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The change of the symmetry of the soft-mode spin wave at the spin–flop transition as observed in $MnTiO_3$ using inelastic polarized neutron scattering

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Abstract. The energy and the eigenvector of the spin waves in $MnTiO_3$ have been studied as functions of the applied magnetic field using inelastic neutron scattering with and without polarization analysis. It is found that the behaviour depends on the distance q from the antiferromagnetic zone centre: for $q \cong 0$ the mode softens completely at the spin–flop field H_{sf}, but it has finite energy for $q > 0$; the eigenvector retains its Ising character for small q up to the highest fields measured (5 T = $0.86H_{sf}$, assuming H_{sf} = 5.8 T), but it changes continuously with field from Ising to Heisenberg character for large q. A very strong, temperature-dependent line width was found at H = 6 T, close to H_{sf}, which is interpreted as further evidence for the soft-mode instability at the spin–flop transition.

1. Introduction

Weakly anisotropic Heisenberg antiferromagnets show a spin–flop transition in a magnetic field applied along the easy axis. At this field, H_{sf}, the Zeeman energy just balances the anisotropy energy; hence with increasing field it becomes energetically favourable for the spins to rotate out of the easy direction into an orientation perpendicular to the easy axis. Consequently the symmetry of the Hamiltonian changes with field:

(i) for $H < H_{sf}$ the system is Ising-like;
(ii) for $H = H_{sf}$ the system has Heisenberg character; and
(iii) for $H > H_{sf}$ the system is xy-like.

As the symmetry determines the universality class and thus the critical behaviour at the phase transition, the phase diagrams and the critical behaviour of such systems have been studied in great detail in the past [1]. Such studies were concentrated on the static critical behaviour, however. Dynamical critical behaviour and the soft mode connected to the spin–flop transition have not been experimentally studied in detail, yet.

In contrast, early theoretical treatments of the spin–flop transition do already make predictions for the soft mode when approaching the transition from above and from below: in both cases the mode at the zone centre should go to zero frequency, but the critical fields need not be the same for the two directions [2, 3]. The existence of two critical fields, H_{c1} and H_{c2}, and in particular the difference between the two reflects the first-order character

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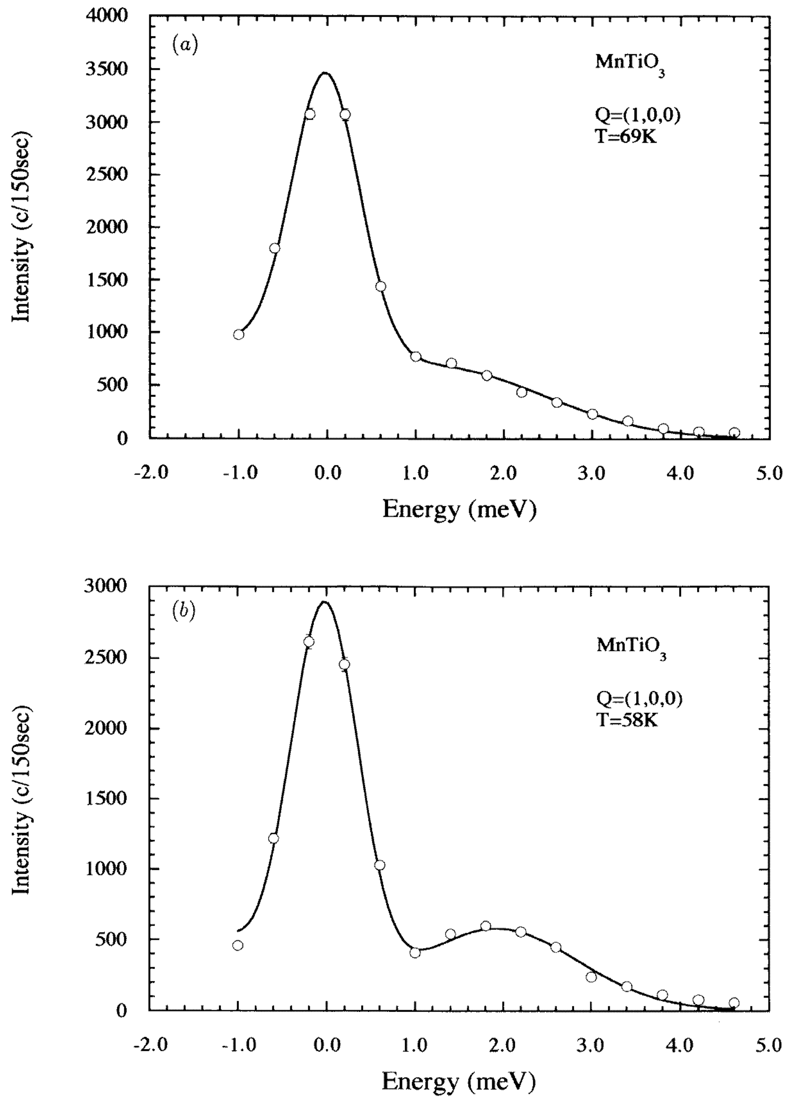

