Upward Renormalization of Fluctuations in $CsMnBr_3$ with Increasing Temperature

C. Reich and P. Böni
Physik-Department E21, Technische Universität München, D-85747 Garching, Germany

B. Roessli
Laboratory for Neutron Scattering, Eidgenössische Technische Hochschule Zürich & Paul Scherrer Institut, CH-5232 Villigen, Switzerland

E. Rastelli
Dipartimento di Fisica dell'Università and Istituto Nazionale per la Fisica della Materia, Parco Area delle Scienze 7/A, 43100 Parma, Italy

(Received 2 May 2003; published 9 October 2003)

The temperature dependence of the spin-wave gap in the triangular antiferromagnet $CsMnBr_3$ was studied above the three-dimensional ordering temperature $T_N = 8.3$ K along the main symmetry directions using inelastic neutron scattering. We find at T_N two gapped dispersive modes, whose energy increases with temperature. Moreover, the width of the spin-wave band along the [110] direction increases also. In a second session, polarization analysis was applied in order to extract explicitly the components with in-plane and out-of-plane character. The results show that both gapped modes (with $\parallel$ and $\perp$ symmetry) renormalize upwards with rising temperature. We show that this behavior is not compatible with spin-wave theory. In addition, we find a new magnetic anomaly in the paramagnetic phase.

DOI: 10.1103/PhysRevLett.91.157203 PACS numbers: 75.50.Ee, 75.10.Jm, 75.30.Ds, 75.40.Gb

Low-dimensional magnetic systems presently attract significant attention because of their novel properties originating from quantum fluctuations. Hexagonal systems of the form ABX_3 (halides) such as $CsMnBr_3$ or $CsNiCl_3$ are of particular interest because they often show, in addition, effects of magnetic frustration depending on the dimensionality of the order parameter of the transition metal atoms. The frustration leads to a wide variety of ground states depending on range, sign of the interactions [1,2], and temperature. The evolution of the fluctuations with T is particularly interesting because the ABX_3 systems often show phase transitions from 3D order to lower dimensional order with increasing T that are accompanied by a renormalization of the spin waves. Mason *et al.* [3] have indeed observed the evolution of critical scattering in $CsMnBr_3$ at $T_N = 8.3$ K and determined the critical exponents that were ascribed to the chiral universality class [4].

The spin dynamics of $CsMnBr_3$ is interesting for several reasons. First of all, we wanted to determine if it is only the acoustic mode (from the three spin-wave modes) that renormalizes at T_N and contributes to the critical scattering as observed by Mason *et al.* [3]. For reasons that will be explained below, this task can be performed only by means of scattering of polarized neutrons. Second, our goal was to determine the T dependence of the energy gaps of the excitation spectra to explore the interplay between short-range exchange and long-range dipolar interactions on the spin dynamics. To our surprise, we find that the spin gaps increase with increasing T. While this result contradicts spin dynamics calculations [2] and simulations [5] that predict a renormalization of the magnetic fluctuations to lower energy with increasing temperature, it is compatible with the work of Mason *et al.* [6].

$CsMnBr_3$ belongs to the hexagonal space group $P6_3/mmc$ (two atoms per unit cell) with $a = 7.609$ Å and $c = 6.52$ Å. The Mn^{2+} ions with spin $S = 5/2$ are responsible for the magnetic properties and are located on a plane hexagonal lattice, while along the c axis $MnBr^-$ units are stacked with an intrachain separation of $c/2 = 3.26$ Å. Because of the large moment, the spins can be considered to behave similar to classical spins. Below $T_N = 8.3$ K, three-dimensional long-range order is established with antiferromagnetic spin coupling along the c axis and a frustrated spin configuration in the basal plane. Hence, the magnetic zone center in the ordered phase occurs at $(\frac{1}{3}\ \frac{1}{3}\ 1)$. From spin-wave measurements, Falk *et al.* [7] found that magnetic properties are well described using an effective Hamiltonian with strong XY-like anisotropy:

