Singlet Ground State Magnetism: III. Magnetic Excitons in Antiferromagnetic TbP

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The dispersion of the lowest magnetic excitations of the singlet ground state system TbP has been studied in the antiferromagnetic phase by inelastic neutron scattering. The magnetic exchange interaction and the magnetic and the rhombohedral molecular fields have been determined.

1. Introduction

The magnetic properties of the rare earth compounds are determined by the crystal field splittings of the rare earth ions, the magnetic exchange coupling and to a lesser degree by the magnetoelastic interaction. The best tool for studying the splittings and the exchange is neutron scattering. The neutron scattering cross section is proportional to the imaginary part of the magnetic dipole susceptibility which is within the RPA given by [1]

$$X(\mathbf{Q},\omega,T)=\frac{g(\omega,T)}{1-g(\omega,T)\cdot J(\mathbf{Q})} \tag{1}$$

where $J(\mathbf{Q})$ is the Fourier transform of the exchange coupling and $g(\omega,T)$ is the dynamic single ion susceptibility

$$g(\omega,T)=\sum_{ij}\frac{|M_{ij}|^2(n_j-n_i)}{(E_i-E_j)^2-\omega^2} \tag{2}$$

$|M_{ij}|^2, n_i, E_i$ are the transition matrix elements, the thermal population factors and the energies of the single ion states; they are the crystal field states in the paramagnetic and the molecular field states in the ordered phases.

A great number of neutron experiments have been carried out on compounds, especially those with cubic symmetry, in the paramagnetic regime, where well above the ordering temperature T_N, X approaches g and the inelastic transitions seen in a neutron experiment occur at the poles of g at $\omega=E_i-E_j$ independent of $\mathbf{Q}$. Fewer experiments have been performed in the ordered phase on single crystals where in addition $J(\mathbf{Q})$ can be determined directly from the dispersion of the excitations. Only a few examples are known where the dispersion is observed already above T_N, because the development of the dispersion in the paramagnetic phase is usually interrupted by the ordering of the crystal field ground state moments. The occurence of the dispersive excitations is therefore most favoured in systems with a non-magnetic crystal field ground state. In cubic symmetry these are the states $\Gamma_1, \Gamma_2, \Gamma_3$ of the non-Kramers ions Pr, Tb, Tm, Ho. But even in the rare case of a non-magnetic ground state the existence of well defined dispersive excitations above T_N is only found if the ratio η of exchange to crystal field energy is about unity [2]. For $\eta \ll 1$ the system will stay paramagnetic down to $T=0$ with little dispersion of the crystal field transitions, for $\eta \gg 1$ the excitations of the paramagnetic phase are found to be overdamped [3]. So far TbP appears to be the best candidate for a comparison of dispersive magnetic excitations above and below the ordering temperature. TbP has a non-magnetic Γ_1 ground state and η is about 1.2. It orders antiferromagnetically at 7.4 K with an ordering wave vector of (1/2 1/2 1/2) [4, 5]. The phase transition is of first order due to a simultaneous alignment of the magnetic dipole and the electric quadrupole moments [5]. A strong dispersion and a splitting of the $\Gamma_1-\Gamma_4$ exciton was observed above T_N which culmi-

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nated in a soft mode behaviour. The evaluation of this result yielded an anisotropic exchange coupling of long range [4, 6].

In the present article we will show results on the magnetic excitations in the antiferromagnetic phase of TbP and compare them with the results on the paramagnetic phase. We propose that the article should be read in parallell with Part I [5] and II [4] of this work and also with the study of Holden et al. on TbSb [3] which has the same crystallographic and magnetic structure as TbP and where the formalism used for the evaluation of the data is described in detail.

2. Experiment and Results

The TbP single crystal with a volume of 0.5 cm^3 was the same as used in Part I and II of this work [4, 5]. The main part of the neutron inelastic scattering experiments was carried out on the triple axis spectrometer IN2 which is situated at a thermal neutron beam of the reactor of the Institut Laue-Langevin at Grenoble. An incident neutron wave vector $k_i = 2.662\,\text{Å}^{-1}$ was used with a pyrolytic graphite double monochromator and a graphite analyser. Higher order contaminations were reduced by a pyrolytic graphite filter. The horizontal collimation was 120′ −40′−40′−40′ along the path of the neutrons. All data were collected in the constant-**Q** mode of operation and with **Q** either in the $(1\bar{1}0)$ or in the (001) plane.

