Experimental Evidence for the Haldane Gap in a Spin-1, Nearly Isotropic, Antiferromagnetic Chain

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Neutron scattering has shown that the lowest spin excitations in the spin-1 antiferromagnet $CsNiCl_3$ in its one-dimensional phase occur at finite frequency. After allowance for the known weak interchain coupling the gap is found to be in good agreement with recent numerical calculations. The results support the Haldane conjecture that in integral-spin chains with isotropic interactions a gap separates the ground state from the excitations.

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A large body of experimental evidence suggests that systems with isotropic spin Hamiltonians exhibit a gapless spin-wave spectrum. Therefore considerable interest has been stimulated by Haldane's conjecture[1] that a gap appears in the excitation spectrum of an antiferromagnetic integer-spin chain but not in that of a half-integer spin. While it has been shown analytically that the spin-$\frac{1}{2}$ antiferromagnetic Heisenberg chain is gapless, an exact solution of the analogous spin-1 chain does not appear to be possible and finite-size scaling methods have been used to investigate its properties. Botet, Jullien, and Kolb[2] estimated the size of the gap for a Heisenberg chain with exchange constant $2J$ and axial anisotropy $D(S^z)^2$ by extrapolating to infinite N the results for finite rings of N spins calculated by the Lanczös algorithm. They found that a gap exists for $-\frac{1}{4} \leq D/2J \leq 0.8$. The gap decreased rapidly for negative D in contrast with the increase expected for classical Ising-type systems. Their results were initially challenged by Bonner and Müller[3] on the basis of similar experience with other Heisenberg chains. Later, Lanczös calculations for $N \leq 14$ and Monte Carlo calculations for $N \leq 32$ by Parkinson *et al.*[4] indicated that a finite gap of order $0.4 \times 2J$ is likely to exist for a Heisenberg antiferromagnetic spin-1 chain at $T=0$. Analytic solutions of the plane-rotation model of the chain have been obtained by Mattis[5] for a restricted set of parameters. His results are in agreement with the work of Botet, Jullien, and Kolb[2] although they do not completely confirm it.

$CsNiCl_3$ is an easy-axis spin-1 antiferromagnetic Heisenberg system in which the Ni atoms form chains parallel to the c axis of the hexagonal lattice. The Hamiltonian is

$$H = J\sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j + J'\sum_{i,k} \mathbf{S}_i \cdot \mathbf{S}_k + D\sum_i (S_i^z)^2, \qquad (1)$$

where J is the intrachain exchange and J' the interchain exchange, and D, the axial anisotropy constant, is negative. Two three-dimensional (3D) phase transitions at 4.85 and 4.46 K have been observed by specific-heat[6] and nuclear magnetic resonance[7] measurements. It has been shown by neutron diffraction[8] that in the lowest-temperature magnetic cell there are three chains ordered antiferromagnetically along their length; on one of the chains the spins point along the chain direction, while on the other two chains, the spins are canted in a plane away from the chain direction by about 60°. The 1D magnetic properties have been investigated by magnetic susceptibility,[9] thermal expansion,[10] heat capacity,[6] and acoustic attenuation,[11] but accurate values for the parameters of the Hamiltonian could not be obtained. We present here neutron-scattering experiments that determine the values of J, J', and D from measurements of the spin-wave dispersion in the 3D ordered phase and show that a gap exists in the 1D phase above 4.85 K.[12] The gap is too large to be caused by the known single-ion anisotropy and lends support to the Haldane conjecture.

Constant-**Q** measurements were made on a single crystal of $CsNiCl_3$ with a triple-axis spectrometer at the NRU reactor, Chalk River. The energy resolution was 0.13 THz for most of the measurements. Spin-wave dispersion relations were obtained in the lower 3D phase at $T \leq 2.7$ K as shown in Fig. 1. A six-sublattice model based on dynamic-susceptibility theory[13] gave an excellent description of the observed peaks when folded with the experimental resolution especially near $(\frac{1}{3}\,\frac{1}{3}\,1)$. The following values for exchange and anisotropy constants were obtained: $J = 0.345 \pm 0.008$ THz, $J' = 0.0060 \pm 0.0005$ THz, and $D = -0.013 \pm 0.002$ THz.[14] These values differ significantly from those obtained in an earlier study.[15] The results confirm that the anisotropy $(D/2J = -0.019)$ and basal-plane exchange $(J'/J = 0.017)$ are sufficiently small that $CsNiCl_3$ may be described as a nearly Heisenberg quasi one-dimensional system. In particu-

