Multiparticle States in the $S = 1$ Chain System $CsNiCl_3$

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A continuum of magnetic states has been observed by neutron scattering from the spin-1 chain compound $CsNiCl_3$ in its disordered gapped one-dimensional phase. Results using both triple-axis and time-of-flight spectrometers show that around the antiferromagnetic point $Q_c = \pi$, the continuum lies higher in energy than the Haldane gapped excitations. At 6 K the integrated intensity of the continuum is about 12(2)% of the total spectral weight. This result is considerably larger than the 1%−3% weight predicted by the nonlinear sigma model for the three-particle continuum.

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The excitations of one-dimensional (1D) Heisenberg antiferromagnets have attracted much experimental and theoretical attention ever since Haldane [1] predicted that the excitations of integer spin and half-integer spin chains are different. Half-integer spin chains have no spin gap and exhibit a spinon continuum extending to zero energy [2,3]. For integer-spin chains the spectrum is at low temperatures dominated by well-defined single particle excitations corresponding to a triplet of spin-1 particles that exhibit a large energy gap [4,5]. These have been thoroughly studied by neutron scattering from spin-1 chain compounds, and it has been shown for $Ni(C_2H_8N_2)_2NO_2ClO_4$ that the well-defined excitations largely exhaust the total scattering [6]. Nonetheless, a continuum of multiparticle scattering was predicted by Haldane and others [7], but as yet no experiment has established its existence. To search for such a continuum we have measured the inelastic neutron scattering of $CsNiCl_3$ in its paramagnetic 1D phase using time-of-flight and triple-axis spectrometers. We have detected a neutron scattering continuum, shown that it extends to energies much higher than the well-defined particle excitation, and find that its spectral weight is larger than predicted for multiparticle scattering.

$CsNiCl_3$ is a quasi-1D spin-1 chain compound in which the Ni chains are antiferromagnetically coupled along the c axis of the hexagonal unit cell. The Hamiltonian is

$$H = J \sum_{i}^{\text{chain}} \vec{S}_i \cdot \vec{S}_{i+1} + J' \sum_{\langle i,j \rangle}^{\text{plane}} \vec{S}_i \cdot \vec{S}_j - D \sum_i (\vec{S}_i^z)^2. \tag{1}$$

The exchange interaction $J = 2.28$ meV along the c axis is much stronger than the exchange interaction in the basal plane $J' = 0.044$ meV [4,8,9]. The weak Ising anisotropy $D = 4$ μeV is small enough that $CsNiCl_3$ is a good example of an isotropic Heisenberg antiferromagnet. Below $T_N = 4.85$ K the interchain coupling causes long-range ordering of the magnetic moments. Above T_N $CsNiCl_3$ is in a 1D magnetic phase for which the magnetic exchange interaction along the c axis dominates the spin dynamics.

The sample of $CsNiCl_3$ was a single crystal $20 \times 5 \times 5$ mm^3 and was mounted with its (hhl) crystallographic plane in the scattering plane. Inelastic neutron scattering experiments were carried out with the time-of-flight spectrometer, MARI, at the ISIS facility of the Rutherford Appleton Laboratory and with reactor-based triple-axis spectrometers, DUALSPEC at the Chalk River Laboratories and RITA at Risø National Laboratory.

For the experiment using MARI the incoming neutron energy was 20 and 30 meV. The scattered neutrons were detected in three detector banks arranged in a half circle vertically below the sample. The energy resolution was 0.35 and 0.4 meV, as determined from the full width at half maximum of the quasielastic peak. The resolution in wave-vector transfer at zero energy transfer was typically 0.02 Å^{-1} along the $c^\star$ axis and along the [110] direction and up to 0.19 Å^{-1} perpendicular to the scattering plane. The measurements at the DUALSPEC triple-axis spectrometer were performed at 8.5 K with a fixed scattered neutron energy of 14.51 meV and with a graphite filter to absorb the higher order reflections from the pyrolytic graphite monochromator and analyzer. The collimation from reactor to detector was 0.65°-0.6°-1.4°-2.0° and gave an energy resolution of 1.94 meV. In the case of the RITA triple-axis spectrometer, supermirror guides and a rotating velocity selector produced a variable energy monochromatic neutron beam which suppressed higher order contamination. The scattered neutrons were analyzed using the Soller geometry with a fixed energy of 5 meV and a cooled beryllium filter between the sample and analyzer. The effective collimation was 1.45°-1.45°-1°-2.0° and the energy resolution was 0.35 meV.