$$H = J_{ab}\sum_{i,\vec{\delta}} \vec{S}_i \cdot \vec{S}_{i+\vec{\delta}} + 2J_c\sum_i \vec{S}_i \cdot \vec{S}_{i+1} + D\sum_i (S_i^z)^2, \quad (1)$$

where $\vec{\delta}$ is a vector joining the site i with its nearest neighbors in the a, b plane. The in- and out-of-plane exchange constants are given by $J_{ab} = 1.7 \pm 0.1$ μeV and $J_c = 0.89 \pm 0.01$ meV, respectively. The effective single-ion anisotropy parameter $D = 12 \pm 1$ μeV leads to a confinement of the spins to the ab plane. Recently, Hummel *et al.* [8] have shown that the in-plane anisotropy can be explained by the dipolar interactions

between the rather large magnetic moment of the Mn^{2+} ions.

In the three-dimensional antiferromagnetic ordered state, three dispersion branches are observed in the hexagonal plane [7]. One branch describes magnons with out-of-plane symmetry ($\perp$), whereas the two remaining magnons have in-plane polarization ($\parallel$). According to Hummel *et al.* [8], the optic character of the out-of-plane mode at the magnetic Brillouin zone center ($\frac{1}{3}$ $\frac{1}{3}$ 1) can be explained by the influence of dipolar interactions that lead to an energy gap in the $\perp$ mode.

The measurements were carried out with the triple-axis spectrometer TASP, located at the neutron spallation source SINQ at the Paul Scherrer Institute, Switzerland. A single crystal of $CsMnBr_3$ (sample mosaic 1.5°, dimensions $7 \times 7 \times 3$ mm^3) was mounted inside an "orange" flow cryostat that has a temperature stability of better than 0.1 K. The crystal was aligned in the $(h\,h\,l)$-scattering plane (setup with unpolarized neutrons) and in the $(h\,0\,l)$-scattering plane (setup for polarization analysis). The spectrometer was mostly operated in the constant final energy mode with $k_f = 1.64$ Å^{-1} using a pyrolytic graphite filter to remove higher-order neutrons. Furthermore, an 80′ collimator was installed in the incident beam between monochromator and sample and a horizontally focusing analyzer was used.

A first series of constant-**Q** scans were performed along the [0 0 l]-crystallographic direction in order to study the behavior of the energy gap at the antiferromagnetic zone center in the paramagnetic phase $T > 8.3$ K. The raw data in Fig. 1 shows that the excitations are very well defined. Remarkably, the peak position of the magnetic modes shifts to higher energy with increasing T.

In order to interpret the data quantitatively, we examine the double-differential cross section for unpolarized neutrons:

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) S^{\alpha\beta}(\mathbf{Q}, \omega), \qquad (2)$$

where $\delta_{\alpha\beta}$ is the Kronecker symbol, α, β are the Cartesian coordinates x, y, z, $(\mathbf{Q}, \omega)$ denote the momentum and energy transfer from neutron to sample and $\hat{Q} = \mathbf{Q}/|\mathbf{Q}|$. The first term in Eq. (2) is a selection rule that implies that only spin components perpendicular to the scattering vector contribute to the neutron scattering cross section. Therefore, measurements with **Q** along the c axis reveal only in-plane fluctuations.

We find that the line shape of the observed excitations is best described by means of a scattering function based on a damped-harmonic-oscillator (DHO) convoluted with the resolution function of the spectrometer:

$$S(\mathbf{Q}, \omega) = \frac{[n(\omega) + 1]}{\pi} \chi(\mathbf{Q}) \frac{2\omega\Gamma_q \Omega_q^2}{(\omega^2 - \Omega_q^2)^2 + 4\omega^2\Gamma_q^2}. \qquad (3)$$

The expression contains the following factors: The term for detailed balance $[n(\omega) + 1] = [1 - e^{-(\hbar\omega)/(k_B T)}]^{-1}$, the damping of the excitations Γ_q, and the renormalized dispersion $\Omega_q = \sqrt{\omega_q^2 + \Gamma_q^2}$. ω_q is the frequency of a damped oscillation. In our description, Ω_q is the physically relevant quantity [9]. The wavelength dependent susceptibility $\chi(\mathbf{Q})$ was treated as a normalization constant during the fitting procedure. The solid lines in Fig. 1 show that the data is well represented by Eq. (3).

