Observation of the Haldane gap in $RbNiCl_3$

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The Haldane gap is observed by neutron scattering in $RbNiCl_3$. The three-dimensional-phase magnetic spectrum of $RbNiCl_3$ is found to be very similar to that of $CsNiCl_3$, even though the two materials differ significantly in the exchange parameters. Application of Affleck's field theory to $RbNiCl_3$ shows that the theory is capable of explaining the dispersion of the gap mode and its relative intensity near the three-dimensional ordering wave vector (1/3,1/3,1). However, the theory does not provide a satisfactory explanation for the nearly degenerate magnon frequencies at (0,0,1). We argue that the degeneracy at (0,0,1) may not be related to the existence of the Haldane gap in integer-spin systems. Rather, it could be a general feature of certain antiferromagnetic materials.

As predicted by Haldane[1] an energy gap is expected to exist in the magnetic excitation spectrum of any one-dimensional (1D) Heisenberg antiferromagnetic (HAFM) system with integer spins. So far, $CsNiCl_3$ and $Ni(C_2H_8N_2)_2NO_2ClO_4$ (NENP) are the only materials in which the predicted gap has been observed and confirmed.[2-5] Both materials consist of chains of spin-1 Ni^{2+} ions with strong intrachain exchange interactions. In $CsNiCl_3$ the chains form a triangular lattice in the hexagonal basal plane. Based on the very low magnetic field required to produce a spin-flop transition it has been argued that the single-ion anisotropy is negligible[3,5] so that the observed gap can only arise from the effects of the spin-1 symmetry. Weak exchange interaction between the chains gives the Haldane mode a weak dispersion in the 1D paramagnetic phase above 4.8 K but does not destroy the gap. The magnitude of the gap was found to agree with numerical computations.[6] For temperatures below 4.8 K the interchain interaction leads to three-dimensional (3D) magnetic order. In the lowest-temperature phase the magnetic moments of Ni^{2+} ions order in a planar 120° structure where all the spins are canted in the crystallographic *a-c* plane.[7] NENP does not show 3D long-range order down to 1 K because the interchain interaction is lower than the critical value for ordering. The single-ion anisotropy is relatively large in this material.[4]

In $CsNiCl_3$ it has been determined that the gap in the 1D phase is between a triplet excited state and a singlet ground state.[8-10] The triplet symmetry is a characteristic feature of a Haldane gap mode that distinguishes it from the doubly degenerate spin waves of the linear theory for antiferromagnets. In NENP the triplet excited state is split into a singlet and a doublet by the single-ion anisotropy.[4]

Even in the 3D phase of $CsNiCl_3$ the integer-spin symmetry influences the magnetic spectrum. The spin excitation spectrum has its triplet degeneracy lifted near the ordering wave vector where it consists of two transverse Goldstone modes and a gap mode; the latter cannot be reproduced by linear spin-wave theory[10] and is related to the longitudinal part of the singlet-to-triplet transition of the 1D phase.

To describe the more complex spin excitations of the 3D phase, Affleck proposed a field theory[11] in which a mass gap, with a phenomenological parameter Δ, is introduced so as to agree in the 1D phase with the predictions of the more fundamental $(1+1)$ dimensional nonlinear σ model. The constrained spin length of the σ model was represented approximately in Affleck's model by a ϕ^4 term, where ϕ is the field variable. The field theory correctly reproduces the triplet in the 1D phase because, in addition to the usual pair of transverse spin excitations, the magnitude of the spin can fluctuate giving rise to an additional longitudinal mode. In the 3D phase the theory requires the existence of longitudinal excitations in addition to the usual transverse excitations. The complete magnetic spectrum consists of three transverse modes and a pair of longitudinal modes. One of the transverse modes corresponds to the spin excitations perpendicular to the planar 120° structure. This is the $\hat{y}$ direction of the Cartesian coordinate system introduced by Morra *et al.*[3] with the $\hat{x}$ and $\hat{z}$ directions parallel to the crystallographic axes *a* and *c*. The predicted dispersion of this transverse *y* mode, T:*y*, is identical to that given by the linear spin-wave theory. The other two transverse modes correspond to the spin excitations within the plane of 120° structure and hence are of *xz* character and mix in with the longitudinal *xz* modes. The dispersion curves of the four rediagonalized modes,

$xz1-xz4$, are very different from those possible to obtain with the linear spin-wave theory. In the limit of a purely isotropic system these modes are of equal x and z character but are neither purely transverse nor longitudinal.