The measurements with MARI at temperatures between 6.2 and 12 K were performed with the c axis of the sample either perpendicular or parallel to the incoming beam. The dynamic structure factor $S(\vec{Q}, \omega)$ was measured for wave-vector transfers along the c axis between $l \simeq 0.175$ and ~ 1.5, where the wave vector along the chain is $\frac{2\pi l}{c}$. Because there are two Ni atoms in each unit cell along c, $l = 1$ corresponds to the antiferromagnetic (AF) wave vector, π, generally used in theoretical work on AF chains. The data with $l > 1.5$ were contaminated by phonon scattering, and so no analysis of the magnetic contribution was then attempted.

Constant-l scans were constructed from the measured $S(\vec{Q}, \omega)$ by mapping on (l, ω) space (Fig. 1). These data were then averaged in stripes with a width $\Delta l = 0.05-0.10$ and corrected for neutron absorption. Figure 1 shows directly the continuum scattering. It is stronger at AF momenta around $l = 1$ than in the region near $l = 0.2$, which is known to carry vanishing magnetic weight [10], and the zone boundary region $l = 0.5$. A detailed description of the analysis of the experiment will be given elsewhere [11]. Here we focus on the scattering close to the AF point. We take data only from the central detector bank so as to limit the wave vectors sampled to lie close to the (hhl) plane. As shown in Fig. 2a the response at $l = 1$ consists of the sharp mode observed previously but also has a component that extends to high frequencies. This continuous spectrum has not been observed before. It is well above background and moreover is seen to be much larger than the scattering near $l = 0$ where the magnetic scattering is expected to be vanishingly small [10]. We will show below that the continuum cannot arise from resolution broadening of the well-defined mode.

The magnetic excitations in the MARI experiment were best fitted by an antisymmetrized Lorentzian peak weighted with the detailed balance factor and convoluted with the line shape of the quasielastic incoherent scattering, which is a good estimate of the resolution line shape particularly at low energy transfers. An intrinsic Lorentzian peak is supported by a recent theoretical prediction [12] and a recent experiment [13]. It gives an excellent fit to the low energy resonant Haldane peak. Nevertheless, we see in Fig. 2a that the scattering intensity at energies above the gap energy is significantly higher than expected from the fits to the sharp peak. The continuum scattering is clearly observed for $0.6 < l < 1.4$

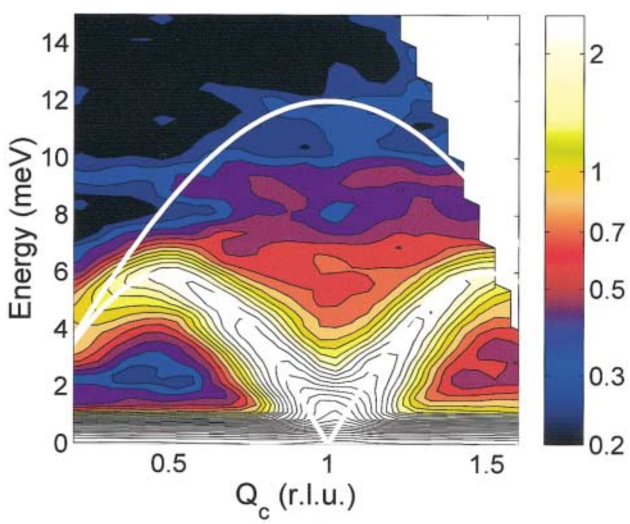

FIG. 1 (color). The neutron scattering intensity observed using MARI as a function of energy transfer and wave-vector transfer along the [001] direction. The data shown are averages of measurements at 6.2 and 12 K measured in all three detector banks of MARI and are given on a logarithmic scale. The intense band of scattering arises from the well-defined Haldane modes and the scattering continuum is at higher energies up to ~ 12 meV for $0.6 < l < 1.4$. The solid lines are the boundaries of the continuum that would be observed for an $S = 1/2$ linear chain if the maximum of the lower boundary was at the same energy as the Haldane excitation for $l = 0.5$.