The q and T dependence of the dispersion along [0 0 1] is shown in Fig. 2 demonstrating clearly that the energy gap of the magnetic modes indeed increases with increasing T above T_N. It is only at 40 K that the linewidth Γ_q exceeds the energy ω_q; i.e., below 40 K the excitations are well defined.

Similar measurements of the in-plane modes along the [1 1 0] direction demonstrate also that the energy gap of the mode increases. The data was analyzed again using a damped-harmonic oscillator [Eq. (3)] yielding the energy of the modes that are plotted in Fig. 3 for $T = 9$, 17.5, and 40 K. Clearly, the energy of the magnetic excitations increases throughout the zone for temperatures up to 40 K. Moreover, the spin-wave band remains broad demonstrating the persistence of strong correlations within the plane. It is only at 40 K that the dispersion becomes small as expected for one-dimensional spin chains.

We note, however, that the dispersion branch measured at $(1 + \zeta, 1 + \zeta, 1)$ is clearly shifted towards higher energy compared with the excitations measured at $(\zeta\ \zeta\ 1)$.

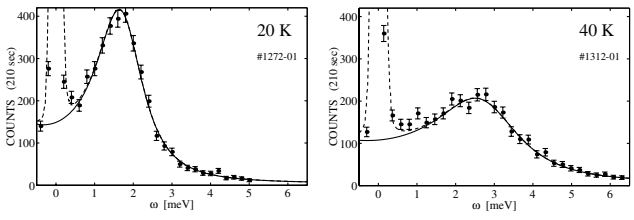

FIG. 1. Fits of scan data around (0 0 1) as measured at $T = 20$ and 40 K.

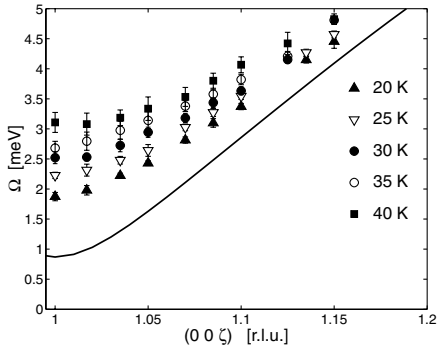

FIG. 2. Dispersion of the in-plane modes along the [0 0 1] direction for $T = 20$, 25, 30, 35, and 40 K. For means of comparison, the solid line shows the dispersion relation (in-plane mode) of the ordered state calculated according to Falk *et al.* [7]. We note that for **Q** along [0 0 1] the out-of-plane modes are not visible in the inelastic neutron spectrum.

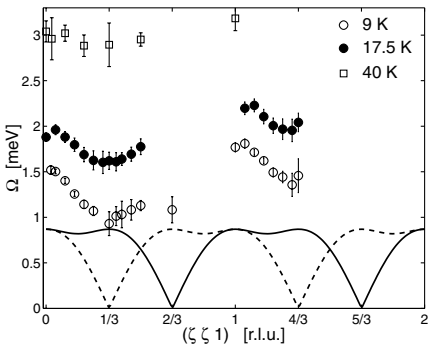

FIG. 3. Dispersion in the plane along $(\zeta\ \zeta\ 1)$ at $T = 9$ K, $T = 17.5$ K, and $T = 40$ K. The data near $(\frac{1}{3}\ \frac{1}{3}\ 1)$ is mostly due to in-plane fluctuations, while near $(\frac{4}{3}\ \frac{4}{3}\ 1)$ it is heavily weighted by the out-of-plane fluctuations. The lines indicate the dispersion below T_N as calculated by Falk *et al.* [7].

