper mass cutoff is included.

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The excitations of one-dimensional (1D) Heisenberg antiferromagnets have attracted much experimental and theoretical attention ever since Haldane predicted that the excitations of integer spin and half-integer spin chains are different. It is now well established that for half-integer chains the excitations have a continuous spectrum extending to zero energy while for integer spin chains there is an energy gap at low temperatures. How the excitations evolve into quasielastic paramagnetic scattering in the high temperature limit is unknown. Recently, the temperature dependence of the gap excitation for an integer spin chain has been discussed by Damle and Sachdev (DS) using the O(3) sigma model of the low temperature excitations. They derive an expression for the temperature dependence of the inelastic neutron scattering line-shape that should apply to all 1D systems that have a gap Δ in the excitation spectrum at low temperatures, k_B T < Δ. They also derive a scaling form for the scattering in energy, momentum and temperature. We have measured the temperature dependence of the neutron scattering and compare the results with the theory. Good agreement is obtained with the predicted line-shape, but the theory fails to describe the observed lifetimes of the excitations. Our results further show that the excitation has a resonant form for high temperatures T of order of the bandwidth of the excitation 2.7J or 6Δ.

The experiments were performed using the quasi-1D antiferromagnet, CsNiCl₃. Previous neutron scattering experiments have shown that the spin excitations of its disordered phase above 4.85 K have an energy gap as predicted by Haldane for S=1 chains, while the excitation is a spin triplet and the dispersion of the excitations has 2π periodicity showing that the symmetry of the spin chain is not broken. All of these properties are consistent with the properties expected for a quantum disordered phase close to a quantum critical point. The bare exchange interaction J along the hexagonal c-axis of the chains is 2.28 meV, the inter-chain interaction J′ is 0.044 meV and the Hamiltonian can be written as

\[ H = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + J' \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j - D \sum_i (\vec{S}_i^2)^2. \] (1)

The single-ion anisotropy D of 4 μeV is small so that CsNiCl₃ is a good example of an S=1 isotropic antiferromagnetic (AF) chain system. The upper limit of the excitation band, 6 meV, is 30% larger than 2J because of quantum renormalisation. Below 4.85 K the inter-chain interactions give rise to three-dimensional (3D) long range AF order. In this 3D phase longitudinal and transverse excitations have been observed and arise from the breaking of the triplet symmetry of the high temperature excitations.

A single crystal of CsNiCl₃ 20 mm × 5 mm × 5 mm was mounted in a cryostat with its (hhl) crystallographic plane in the horizontal scattering plane of the neutron scattering instrument, and the temperature was controlled with an accuracy of 0.1 K between 1.5 and 70 K. The experiments were performed with the RTIA triple axis crystal spectrometer at the DR3 reactor of the Risø National Laboratory. The energy of the neutrons thermalised in a cold source was selected by a vertically focusing pyrolytic graphite monochromator. A rotating velocity selector before the monochromator suppressed unwanted neutrons that would be Bragg reflected by its higher order planes. Supermirror guides with n = 3 (θ_c = 1.2° at 4 Å) were located before and after the monochromator, and the beam was 20 mm wide. The scattered neutron beam was filtered through cooled beryllium, passed through a 50 mm wide 1° Soller collimator, and analysed by reflection from the central two blades of a 7-component flat pyrolytic graphite analyser aligned so that each blade reflected the same energy of neutrons, 5 meV. The Soller geometry meant that the beam reflected by the analysers was about 20 mm wide and located in the central 30 strips of a position sensitive detector. Because the detector was 120 pixels wide (~ 120 mm) the side strips were used to estimate the temperature independent background, which was sub-
tracted from the data. Turning of either analyser or monochromator from their reflecting position confirmed that the side pixels gave a good representation of the background arriving at the centre of the detector with the signal. With this arrangement the low-energy resolution was typically 0.26 meV (FWHM) in energy. The longitudinal and transverse wave-vector width of the (002)-peak was 0.01 and 0.016 (FWHM in reciprocal lattice units) and the calculated vertical resolution was 0.22 Å⁻¹.

Measurements were made for wave-vector transfers along the [ηη1] direction, which corresponds to a π phase difference between the Ni spins along the chains. In the absence of the interactions between the chains, the energy of the spin excitations would be independent of the wave vector perpendicular to the chain direction or c-axis. There is however a significant dispersion that is proportional to the Fourier transform of the inter-chain exchange interactions. The minimum of the dispersion relation along the [ηη1] direction occurs when η = 1/3, which is the ordering wave vector of the low-temperature AF structure. For most of our measurements we set η = 0.81, where the Fourier transform of the inter-chain interactions is zero, so that to first order our results are characteristic of independent S=1 chains. Scans were performed by varying the energy transfer between 0 and 13.5 meV, and were repeated for 16 temperatures between 1.5 and 70 K.