Figure 1. Inelastic neutron spectra for $MnTiO_3$ at $Q = (1, 0, 0)$ at different temperatures ($T_N = 64$ K): (*a*) $T = 69$ K; (*b*) $T = 58$ K; (*c*) $T = 50$ K; and (*d*) $T = 9$ K. Only the spin-wave-creation part of the spectrum is shown together with the scattering at zero energy (mainly incoherent background).

and the hysteresis due to the different stability regions of the two phases. It is thought that the magnetic excitations in the different regimes reflect in their eigenvectors the different symmetries as well.

We have investigated the spin waves in $MnTiO_3$ in an applied field using inelastic neutron scattering with and without polarization analysis. For the first time we observed the soft mode at the antiferromagnetic zone centre with increasing H. Up to now measurements using afmr (antiferromagnetic resonance) have been performed at the spin–flop transition at $Q = 0$ only. We could in particular study the eigenvector of the lowest mode and

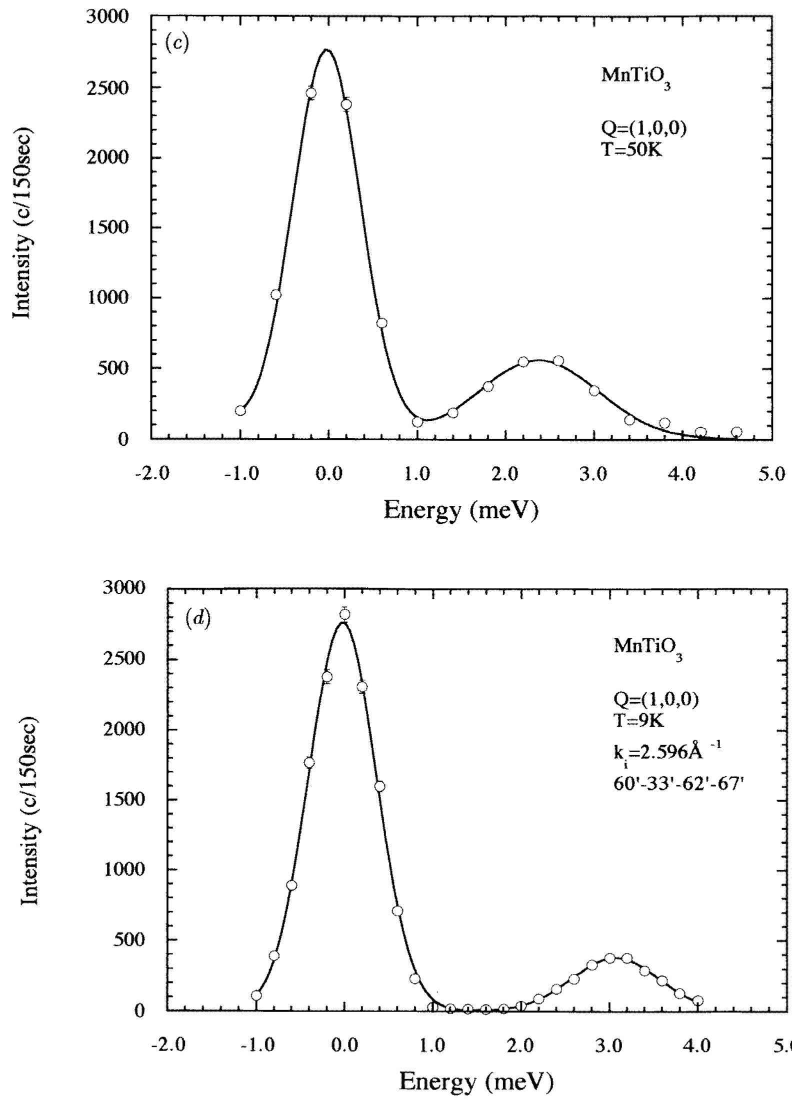

Figure 1. (Continued)

its variation with H for different values of the wave vector q, the distance from the antiferromagnetic Brillouin zone centre. It is found that for small q the eigenvector does not change up to the highest available fields of $0.86H_{sf}$, while at large q a continuous change of the character of the mode from Ising towards Heisenberg character was observed.

2. The system $MnTiO_3$

$MnTiO_3$ has been studied using different techniques in the past [4]. More recently the exchange energies in this system have been determined using inelastic neutron scattering and by the comparison of these results with spin-wave calculations ([5], and references therein). The results obtained can be summarized as follows.

(i) The structure is of Ilmenite type and can be described in a quasi-hexagonal unit cell with $a = 5.138$ Å and $c = 14.283$ Å. The layered character of this structure comes about due to the arrangement of the constituents Mn, Ti and O in separate layers with the Mn^{2+} and Ti^{4+} layers separated by an O layer.