This indicates that two modes contribute to the scattering because the contribution from the out-of-plane fluctuations becomes large for **Q** away from (0 0 1). We show next that the two modes can be easily separated by means of polarization analysis as shown below.

The inelastic polarized neutron measurements were performed at (1.3, 0, 1) at different temperatures below and above T_N, i.e., $4\ \text{K} \leq T \leq 25\ \text{K}$. At this position, only two modes are visible because the two in-plane modes are degenerate. To perform full-polarization analysis remanent supermirror benders [10] were inserted after the monochromator and before the analyzer. The orientation of the polarization was chosen perpendicular to the scattering plane that is defined by the crystallographic axes [1 0 0] and [0 0 1]. With this setup, it is possible to distinguish the non-spin-flip scattering from the spin-flip scattering, respectively. Because magnetic fluctuations with polarization factor parallel to the neutron spin occur in the non-spin-flip channel, the non-spin-flip data (NSF) contains only in-plane-fluctuations. On the contrary, in the spin-flip channel (SF), both in-plane and out-of-plane fluctuations are present and the inelastic intensity is a superposition of weighted contributions

$$I_{\text{SF}} = A^{\parallel}\sin^2(\alpha)S^{\parallel}(\mathbf{Q}, \omega) + A^{\perp}\cos^2(\alpha)S^{\perp}(\mathbf{Q}, \omega). \quad (4)$$

$A^{\parallel}$ and $A^{\perp}$ are the dynamical structure factors of the two modes and α the angle between the scattering vector **Q** and the [1 0 0] crystallographic direction.

Typical inelastic data obtained in the paramagnetic phase is shown in Fig. 4. The NSF data contain a single $\parallel$ magnon, whereas in the SF channel both the $\perp$ and $\parallel$ excitations are visible. Obviously, the data analysis has to be conducted first on the NSF data $I_{\text{NSF}} = A^{\parallel}S^{\parallel}(\mathbf{Q}, \omega)$. The solid lines in Fig. 4 show fits assuming a DHO function [Eq. (3)]. In the next step, the in-plane contribution in Eq. (4) was kept fixed and the spin-flip channel was fitted to extract $S^{\perp}(\mathbf{Q}, \omega)$.

The renormalized energies of the magnetic fluctuations are plotted in Fig. 5 as a function of temperature. It is

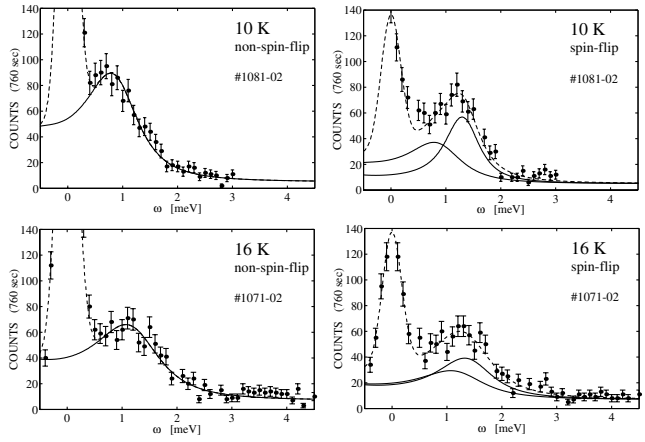

FIG. 4. Fitted scans performed with $\mathbf{Q} = (1.3, 0, 1)$ at $T = 10$ K and $T = 16$ K, convoluted with the resolution function. On the left side is the NSF data and on the right the SF data. The full lines denote the observed spin-wave peaks. The central peak is due to incoherent scattering.

clearly seen that in the ordered phase the in-plane and out-of-plane components have a different temperature dependence. The energy $\Omega_{\parallel}(\mathbf{Q})$ of the in-plane mode rises linearly with increasing temperature even in the disordered phase. The out-of-plane energy $\Omega_{\perp}(\mathbf{Q})$ shows no temperature dependence up to $T_z = 14$ K, where it starts to increase linearly with increasing T. Above T_z both dispersions are indistinguishable. This degeneracy of the modes in the paramagnetic phase explains why in the spectra obtained with unpolarized neutrons (Figs. 2 and 3) only one excitation peak was observed. The important clue is that the gap of the in-plane modes increases with increasing T as we observed at other reciprocal lattice points with unpolarized neutron scattering.