The results for two temperatures are shown in Fig. 1. It is clear that both the energy and the width of the excitations increase rapidly with increasing temperature. Surprisingly we find that the excitations are reasonably well defined up to 70 K.

FIG. 1. Neutron scattering intensity at 9 K and 50 K at (0.81 0.81 1) wave-vector transfer as a function of energy transfer. The energy resolution ∆ = 0.26 meV is shown as a horizontal bar. The solid line is a fit of a Gaussian to the quasi-elastic peak and a double Lorentzian for the magnetic excitation as explained in the text.

The experimental results were analyzed by fitting the results at low temperature, 1.5 K, to a Lorentzian form, which gave a better fit than the Gaussian form. At this temperature the magnetic structure is an ordered antiferromagnet and the excitation is expected to be a long-lived spin wave. We therefore assume that the width of 0.26 meV at 1.5 K is a good measure of the experimental resolution function. As the temperature is raised in the 1D phase the response is found to have a Lorentzian spectral form (Fig. 1). This is in agreement with the DS prediction based on a model of collisions between the injected Q = π spin excitation and a gas of thermally activated excitations near the bottom of the gapped band. The gas particles were given classical dispersion. Our data was described by a constant background, a quasi-elastic Gaussian for the incoherent scattering, and, for the excitation, a double Lorentzian form:

\[
S(E) = A \cdot (n(E) + 1) \cdot \frac{\Gamma}{(E - \epsilon(0))^2 + \Gamma^2} - \frac{\Gamma}{(E + \epsilon(0))^2 + \Gamma^2},
\]

where \( E \) is the energy transfer, \( n(E) \) is the Bose factor, the energy width is given by \( \Gamma \) and the gap energy by \( \epsilon(0) \) and \( A \) is a constant. The parameters \( \Gamma, \epsilon(0) \) and \( A \) were fitted at each temperature and, as shown in Fig. 1, the model gave a good description of the data. The results for the widths are shown in Fig. 1 and the resonant energies \( \epsilon(0) \) are shown in Fig. 1. Both show a rapid initial increase with increasing temperature. By a temperature of about 2\( J/k_B \) the energy has increased by more than a factor of 3 and the excitation is still well defined. We have found that a non-resonant overdamped Lorentzian cannot account for the data at any temperature. This confirms that the excitations remain as a resonance to high temperatures.

The temperature dependence of the excitations in CsNiCl₃ has also been studied by Zaliznyak et al. They measured, however, were at the 3D minimum of the excitations at a wave-vector transfer of (0.33,0.33,1) and for temperatures below 20 K. They observed an increase in the line-width and energy with increasing temperature but their results are strongly influenced by 3D effects and so cannot be directly compared with the theory of quantum disordered chains.

The initial motivation for these experiments was the theory of the neutron scattering cross-section in 1D gapped antiferromagnets by DS. They suggested that for \( k_B T < \Delta \) the cross-section is given by a scaling form:

\[
S(Q, E) = \frac{A e}{\Gamma \Delta} \Phi \left( \frac{E - \epsilon(q)}{\Gamma} \right)
\]

where \( A \) is a constant. They described the dispersion of the excitations by a classical approximation to the non-linear sigma model (NLσM) namely:

\[
\epsilon(q) = \Delta + \frac{e^2 q^2}{2\Delta}.
\]

The difference between the wave-vector transfer, \( Q \), and the AF wave vector is \( Q - \pi = q \). The energy broadening is proportional to the density of excited excitations times their root mean square velocity, which DS obtain analytically as

\[
L^{-1}_q = \Gamma = \frac{3k_B T}{\sqrt{\pi}} \exp \left( -\frac{\Delta}{k_B T} \right),
\]

where \( L_q \) is the excitation lifetime. The scaling function \( \Phi(z) \) was calculated numerically and is found to be given closely by a Lorentzian form:

\[
\Phi(z) = \frac{\pi \alpha}{2(\alpha^2 + z^2)}
\]

with the constant \( \alpha = 0.71 \sim 1/\sqrt{2} \). Thus the theory predicts that the observed half-width should be \( \alpha \cdot \Gamma \), with \( \Gamma \) from Eq. 1.
In the case of CsNiCl$_3$, the energy gap at absolute zero cannot be reliably obtained because it enters the 3D phase transition below 4.85 K. The best estimate is obtained from the exchange constants, in agreement with an earlier estimate, using the relation $\Delta_0 = 0.41J$ to give $\Delta_0 = 0.93$ meV $\approx 11$ K.

**FIG. 2.** The half-width, $\Gamma$, of the excitation. The points are the experimental half-widths and the solid line is the NL\(\sigma\)M prediction by DS. The inset shows the widths for $T < 15$ K. The dashed line is our modification of the DS theory to include the relativistic dispersion.