(ii) The Néel temperature is $T_N = 64$ K; the magnetic structure is characterized by an antiferromagnetic arrangement along the c-axis as well as in the plane; the spins point along the c-axis; the anisotropy responsible for this amounts to 1/1000 of the exchange energy corresponding to a gap energy of 156 GHz (or 0.64 meV).

(iii) The two-dimensional character of the system is reflected in a broad peak in the susceptibility well above T_N; the dispersion of the spin waves is found to be strongly anisotropic with respect to the c-axis: there is much weaker dispersion along the c-axis than perpendicular to it; spin-wave analysis of this observation reveals that the 2D character is due to an accidental cancellation of the interplane exchange interaction: the dominating in-plane interaction is $J/k = -7.3$ K while the different interlayer interactions are $J'/k = -2$ K; see [5]. The weighted ratio of these interactions is $J'/J = 0.04$, explaining the observed 2D character.

Thus $MnTiO_3$ appears to be a good candidate for the search for nonlinear excitations in the 2D xy-regime.

3. The experiment and experimental results

Unpolarized as well as polarized inelastic neutron scattering experiments have been performed on triple-axis instruments at Risø National Laboratory (TAS 1 using cold neutrons) and at the Institut Laue–Langevin in Grenoble (IN 12 and IN 20 using cold and thermal neutrons respectively). Pyrolytic graphite was used as monochromator and analyser for the unpolarized experiments and at IN 12, together with a supermirror bender, as polarizer and analyser for the polarized experiments. At IN 20, Heusler crystals were used as monochromator and polarizer and as energy and spin-state analyser. To study the field dependence of the excitations a vertical as well as a horizontal field was used to profit from the selection rules for polarized neutron scattering. The orientation of the 0.4 cm^3 crystal was chosen according to the field orientation: the c-axis was parallel to the magnetic field. Most of the experiments were performed well below the Néel temperature, but some data were obtained close to it.