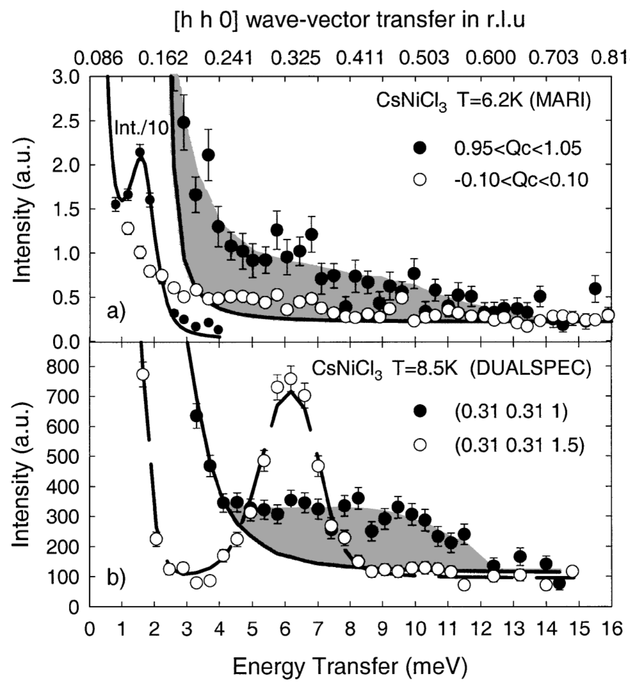

FIG. 2. (a) Neutron scattering intensity at 6.2 K as a function of energy transfer at $l = 0$ and $l = 1$ as measured in the central detector bank of the time-of-flight spectrometer MARI and after correction for neutron absorption. The wave-vector transfer describing the in-plane wave vector $[hh0]$ varies between $h = 0.09$ and 0.81. The solid line is the fit described in the text. (b) Neutron scattering counts at 8.5 K as a function of energy transfer as measured using the triple-axis spectrometer DUALSPEC and corrected for neutron absorption. The energy scan at the zone boundary (0.31 0.31 1.5) shows that the magnetic excitation peak is at ~ 6 meV and that the background at low and high energy transfer is considerably lower than the neutron scattering at (0.31 0.31 1) between 4 and 10 meV. The solid lines are fits described in the text including the resolution function. The shaded areas are a guide to the eye.

(Fig. 1). At 6.2 K, the integrated intensity of the continuum is 10(4)% of the total magnetic scattering at the AF point. The continuum was also observed in an experiment in a different configuration at 12 K, where the c axis was parallel to the incoming beam.

Calculations were made using an ISIS spectrometer simulation program which takes into account the spectrometer parameters such as the detailed pulse line shape, chopper characteristics, etc., and predicts the scattering line shape for a particular sample orientation and model of the scattering cross section. We find that the resolution function reproduced the measured line shape of the quasielastic incoherent scattering and of the well-defined excitations, but that it cannot give rise to a high energy tail in the region of the continuum.

The continuum scattering was investigated further using the triple-axis spectrometer DUALSPEC at Chalk River Laboratories and constant-$\vec{Q}$ scans were performed at 8.5 K for various wave vectors in reciprocal space. The energy scans close to the AF point $l = 1$ revealed considerable continuum scattering above the well-defined Haldane excitation. The continuum extends up to 12 meV as shown in Fig. 2b for the energy scan at (0.31 0.31 1). This wave vector was chosen to be close to the 3D ordering wave vector such that the Haldane excitation was at the lowest energy to give the largest possible energy window for the observation of the continuum. The scattering intensity at the AF zone boundary, $l = 1.5$, below and above the sharp excitation is considerably lower than the intensity at $l = 1$. The magnetic excitation was then fitted by a dispersion relation (an antisymmetrized Lorentzian weighted by the Bose factor) convoluted with the resolution ellipsoid given by Cooper-Nathans's expression [14]. The dispersion relation has been given by [4,6], and at 8 K the zone boundary energy is 6 meV, the gap at (0.81 0.81 1) is 1.35 meV [13] and the bandwidth of the gap along the [110] direction is given by the gap at (0.33 0.33 1), which is 0.75 meV [15]. The Lorentzian half-width of the excitation is 0.35 meV [13]. The fit gives an excellent account of the right-hand side of the peak (Fig. 2b), but it cannot explain the more slowly decreasing continuum at energies above 4 meV. This result is robust against changes of the vertical collimation settings because at $l = 1$ the dispersion perpendicular to the chain axis extends only up to about 2 meV.