The major result of the present work is twofold. First, we find unexpectedly that the energy gap in $CsMnBr_3$ increases linearly with increasing temperature in the paramagnetic phase, as shown in Fig. 5. Second, we have found a new transition near $14\ \text{K} > T_N$ where the in-plane and out of-plane mode become degenerate. In the

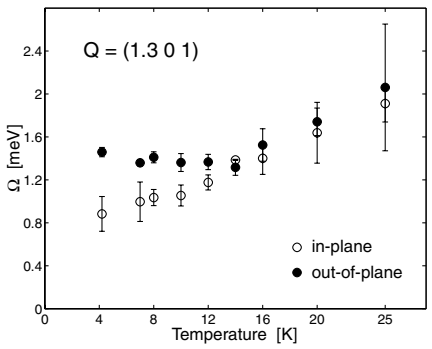

FIG. 5. Energies $\Omega_{\parallel}$ and $\Omega_{\perp}$ of the in-plane and out-of-plane components, respectively, measured at (1.3,0,1) at different temperatures.

following, we show that the upward renormalization cannot be explained by linear spin-wave theory.

We recall that in $CsMnBr_3$ the ratio $J_c/J_{ab} \approx 460$ of the exchange parameters shows that the magnetic interactions along the c axis are significantly stronger than within the ab plane. Therefore, it seems legitimate to us to treat $CsMnBr_3$ as an example of a quasi-one-dimensional antiferromagnet. For a one-dimensional Heisenberg antiferromagnet with nearest neighbor exchange J and including dipolar interactions, we find with linear spin-wave theory for the dispersion of the magnetic excitations

$$\omega(q_c) = \sqrt{[2|J|S(1-\cos q_c) + 2\omega S f(q_c)][2|J|S(1+\cos q_c) + 2\omega S g(q_c)]}, \tag{5}$$

with $S = 5/2$, $f(q_c) = -\sum(-1)^n/n^3(1-\cos nq_c)$, $g(q_c) = -\sum 1/n^3[(-1)^n + 2\cos nq_c]$, and $\omega = (g\mu_B)^2/(c/2)^3 = 0.006$ meV, where $c/2$ is the nearest neighbor distance.

The temperature dependent part of the spectrum is obtained from perturbation theory and yields after some lengthy calculations the temperature dependent renormalization of the energy gap at $q_c = \pi$:

$$\Delta\omega_\pi = -\sqrt{\frac{2\omega|J|}{g(\pi)}}\frac{1}{\pi}\int_0^\pi \frac{(1-\cos q)[g(\pi)(2+\cos q) + g(q) - f(\pi - q)]n_q}{\sqrt{[1-\cos q + (\omega/|J|)f(q)][1+\cos q + (\omega/|J|)g(q)]}}\,dq, \tag{6}$$

where n_q is the Bose occupation number. Equation (6) provides a downwards thermal renormalization. For instance, numerical evaluation gives $\Delta\omega_\pi = -0.094$, -0.343, -0.640, and -0.957 meV for $T = 10$, 20, 30, and 40 K, respectively. Analogous calculations have been performed at the same temperatures for $q_c \to 0$ and for $q_c = \pi/2$ giving $\Delta\omega_{q_c\to 0} = -0.026q_c$, $-0.129q_c$, $-0.313q_c$, and $-0.549q_c$ meV, and $\Delta\omega_{\pi/2} = -0.030$, -0.145, -0.341, and -0.592 meV, respectively.