Affleck[11] showed that the observed magnon frequencies in $CsNiCl_3$ at the ordering wave vector, $\mathbf{Q}_0=(1/3,1/3,1)$, can be accurately represented by the y mode and the two lower xz modes, $xz3$ and $xz4$. The predicted intensities of $xz1$ and $xz2$ are relatively weak so that it is hard to observe them at $\mathbf{Q}_0$. In contrast, $xz3$ and $xz4$ are predicted to be weak at (0,0,1) where $xz1$ and $xz2$ are strong. The frequencies of the latter pair, ω_{xz1} and ω_{xz2}, are very close to the y-mode frequency, ω_y. This accidental near degeneracy at (0,0,1) is a major support to the field theory since it removes the so-called "$\sqrt{2}$ problem" encountered by the linear spin-wave theory.[10,12]

In spite of such excellent agreements, one possible discrepancy emerges when the field theory is compared to additional experimental data available on $CsNiCl_3$. It concerns the prediction of a second gap mode, $xz2$, above the observed gap mode, $xz3$. The expected intensity of $xz2$ at $\mathbf{Q}_0$ is $\sim 1/3$ of the observed gap but one of our scans (unpublished) near $\mathbf{Q}_0$ sets a limit of $\leq 1/4$ on this intensity ratio. This observation, of course, is not a definitive evidence against the field theory because the $xz2$ mode could become very weak due to heavy damping.

The experimental results that suggest such discrepancies exist are limited in $CsNiCl_3$ in part by the weak exchange interactions and therefore low energies. In addition, the accidental near degeneracy at (0,0,1) deserves further investigation. It was therefore decided to look for the Haldane gap in a second triangular material. The system selected should have higher exchange energies for ease of measurement. It should also have a different ratio of exchange interactions in order to lift the near degeneracy at (0,0,1). The system chosen was a high quality crystal of $RbNiCl_3$ where the ratio of the exchange between chains, J', to the exchange within chains, J, is about 80% greater than in $CsNiCl_3$. It has a further advantage that the single-ion easy-axis anisotropy, D, in the following Hamiltonian:

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

is known to be small ($|D|<0.0026$ THz) from spin flop field measurements,[13,14] and therefore unimportant in accounting for gap energies. Because of the J' interaction the material undergoes 3D magnetic long-range order into the 120° structure at $T_N=12$ K.

Inelastic neutron scattering experiments were carried out on the L3 triple-axis spectrometer at the National Research Universal (NRU) reactor, Chalk River. The single-crystal specimen with dimensions $8\times8\times10$ mm^3 was mounted with its (hhl) plane in the scattering plane of the spectrometer. It was cooled to 1.5 K with no applied magnetic field. The 3D ordered phase was therefore expected to be equally distributed among three different magnetic domains, each with Ni^{2+} spins canted in one of the three symmetry-equivalent xz planes. The instrumental resolution was 0.18 THz for the measurements near the ordering wave vector (final neutron energy $E_1=2.0$ THz), and 0.26 THz for most of the other measurements ($E_1=3.0$ THz).

A constant-Q scan at (1/3,1/3,0.96) is shown in Fig. 1. The mode observed at 0.56 THz is resolution limited and completely resolved from lower energy Goldstone modes (at 0.25 THz). A scan at exactly the ordering wave vector $\mathbf{Q}_0=(1/3,1/3,1)$ gave a gap mode at 0.51 THz, well resolved from the strong quasielastic central peak. The weak anisotropy cannot account for such a high-frequency mode at the zone center. We therefore identify it as the longitudinal member, according to the field theory,[11] of the triplet Haldane gap persisting into the 3D phase. Consequently, the low-frequency peak is expected to consist of two transverse Goldstone modes with approximately the same frequencies. The field theory applied to $RbNiCl_3$ in a similar way as in $CsNiCl_3$, i.e., fitting the frequency ω_{xz3} at $\mathbf{Q}_0$ to the observed gap frequency,[15] is found to reproduce the gap mode and the Goldstone modes satisfactorily. The predicted frequencies of the modes with appreciable intensities are indicated in Fig. 1 by the arrows. The associated numbers are the spectral weights given by the theory modified by the $(1-\hat{Q}_\alpha^2)$ Lorentz factors ($\alpha=x,y,z$) for a multidomain sample. The observed relative intensity of the gap mode compared to the combined intensity of the Goldstone modes is in agreement with the theory, supporting our as-