With unpolarized neutrons the dispersion within and perpendicular to the plane at temperatures below and above T_N in zero field have been measured. Figure 1 shows typical spectra at different temperatures for $\boldsymbol{Q} = (1, 0, 0)$. The solid lines in the figures are results of fits with three gaussians: one gaussian due to incoherent scattering from Ti and Mn and background at zero energy, and the other two representing SW excitations for energy gain and loss whose strengths are related by detailed balance. As the peaks are symmetric and well resolved except at the highest temperature, this procedure appears sufficient for the present purpose. The parameters for the incoherent peak are held fixed to the value obtained at the lowest temperature ($T = 9$ K). The dispersions obtained agree well with the earlier results [5]. The energies and line widths obtained from these fits are shown in figures 2(a) and 2(b). The softening and broadening of the SW excitation with increasing temperature are clearly visible. T_N for the sample was checked by looking at the sublattice magnetization. It agrees very well with $T_N = 64$ K as determined in the earlier work.

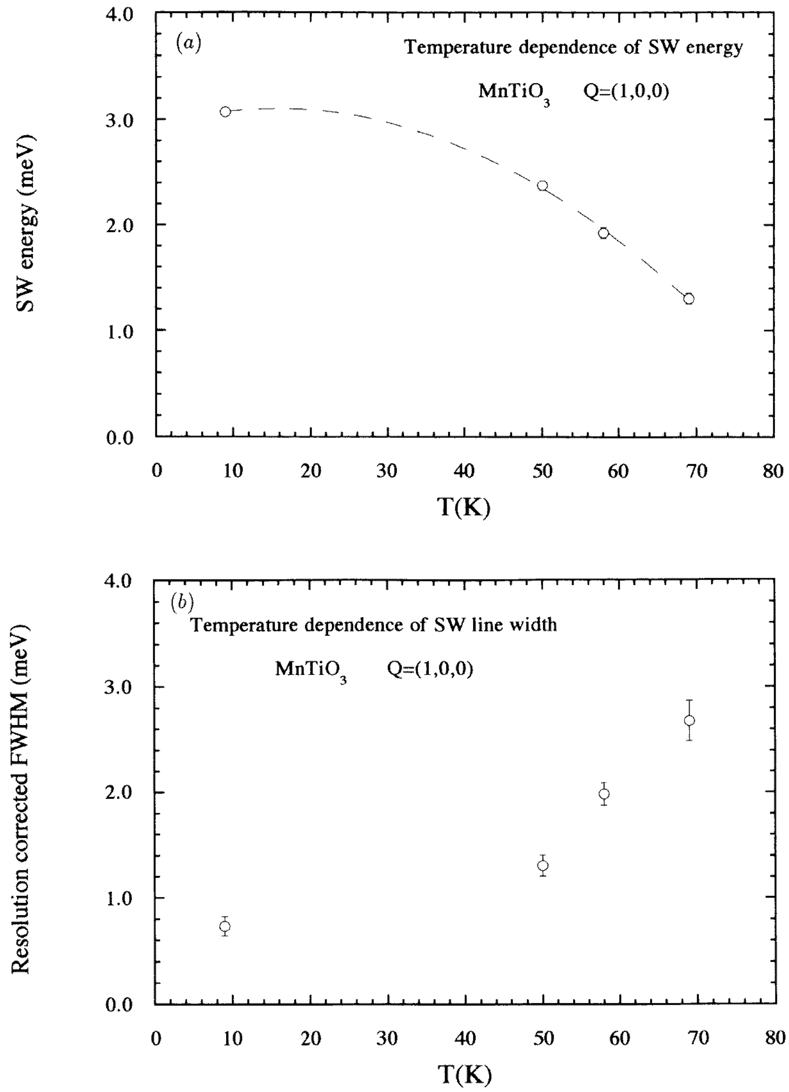

Figure 2. The temperature dependence of (a) the spin-wave energy and (b) the spin-wave line width in $MnTiO_3$ for the mode at $\boldsymbol{Q} = (1, 0, 0)$ at $H = 0$.