The integrated intensity for the DUALSPEC data at the AF point $l = 1$ was inferred by scaling the peak intensity for $l = 1.5$ according to the l dependence of the intensity measured by the MARI experiment. The integrated intensity of the continuum at 8.5 K is found to be about 12(3)% of the overall scattering at the AF wave vector. This confirms the results obtained using the MARI spectrometer.

The temperature dependence of the continuum scattering was further investigated using the RITA triple-axis spectrometer at Risø and constant-$\vec{Q}$ scans were performed at the 1D point (0.81 0.81 1). In Fig. 3 we show that the peak broadens and increases in energy with increasing temperature as reported elsewhere [13]. The well-defined peak was well fitted by an antisymmetrized Lorentzian weighted by the Bose factor and convoluted with the resolution ellipsoid. The flat background was determined from the scattered intensity below 25 K at the highest energy transfers measured ($\omega > 12$ meV), where the scattering was temperature independent and assumed to be nonmagnetic. At low temperatures and energies higher than the well-defined peak energy, there was considerable continuum scattering (Fig. 3). After correction for neutron absorption, the total integrated intensity at 6 and 12 K was about 14(3)% and 13(6)% of the integrated scattering at $l = 1$, respectively. At higher temperatures, the Lorentzian peak increases in energy and broadens so that the continuum could not be clearly identified. Nevertheless, there was more scattering around 8–12 meV energy transfer at 6 and 9 K than at 30 K (see Fig. 3).

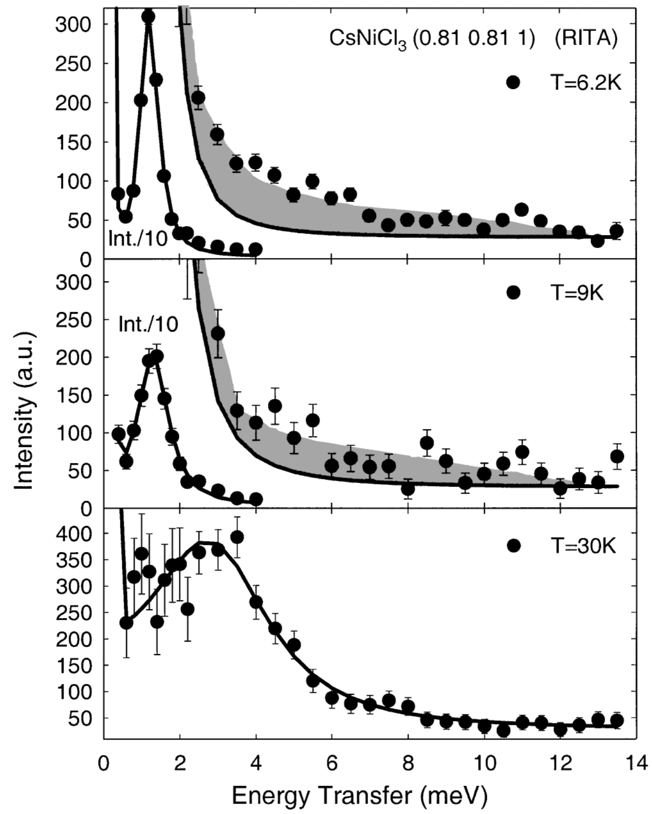

FIG. 3. Neutron scattering intensity at $l = 1$ wave-vector transfer as a function of energy transfer measured using the triple-axis spectrometer RITA for three different temperatures. The data are corrected for neutron absorption. The solid lines are the fits explained in the text including the spectrometer resolution. The shaded areas are a guide to the eye.