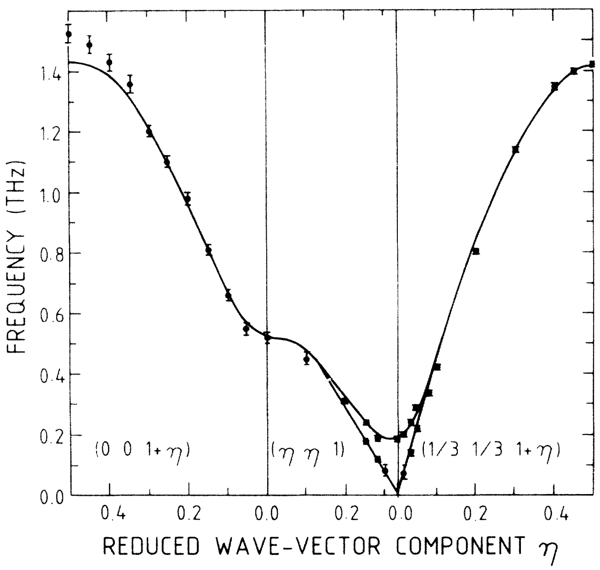

FIG. 1. Spin-wave peak frequencies measured in the 3D phase of $CsNiCl_3$ for 1.8 K $\leq T \leq$ 2.7 K, compared with frequencies obtained from a convolution of the theoretical spin-wave spectrum with the experimental resolution. Only near $(\frac{1}{3}\,\frac{1}{3}\,1)$ can two peaks be resolved.

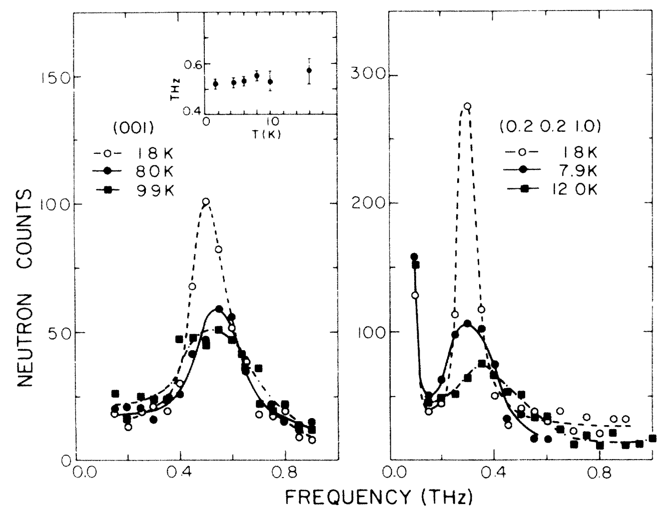

FIG. 2. Temperature behavior of spin-wave peaks at (001) and (0.2 0.2 1.0). The inset shows that the peak at (001) does not shift in frequency from 2 to 16 K.

lar, the D largely arises from single-ion anisotropy so that it will be of the same magnitude in the 1D phase. $CsNiCl_3$ is therefore suitable for testing the conjecture of Haldane, provided due account is taken of the small but nonnegligible effects of D and J'.

To determine whether an energy gap exists scans were carried out along $(\eta\,\eta\,1)$ as a function of temperature above T_N. It was found that spin excitations remain well defined with little change in frequency up to at least 10 K. No evidence was found for growth of a central peak. It may be seen from Fig. 2 that the spin-wave group at (001) with frequency ≈ 0.5 THz persists up to 10 K. By 16 K the peak becomes very broad and weak, but no softening is observed (inset). Similarly, at (0.2 0.2 1), the peak frequency of 0.3 THz is little changed from its low-temperature value. At (0.25 0.25 1) and (0.28 0.28 1) the two peaks that are distinguishable at 2.1 K are replaced at 8.0 K by one broad peak. Our results for the basal-plane dispersion in the temperature range 8–10 K are shown in Fig. 3. All modes occur at finite frequencies. Other experiments show that the frequency of the mode in the 1D phase at $(\frac{1}{3}\,\frac{1}{3}\,1)$ is also finite and only softens to zero as T_N is approached.[16] The results, together with the absence of a central quasielastic peak, suggest that the spectrum of isolated spin-1 antiferromagnetic chains may indeed exhibit a gap, but that the 3D coupling provides significant dispersion above T_N.

To allow for 3D coupling and thus derive the value of the gap-mode frequency ν_0 of an isolated chain (i.e., when $J'=0$) we apply perturbation theory in the spirit of Scalapino, Imry, and Pincus[17] to the system of weakly coupled 1D chains. Above T_N the canting is absent and all chains are equivalent with spis along $\pm\mathbf{c}$ so that there is one chain per cell. Each chain has strong correlations along its length; its lowest-frequency dynamic response, which occurs at wave vector (001), is that of an oscillator resonating at the minimum frequency ν_0,

$$g(\nu)=A/(\nu^2-\nu_0^2). \tag{2}$$

When the set of oscillators is coupled at right angles to

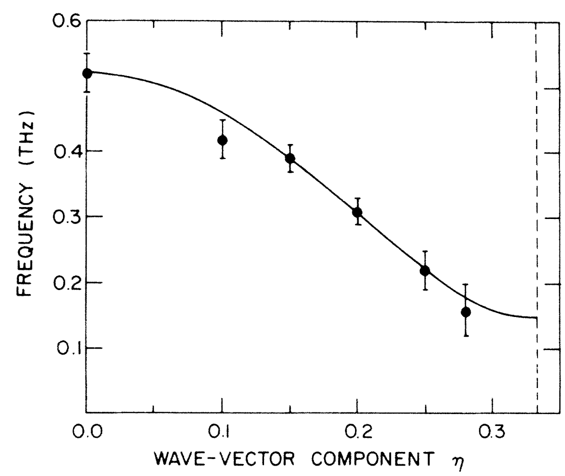

FIG. 3. Spin-wave peak frequencies measured along $(\eta\,\eta\,1)$ at 8–10 K. The line is the dispersion given by Eq. (4) from which a frequency of 0.32 ± 0.03 THz is determined for the Haldane gap mode.