With polarized neutrons and polarization analysis two configurations, in both cases with the field direction parallel to the c-axis, have been used.

(i) *H vertical, i.e. perpendicular to the scattering plane.* In this configuration only Brillouin zones with centres of the type $(h, k, 0)$ could be investigated. Consequently no 3D antiferromagnetic zone centre could be reached. It is however a particular situation as far as the selection rules for polarized neutrons are concerned: spin-flip (SF) scattering is due to spin fluctuations in the plane, i.e. perpendicular to the c-axis only. Typical spectra for different fields at 1.7 K are shown in figure 3 for SF and NSF scattering. Analysis of such data yields the field dependence of the spin-wave energy and the intensity of the

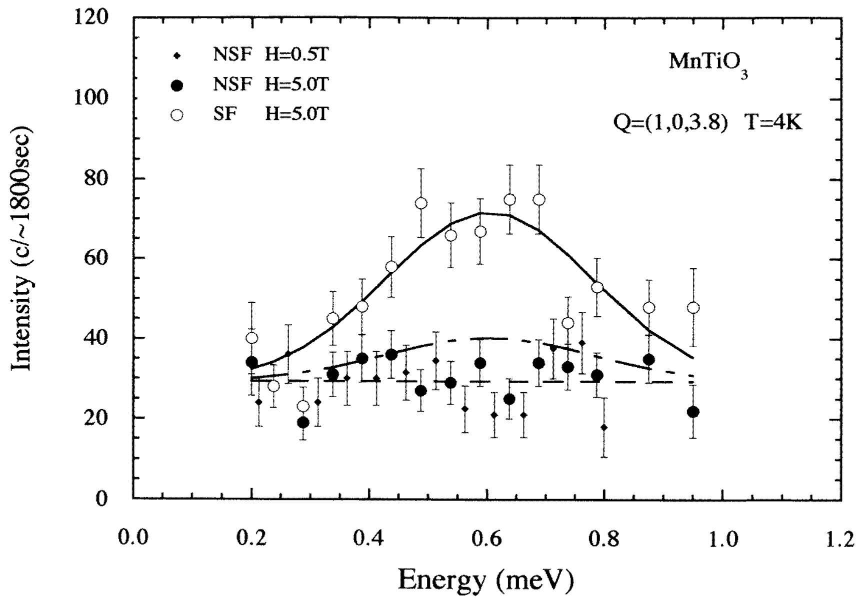

Figure 3. Polarized neutron spectra, spin-flip (SF) and non-spin-flip (NSF), from spin waves in $MnTiO_3$ are shown for different fields along the c-axis at 1.7 K, together with the relative strengths of the NSF (- · -) and SF (—) lines as calculated from neutron beam polarization.

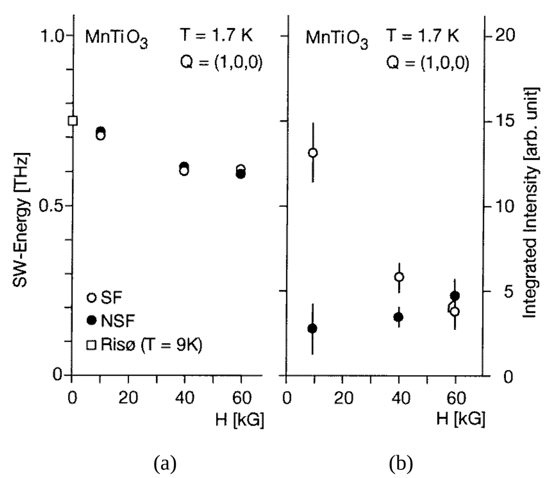

Figure 4. The field dependence of (a) the spin-wave energy and (b) the intensity of the SF and NSF parts of the spin-wave scattering as obtained from data as shown in figure 3.

SF and the NSF scattering as displayed in figure 4. A surprising result is found for the temperature dependence of the line width at large (6 T) field (see figure 5), which is quite different from the zero-field result shown in figure 2(b).