In Fig. 2 we compare the half-width of the excitations with the prediction of $\sigma^{-1}$ from Eq. 5 and 6 with $\Delta = \Delta_0$, the gap at $T = 0$ K. For low temperatures, $k_B T < \Delta$, where the theory is applicable, the theoretical widths are much less than the observed widths. Around 10 K, the experimental widths are about 40% times the predicted width. This discrepancy may be due indirectly to 3D interactions which are still appreciable in this temperature range. The energy of the spin excitation measured at the 1D point, (0.81 0.81 1), up to 15 K are noticeably larger than at the 3D ordering wave vector, but it is lower than at other wave-vectors, but the average effect may still not fully cancel at the 1D point we have selected to study. However, good agreement between theoretical and experimental width is achieved, we have found (Fig. 2), if the classical dispersion in DS’s model is replaced by the relativistic dispersion of the non-linear sigma model NL\(\sigma\)M ($\epsilon(q) = (\Delta^2 + q^2)^{1/2}$). The calculation of $\Delta$ must be done numerically. At temperatures above about 20 K, the rate of increase in the observed width decreases, an effect which is not reproduced by the theory. In this temperature region the NL\(\sigma\)M is no longer expected to apply. We find that including the temperature dependence of the excitation energy does not improve the agreement of the theory.

**FIG. 3.** The measured excitation energy is compared with the theoretical predictions. The solid line is the prediction of Jolicoeur from the NL\(\sigma\)M and the dashed line is the model of Köhler and Schilling. The inset shows the gap for $T < 15$ K compared with the prediction of the NL\(\sigma\)M.

The energy of the excitation shown in Fig. 3 increases by a factor of 3.8 from 1.22 meV at 5 K to 4.6 meV at 70 K. This substantial increase in the excitation energy of a gapped quantum chain has not been previously reported and contrasts with the decrease seen in most two- and three-dimensional antiferromagnets. This fast upward renormalisation is the reason that the excitation remains resonant to high temperatures, much higher than observed in earlier surveys of the temperature dependence of the excitation energy. The measured energy at 9 K agrees well with the original estimate of the energy.

The upward renormalisation of the excitation energy is compared in Fig. 3 with the calculation based on the self-consistent NL\(\sigma\)M theory of Jolicoeur and Golinelli using $\Delta_0 = 0.93$ meV and a relativistic dispersion. The theory describes the measured energy quite well between 8 and 15 K, where it predicts a slightly lower gap energy than observed. The difference of a few percent lies within the error of $J$, with which the predicted gap energy scales for all $T$. The upward gap renormalisation is not included in the theory by DS, although their theory should be valid for $k_B T < \Delta = 11$ K.

Below 6 K, the observed energy flattens off with decreasing temperature. This is possibly because, as the Néel temperature is approached, the interactions between the chains reduce the effective excitation energy so that the gap must become larger than for a pure 1D system, so as to conserve the total spin. The greater thermal excitation increases the gap energy above that of the purely 1D NL\(\sigma\)M.

The decreasing temperature dependence of the measured excitation energies above 50 K contrasts with the steadily increasing gap energy of the NL\(\sigma\)M. This partly reflects the assumption of an infinitely large distribution of possible energies in the continuum NL\(\sigma\)M. If we constrain the upper momentum to $2\pi$ because of the lattice, the energies tend to level off at higher temperatures. It is recognized, however, that the mapping of the 1D Heisenberg Hamiltonian to the NL\(\sigma\)M is not applicable at such high temperatures.

Köhler and Schilling have described the temperature dependence of the excitations in terms of a restricted set of zero-spin defect states and treated them with a Hartree-Fock approximation. Their result describes the energy very well for $T < 20$ K (Fig. 3), but only if $J = 2.8$ meV is used as fit parameter. At higher temperatures, the theory predicts a levelling off of the energy as observed, but it underestimates the energy in the high temperature limit. The upturn of the energy at low temperatures may be an artefact of the theory.

The excitation remains resonant up to at least 70 K $\sim 2.7J$. This is more than twice the temperature of the maximum in the magnetic susceptibility and in the specific heat, which has previously been taken to indicate the breaking of the 1D correlations. Our results are in sharp contrast with a quantum Monte Carlo calculation where the peak in the spectral function persists only to $0.5J \sim 13$ K.

In summary, we find
1. that the excitations for the AF wave-vector persist as a resonant feature at temperatures greater than the spin band energy;
2. that a scaling form of the theory, in its expected range of validity, overestimates the lifetime of the excitations by 40%;
3. that the upward renormalisation of the energy of the excitations predicted by the NL\(\sigma\)M theory is accurate only in a narrow range and fails at high temperatures.

A theory is needed that includes the persistence of the resonance, the strong temperature dependence of the excitation energy, and the correct line-width.
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CsNiCl$_3$ (0.81 0.81 1)

$\Delta E = 0.26$ meV

$T = 9$ K

$T = 50$ K