the chain by an effective coupling $\bar{J}'$ the coupled susceptibility for wave vector $\mathbf{q}_a = (\eta\,\eta\,0)2\pi/a$ is found to be

$$G(\mathbf{q}_a,\nu) = g(\nu)/[1-\bar{J}'(\mathbf{q}_a)g(\nu)], \tag{3}$$

resulting in a spin-wave dispersion

$$\nu(\mathbf{q}_a) = [\nu_0^2 + A\bar{J}'(\mathbf{q}_a)]^{1/2}. \tag{4}$$

The dispersion of Fig. 3 thus arises because the coupling at (001), i.e., for $\eta = 0$, is $+6\bar{J}'$ and increases the observed frequency above ν_0, whereas at $(\frac{1}{3}\,\frac{1}{3}\,1)$ where $\eta = \frac{1}{3}$ the coupling is $-3\bar{J}'$ and depresses the frequency below ν_0. The line in Fig. 3 shows that Eq. (4) gives an excellent description of the dispersion in the 1D phase with parameters $A\bar{J}' = 0.028 \pm 0.005$ THz^2 and a gap-mode frequency of 0.32 ± 0.03 THz. Note that the dispersion occurs in the absence of direct interchain spin correlations which are weak at $T \approx 2T_\mathrm{N}$; it requires only the long correlation length along each chain that exists at 10 K. Indeed the dispersion is in a sense a consequence of the finite minimum resonance frequency of each chain. A further check that Eq. (4) gives a reasonable physical description of the effects of 3D coupling above T_N is that the value of $A\bar{J}'$ is of approximately the size expected. Thus if the classical value of A is taken, $8JS = 2.76 \pm 0.06$ THz, then $\bar{J}' = 0.009 \pm 0.002$ THz is found, close to the value, $J' = 0.0060 \pm 0.0005$ THz, known from the spin-wave spectrum of the 3D phase. Given the presence of critical and nonlinear effects included in the effective coupling $\bar{J}'$, the description of Eq. (4) is therefore a reasonable physical approximation. It allows the 3D effects to be removed so as to derive an estimate of the gap frequency, $\nu_0 = 0.32$ ± 0.03 THz, of a single isolated chain for comparison with theory.

For classical spins the observed gap of 0.32 THz would require an anisotropy $D = -0.037 \pm 0.007$ THz. This is three times larger than the known value of -0.013 ± 0.002 THz determined from the spin-wave dispersion in the 3D phase. Hence the observed gap cannot arise from anisotropy. For $D = 0$ the gap for a quantum spin-1 chain has been predicted by Botet, Jullien, and Kolb[2] to be $0.25(2J) = 0.17$ THz and by Parkinson *et al.*[4] to be $0.40(2J) = 0.28$ THz for $CsNiCl_3$. Our gap agrees with the latter within 2 standard deviations. The larger value of Ref. 4 occurs because the gap as a function of $1/N$ levels off for $N > 14$ whereas the calculations for $N \leq 10$ in Ref. 2 do not sample this asymptotic behavior.

Further confirmation of the existence of a gap for $T > T_\mathrm{N}$ has been obtained from measurements of $S(\mathbf{Q},\nu = 0)$ along $(\eta\,\eta\,1)$ with a frequency resolution of 0.25 THz. At 10 K no evidence for elastic 3D critical scattering is observed at $\eta = \frac{1}{3}$, $\frac{2}{3}$, or $\frac{4}{3}$. This is expected as the lowest mode lies at a finite frequency beyond the resolution function of the spectrometer. By a change of the frequency transfer to $\nu = 0.1$ THz, weak broad peaks were observed at the 3D positions consistent with the intersection of the resolution function with the finite-frequency peaks of Fig. 3. Thus, all the critical scattering is in the excitations.

Experiment, therefore, supports Haldane's conjecture that the isotropic spin-1 antiferromagnetic chain exhibits a gap in its excitation spectrum. Its magnitude for $CsNiCl_3$ agrees with that predicted by recent calculations for spin-1 antiferromagnetic chains near the Heisenberg point.

If confirmed by further work our results suggest that the apparent parameters (i.e., those obtained with the aid of linear theories) are in fact determined by the many-body interactions. For we would expect that $CsNiCl_3$, $RbNiCl_3$, and $CsNiF_3$ would all have the same sign of anisotropy. All mechanisms (e.g., dipole, orbital effects from the nonideal c/a ratio) would lead to an XY-like anisotropy. In fact only for $CsNiF_3$ where the ferromagnetic coupling should lead to small many-body effects is the system strongly XY like. For the others the antiferromagnetic coupling and the Haldane effect apparently overcome the intrinsic anisotropy to produce systems with Ising-type gaps.

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