(ii) *H horizontal, i.e. in the scattering plane.* In this configuration antiferromagnetic zone centres can be reached, although the horizontal superconducting split-pair coil puts severe restraints on the accessible Q-values. In figure 6 typical spectra for SF and NSF

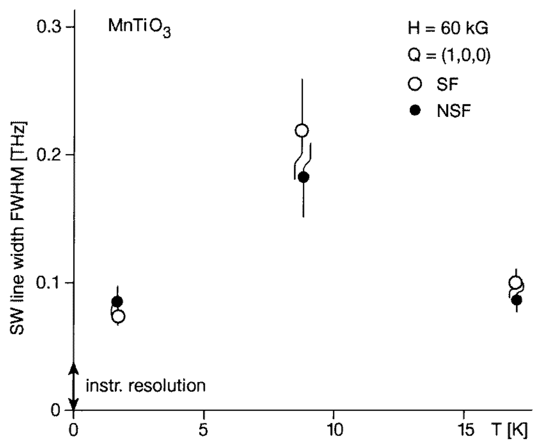

Figure 5. The temperature dependence of the SF and NSF parts of the line-width spin-wave peak as obtained at 6 T.

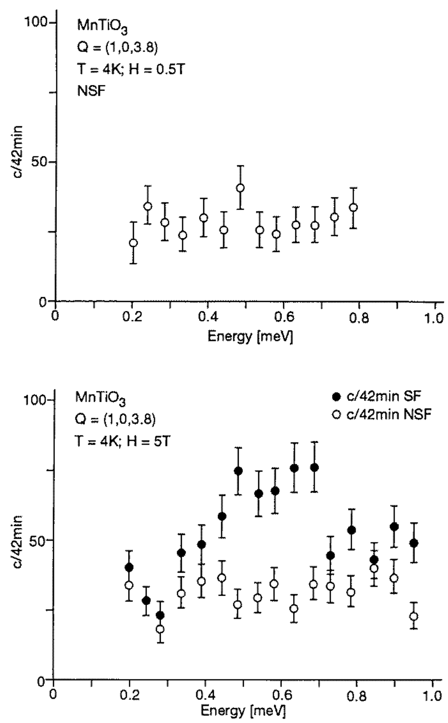

Figure 6. The SF and NSF parts of the spin-wave scattering at $q_c = 0.2$ at 4 K and a horizontal field $H = 5$ T, along the *c*-axis. For comparison, the NSF part is shown for small fields as well.

scattering measured at low and at high magnetic field close to the magnetic zone centre, $q_c = 0.2$ r.l.u., are shown. In figure 7 the field dependence of the mode at the zone centre and slightly away from it is shown as measured at 4.2 K.

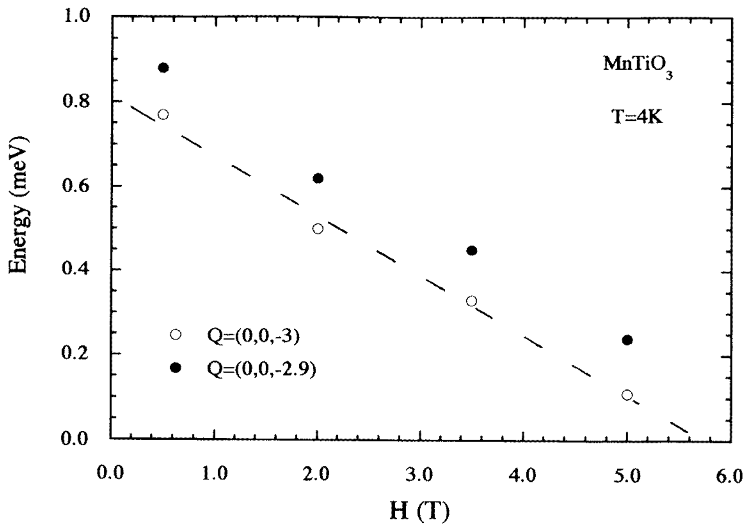

Figure 7. The field dependence of the spin-wave energy at the afm zone centre and slightly off the centre at 4.0 K.