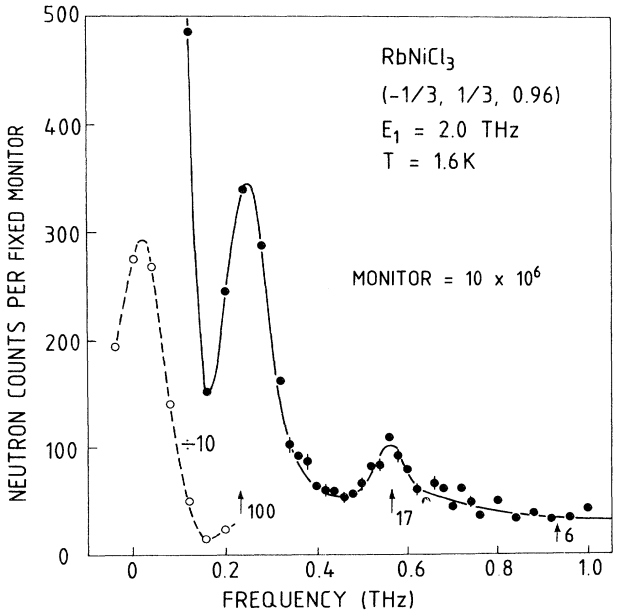

FIG. 1. Constant-Q scan near the magnetic ordering wave vector $\mathbf{Q}_0=(1/3,1/3,1)$. Magnon frequencies predicted by the field theory (Ref. 11) are shown by arrows while their expected intensities normalized to the total intensity of Goldstone modes (peak at 0.24 THz) are given by the associated numbers. Note that the intensities are calculated assuming that the sample is ordered into three equal domains of planar 120° spin structures.

sumption that there are two Goldstone modes in the low-energy peak. However, the counting statistics of our scan is not sufficient to observe the second gap at $\omega_{xz2}=0.93$ THz.

In Fig. 2 we show constant-Q scans at (0,0,1) and the equivalent wave vector (1,1,1). The width of the single peak observed at (0,0,1), FWHM=0.40 THz, is almost a factor of 2 broader than the resolution width, FWHM=0.2 THz, deduced from quasielastic scattering of a vanadium powder sample and corrected for the energy transfer of ~1 THz. It is therefore reasonable to postulate that the single peak consists of y and xz modes approximately separated by the resolution width. The scan at the equivalent wave vector (1,1,1) gives essentially the same peak position and width, but a lower intensity consistent with the reduced magnetic form factor at the larger $|Q|$. Since the $(1-\hat{Q}_\alpha^2)$ Lorentz factors are significantly different at the two wave vectors, any difference in ω_y and ω_{xz} that was comparable to the resolution width would have given a shift or a different peak shape at (0,0,1) and (1,1,1). The scans in Fig. 2 therefore allow us to draw an important conclusion: the excitations at (0,0,1) are degenerate or nearly degenerate as in $CsNiCl_3$.

The above observations clearly show that the magnetic excitations in $CsNiCl_3$ and $RbNiCl_3$ are qualitatively the same even though the two materials differ significantly in the magnitude of exchange interactions J and J'. More importantly, they show that the near degeneracy at

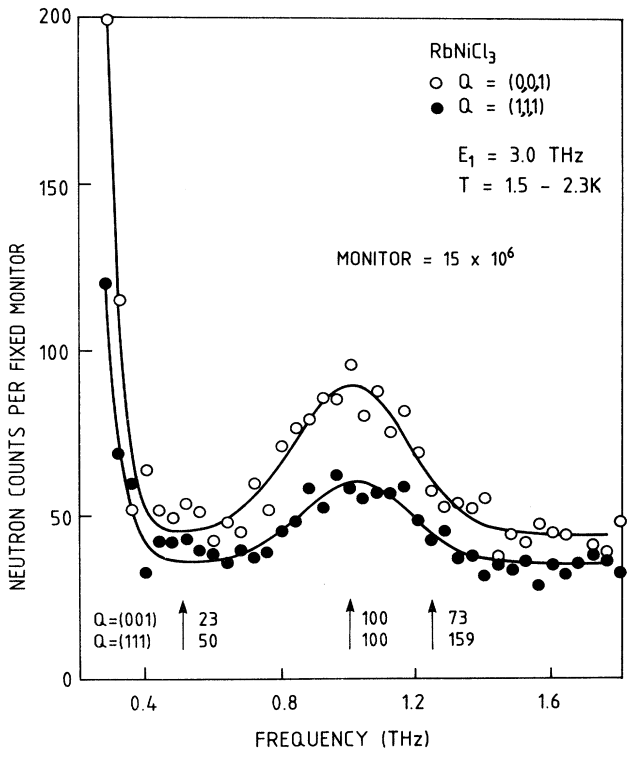

FIG. 2. Constant-Q scans at (0,0,1) and (1,1,1) normalized to the same incident-beam monitor.