The portion of the intensity in the continuum scattering for $CsNiCl_3$ at 6 K is about 12(2)% for $l = 1$. The scattering continuum is consistent with the Hohenberg-Brinkman sum rule for $\int d\omega\, \omega S(Q, \omega) = F(Q)$ [16]. For nearest neighbor exchange interaction the sum rule gives $F(l) \propto [1 - \cos(l\pi)]$ and the ratio $R = F(0.5)/F(1) = 0.5$. Numerical integration of the measured spectra gives $R = 0.52(0.02)$, if the continuum at $l = 1$ is included, and

$R = 0.84(0.11)$, if it is not. This result shows that our data are consistent with the sum rule only if the continuum scattering is included. Indeed, it is because the continuum at high energies carries much spectral weight that the single particle weight increases by only a factor of 5.4 between $l = 1.5$ and $l = 1$, much less than the theoretical prediction of 8.9 from the single-mode approximation (Eq. 5 in Ma *et al.* [6]).

There are a number of theoretical predictions for the strength of a continuum at $l = 1$. A numerical diagonalization of a spin-1 chain with $N = 20$ sites and nearest neighbor exchange interaction showed that at zero temperature the continuum above the Haldane excitation carries 3% of the total weight [17]. In the nonlinear sigma model (NLσM) the continuum arises from three-particle scattering, and carries about 2% of the spectral weight [18,19]. If the coupling of the magnetic chain is taken into account via a random-phase approximation (RPA), the three-particle scattering becomes dependent on the wave-vector transfer perpendicular to the 1D axis, but its integrated intensity remains between 0.5% and 2.25% of the total spectral weight [19].

A much larger three-particle weight of 17% is predicted by the Majorana fermion theory (MFT) [19]. It is based on a perturbation to the Heisenberg Hamiltonian from a model where biquadratic and bilinear exchange are equal. Its validity at the Heisenberg point is unclear. The peak it predicts at 4 times the gap energy does not occur in our data. Moreover, the MFT results disagree with the numerical calculations of Takahashi [20].

In order to confirm that the continuum scattering arises from three-particle scattering as predicted by the NLσM we have searched for the onset of the continuum at 3Δ and for the pronounced maximum of the continuum at 6Δ as predicted by the NLσM. With $\Delta = 0.94$ meV, our resolution is more than adequate to observe an increasing continuum intensity between $3\Delta = 2.8$ meV and $6\Delta = 5.6$ meV, but instead the spectrum shows a steadily decreasing intensity (Figs. 2 and 3). This may arise because the 3D interactions in $CsNiCl_3$ cause a change in the excitation spectrum which is not properly taken into account via RPA and the pronounced maximum at 6Δ gets much broader as expected from kinematics. Possibly the effect can also account for the observed continuum intensity being higher than predicted for a 1D chain and for the spectral differences of the continuum in the three experiments.

The observed continuum, Figs. 1, 2, and 3, has intensity extending to approximately 12 meV, which is twice the maximum one-particle energy for $CsNiCl_3$. Because similar measurements near $l = 0$, 2 show no evidence of scattering, we conclude that the continuum is strongest in a broad region where the AF fluctuations are largest. It is then worth commenting that qualitatively the continuum has qualitatively similar features (Fig. 1) to the continuum found for $S = 1/2$ systems [2].

It is clear that further theoretical work is needed to understand these results. It is unclear first whether a quantitative theory can be obtained from the three-particle picture of the NLσM or whether it is more appropriate to use another development such as the MFT approximation [21] to the Heisenberg model with biquadratic exchange and second whether the form of the scattering depends on the interchain coupling or is characteristic of coupled chains.

In summary, we have measured the continuum scattering of the spin-1 chain compound $CsNiCl_3$ in a broad region that favors antiferromagnetic fluctuations and shown that it is stronger than expected for an ideal spin-1 chain both from numerical diagonalization and from field theoretical calculations involving the NLσM. These results are presented as observations from experiment, and while we cannot explain them we hope that they will stimulate further theoretical work.

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