4. Discussion

Inelastic neutron scattering in connection with polarized neutrons and polarization analysis involves more selection rules for scattering from a magnetic system than conventional unpolarized experiments [6]: in addition to energy and momentum conservation, which allow the determination of the dispersion surfaces, spin conservation is probed as well. This together with the well known fact that only those spin components which are perpendicular to the momentum transfer $\boldsymbol{Q}$ contribute to the scattering allows the direct determination of eigenvectors of spin waves. The applied field defines the direction, parallel or antiparallel to which the neutron spin may be polarized. Then spin fluctuations along the field direction are seen in the NSF channel, while fluctuations perpendicular to the field yield SF scattering. Therefore, if we expect a symmetry change in a system the corresponding change in the eigenvectors can be monitored directly by measuring the SF and the NSF channels: in an Ising system spin waves, which by definition are transverse fluctuations, correspond to fluctuations perpendicular to the easy axis. Thus with H parallel to the easy axis, spin waves can show up in the SF channel only. In contrast, if a Heisenberg system is considered, then no quantization axis exists and spin-wave fluctuations appear in all spin components. Thus in a field small compared to the exchange field but comparable with the anisotropy energy, spin waves will show up in both the SF and the NSF channel.

We are not going to discuss the overall features of the SW dispersions in the 3D ordered state, as they agree very well with previous results [5]. But the temperature dependence of the SW energy and the line width at $\boldsymbol{Q} = (1, 0, 0)$, as shown in figure 2, will be discussed. This reciprocal point is a zone-boundary point with respect to the interplanar ordering below T_N and a zone centre with respect to the intraplanar correlations above T_N. One therefore would expect a closing of the gap at T_N, if the 2D system exhibited an xy- or (isotropic) Heisenberg-like character. The results shown in figure 2(a) clearly show that a finite gap remains at T_N. This indicates that a small Ising-like anisotropy exists which is consistent with the results of [5]. The increase of the line width as T_N is approached can clearly be seen in figure 2(*b*). But it is remarkable that it does not seem to diverge at T_N. A more detailed study is needed to determine at which temperature the gap vanishes and the line width diverges. The existence of reasonably well defined spin waves for $T > T_N$ is to be attributed to the significant 2D correlation at these temperatures [7], as observed for other 2D magnets [8].

As discussed above, different symmetry yields different eigenvectors and this can be directly observed by measuring the SF and NSF parts of the scattering. The magnetic field applied along the easy axis leads at the spin–flop transition to a transition from Ising to Heisenberg symmetry, and beyond the spin–flop field, xy-symmetry is obtained. In what follows, we will concentrate on $H < H_{sf}$ and thus on the Ising–Heisenberg transition. This transition would correspond to a transition from purely SF scattering to SF and NSF scattering of equal strength.