The linear upward renormalization of the spin-wave gap in $CsMnBr_3$ is unusual. Generally, in a magnetically ordered system, the gap decreases with increasing temperature. This is understandable because the gap, usually entered by a single-ion easy-axis anisotropy term in the Hamiltonian, renormalizes similar to the sublattice magnetization [2]. For instance, this behavior has been observed in K_2NiF_4 [2,11] or Li_2CuO_2 [12]. Even in frustrated systems such as $Sr_2Cu_3O_4Cl_2$ [13], where the magnetic ordering of the two subsystems (Cu_I and Cu_{II}) originates from quantum fluctuations that lift the classical degeneracy owing to the frustration of the intersubsystem interactions, giving an example of *order out of disorder* [14], the "quantum" gap renormalizes downwards at increasing temperature, as shown in Fig. 2(b) of [13].

The only examples of upward renormalization were found in the $S = 1$ system $CsNiCl_3$ due to the Haldane gap [15] and in the square [16] and triangular [17] planar models, where two-component classical spins interact via dipole forces. For the latter (dipolar) systems, the ground state is "columnar" with alternating rows of parallel spins and ferromagnetic spins for the square lattice and the triangular lattice, respectively. In both cases, order by thermal disorder lifts the continuous degeneracy of the classical ground state and the elementary excitation spectrum becomes gapped at finite temperature, and the gap is found to increase linearly with temperature. However, the results for the quantum linear antiferromagnetic chain with three-component spins coupled by a strong exchange and a (weak) dipole interaction show that the presence of dipole interaction does not assure upward renormalization at increasing temperature. For this reason, we think that the upward renormalization of the magnetic excitation energy we have observed in $CsMnBr_3$ is a unique behavior never recorded before in magnetic systems with half-integer spins that cannot be understood in the frame of spin-wave theory. In particular, one has to take the in-plane correlations into account in order to explain the strong dispersion of the in-plane modes above T_N.

We also observe near $T_z = 14$ K a merging of the spin-wave gaps for the in-plane and out-of-plane modes. If the confinement of the spins to the hexagonal plane was caused by dipolar interactions only, we would expect the transition to take place at T_N. In contrast, the degeneracy vanishes at T_z indicating that the single-ion anisotropy D persists at least up to T_z.

This work was partially performed at the spallation neutron source SINQ, Paul Scherrer Institut, Villigen, Switzerland.

[1] C. Pich *et al.*, Phys. Rev. B **47**, 7957 (1993).
[2] E. Rastelli *et al.*, J. Phys. C **7**, 1735 (1974).
[3] T. Mason *et al.*, Phys. Rev. B **39**, 586 (1989).
[4] H. Kawamura, J. Appl. Phys. **63**, 3086 (1988).
[5] K. Nho *et al.*, Phys. Rev. B **66**, 174403 (2002).
[6] T. Mason *et al.*, J. Magn. Magn. Mater. **104–107**, 197 (1992).
[7] U. Falk *et al.*, Phys. Rev. B **35**, 4888 (1987).
[8] M. Hummel *et al.*, Phys. Rev. B **63**, 094425 (2001).
[9] B. Fåk *et al.*, Physica (Amsterdam) **234B–236B**, 1107 (1997).
[10] F. Semadeni *et al.*, Physica (Amsterdam) **297B**, 152 (2001).
[11] R. J. Birgeneau *et al.*, Phys. Rev. B **3**, 1736 (1971).
[12] M. Boehm *et al.*, Europhys. Lett. **43**, 77 (1998).
[13] Y. J. Kim *et al.*, Phys. Rev. Lett. **83**, 852 (1999).
[14] J. Villain *et al.*, J. Phys. (France) **41**, 1263 (1980).
[15] M. Kenzelmann *et al.*, Phys. Rev. B **63**, 134417 (2001).
[16] A. Carbognani *et al.*, Phys. Rev. B **62**, 1015 (2000).
[17] E. Rastelli *et al.*, Phys. Rev. B **67**, 094429 (2003).