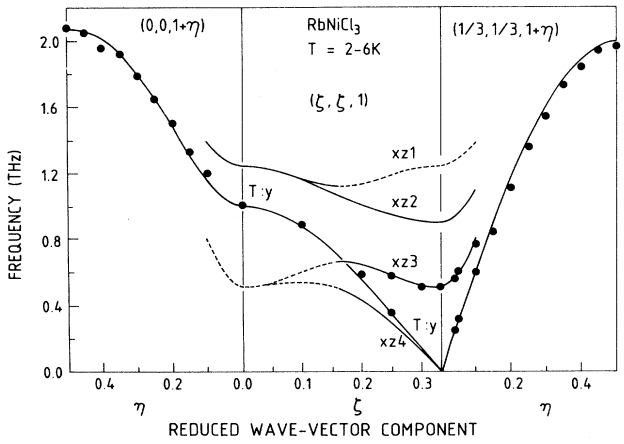

FIG. 3. Measured magnon frequencies and dispersion curves predicted by the field theory (Ref. 15) with parameters $J=0.485$ THz, $J'=0.0143$ THz, and $\Delta_L=0.9$ Thz.

(0,0,1) is not a result of a particular combination of parameters in one isolated example. Related to this conclusion is the question of whether the parameters in the field theory could be readjusted to produce nearly degenerate modes in $RbNiCl_3$. Our analysis shows it is possible only if we represent the observed gap with the $xz2$ mode instead of the $xz3$ mode. However, the $xz3$ mode should then appear at 0.42 THz in the scan of Fig. 1. This is clearly not the case and such a scheme is acceptable only if the absence of $xz3$ mode at $\mathbf{Q}_0$ could be explained.

In order to assess the overall agreement obtained by the field theory in $RbNiCl_3$ the observed magnon frequencies (points) and the predicted magnon branches (curves) are shown in Fig. 3. The branches shown are calculated with the parameters[15] $J=0.485$ THz, $J'=0.0143$ THz, and $\Delta_L\equiv(96JJ'-2\Delta^2)^{1/2}=0.9$ THz in the limit of zero single-ion anisotropy. The xz modes are plotted only to $|Q_z|<1.1$ since the field theory is a long-wavelength limit theory valid for $|Q_z|\approx 1$ only. The unexplained degeneracy at (0,0,1) causes an ambiguity in determining J'; it was chosen to fit ω_y to the center of the observed peak. The frequencies ω_{xz1} and ω_{xz2} then came out slightly too high. The parameter Δ_L was subsequently chosen so that ω_{xz3} at $\mathbf{Q}_0$ is equal to the observed gap frequency, 0.51 THz. One consequence of this choice is that the gap parameter Δ^2 is a negative quality. This implies that, unlike in $CsNiCl_3$, the value of $\Delta/2J$ in the 3D phase of $RbNiCl_3$ is significantly renormalized from its value, 0.41, predicted by numerical simulations[6] on 1D finite chains.

We do not know what causes the discrepancies between experiments and the field theory for $RbNiCl_3$ but useful insight can be obtained by reviewing what is known about other triangular HAFM materials. $CsMnI_3$ is an isostructural material with spin-5/2 Mn^{2+} ions. As for the Ni compounds, its Hamiltonian is highly isotropic with a small easy-axis anisotropy ($D/J\simeq 0.003$). Because of its large noninteger spin the magnetic spectrum of $CsMnI_3$ was expected to exhibit classical spin-wave be-

havior. However, recent measurements by Harrison *et al.*[16] show that this is not the case. Although there is a small energy gap at the ordering wave vector (1/3,1/3,1), which is consistent with the weak single-ion anisotropy, the high-energy optical mode predicted by the linear theory could not be found. Further, only a single broad peak is observed at (0,0,1) although the spectrometer resolution was good enough to resolve the modes separated by the expected $\sqrt{2}$ ratio.[10] In light of these results the near degeneracy at (0,0,1) is likely to be a general feature of certain HAFM materials and not related to the Haldane gap phenomenon.

In the above context we stress that the linear spin-wave theory does not fail for every triangular magnet. For example, it provides a good description of spin waves in $CsMnBr_3$, a triangular HAFM but with a relatively strong *xy anisotropy.* For this material the optical magnons at (1/3,1/3,1) are clearly observed.[17] At (0,0,1), two magnons with different frequencies can be seen but the frequency ratio is, as expected, significantly larger than $\sqrt{2}$ because of the strong anisotropy. The situation is far from clear in $CsVX_3$ (X=Cl, Br, I), another easy-plane HAFM with noninteger spins, due to the limited experimental data available[18] between the wave vectors (0,0,1) and (1/3,1/3,1).

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