We shall first consider the field dependence of the spin-wave energies as shown in figures 4(a) and 7. As expected [2, 3], the energy decreases with increasing field, but complete softening is found at the afm zone centre only. In agreement with the theoretical expectations the energy is found to vary linearly with H. Linear extrapolation to energy zero yields as a critical field $H_{sf} = 5.7$ T and the slope yields a magnetic moment of 2.5 μ_B. These values agree well with values obtained before [9, 10]. The agreement with afm resonance demonstrates that the dispersion is symmetric with respect to the zone boundary. Therefore results of the type presented here should be similar to results obtained by afm resonance at $\boldsymbol{Q} = 0$. This is indeed the case for $H < H_{sf}$ [11]. Although our results are in good agreement with theory, there is one piece of information missing: the gap mode should split into two modes, one increasing and the other decreasing with increasing field. We have not observed the upper mode. As we have not searched systematically, no definite statement about its existence can be made. Although the above-discussed softening of the afm gap mode is the first observation of the soft mode associated with the spin–flop transition, the physically more interesting question to experimentally answer is the change of the symmetry at H_{sf}. The corresponding results are shown in figures 4(b) and 6. As can be seen clearly, at small fields the scattering is essentially SF for both Q-values ($q = \pi$ and $q = 0.1\pi$). On increasing the field, no change is observed for $\boldsymbol{Q} = (1, 0, 3.8)$ or close to it, while for $\boldsymbol{Q} = (1, 0, 0)$ the SF contribution decreases, with correspondingly increased NSF scattering. This means that for $\boldsymbol{Q} = (1, 0, 3.8)$ the mode retains its Ising character up to the highest magnetic field used in this experiment, $H = 0.86H_{sf}$, while at $\boldsymbol{Q} = (1, 0, 0)$ the mode continuously changes character from Ising to Heisenberg behaviour with increasing magnetic field. The observed behaviour can be understood in terms of the different types of zone centre used in the experiment: (0, 0, 3) and (1, 0, 4) are 3D afm zone centres, while (1, 0, 0) is not. At (0, 0, 3) and at (1, 0, 4) the mode with $q \cong 0$ 'senses' the *complete 3D antiferromagnetic intra- and interplanar structure* of Ising character, while the mode at (1, 0, 0) senses the 2D *antiferromagnetic correlation in the planes* only. In addition, at (0, 0, 3) only the x- and y-components of the spins are seen, while at (1, 0, 0) the y- and the z-components can be seen simultaneously. The results for (1, 0, 0) have therefore to be interpreted in the following manner: the observed equal intensity for SF and NSF scattering at 1.7 K and 6 T demonstrates the isotropic character of this mode. Since this mode does not sense the full 3D afm structure it need not show the abrupt change in symmetry as reflected by the first-order spin–flop transition. On the other hand the results near (1, 0, 4) do indeed show no change in the character of the mode with field as the ratio of the SF to the NSF scattering stays essentially unchanged. The measured ratio is very close to the one expected for the measured polarization of the neutron beam. As the z-component of the spins does not fully contribute near (1, 0, 4) (at the Heisenberg point SF would still be stronger than NSF scattering), we have calculated the corresponding strength of the NSF signal for a Heisenberg system. This is drawn as the dashed–dotted line in figure 3, which is not in disagreement with the observation. If the isotropic character near (1, 0, 4) were the same as the one observed at (1, 0, 0), it should have been observable under the experimental conditions.

As the last point, the observed T-dependence of the spin-wave line width at (1, 0, 0) has to be discussed. The results shown in figure 5 demonstrate that for all temperatures at 6 T the line width is significantly larger than the resolution. At 10 K the width is approximately seven times larger than the resolution, for both SF and NSF! We can only speculate about the underlying physics: 6 T is very close to the best experimental value for H_{sf} (5.8 T) but slightly beyond it. Assuming the spin–flop transition to be shifted to higher fields with increasing T, which is not inconsistent with measured phase diagrams [12], one could imagine that around 10 K the system is exactly on the spin–flop line. In this case, the system is at the stability limit, and all excitations and in particular those at the lowest energies are strongly affected and could show significant damping as observed. Further experiments and in particular further theoretical treatments are needed to understand this observation fully.

In conclusion, we have measured for the first time the soft mode at the spin–flop transition of a Heisenberg–Ising antiferromagnet and find agreement with theoretical predictions. We have shown that the eigenvector of the spin wave at the 3D afm zone centre stays unchanged up to $0.86H_{sf}$ (the highest available field for this experimental configuration), while the eigenvector at a zone centre, which does not correspond to an afm Bragg peak, changes continuously with field from Ising to Heisenberg behaviour at 6 T ($\geqslant H_{sf}$). This is physically plausible but no theory is available for this phenomenon. We observe very strong broadening of the spin waves, which is interpreted as another indication for the instability of the system at the spin–flop transition.

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