In the antiferromagnetic phase of TbP the Tb-moments are constrained by the crystal field anisotropy to point along the ⟨111⟩ directions. Thus there are four magnetic domains corresponding to the [111], $[1\bar{1}1]$, $[\bar{1}11]$, $[\bar{1}\bar{1}1]$-direction, each one having its own magnetic reciprocal lattice which is superimposed on the nuclear reciprocal lattice (see Fig. 2 in [3]). For the sake of brevity we specify the momentum transfer **Q** in terms of the Miller indices of the conventional cubic cell of the *fcc* nuclear lattice, rather than translating **Q** into the sum of a Bragg point τ_d and a reduced wave vector $\mathbf{q}_d$ for each domain separately.

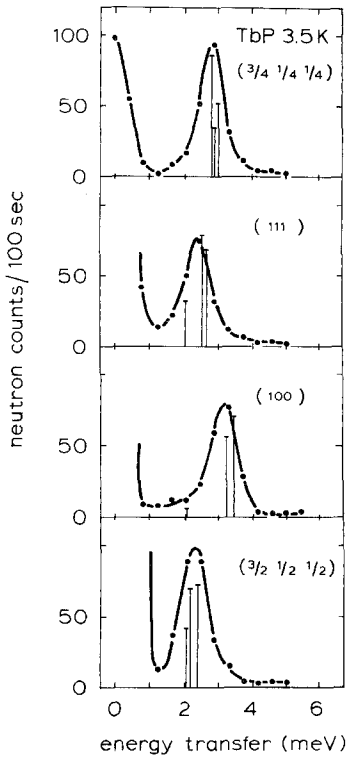

Fig. 1. The scattered neutron intensities for several const. $-\mathbf{Q}$ scans collected with $k_i = 2.662\,\text{Å}^{-1}$ at 3.5 K. The solid lines are guides to the eye. The vertical bars give the positions and intensities of the magnetic excitations as calculated from the theoretical model described in the text

Some scans taken at 3.5 K, which is about half of T_N, are shown in Fig. 1. The dispersion of the magnetic excitation is presented in Fig. 2. The intensity of the scattered neutron groups was found to be almost inde-

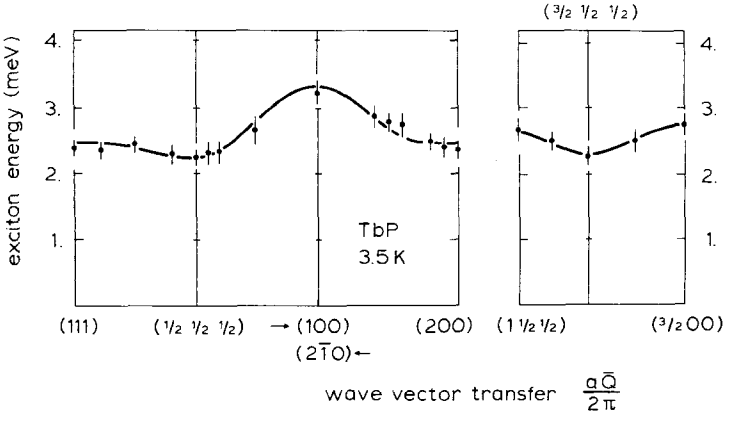

Fig. 2. The dispersion of the lowest magnetic excitation. The solid line is the theoretical result for the averaged mode

pendent of **Q** when corrected properly for the magnetic form factor, the Bose factor and the spectrometer efficiency according to (3) of Part II.

As will be described later, the theoretical treatment of the antiferromagnetic phase predicts several modes in the energy range studied. For this reason we also show some high resolution scans which were performed at a cold neutron source spectrometer at Risø during the measurements reported in [4]. These data show the recovery of the two soft modes of the paramagnetic phase when crossing T_N. Note that the **Q**-value of Fig. 3 is the one where the largest relative splitting of the paramagnetic $\Gamma_1-\Gamma_4$ exciton was observed. The results at 7.37 K are indications for the coexistence of ordered and non-ordered parts of the crystal, the data at 7.25 K are already representative of the antiferromagnetic phase, though of course in a comparison to the results at 3.5 K one should take into account that in spite of the first order phase transition the magnetization and the excitation energy have not yet quite reached their fully saturated values. Nevertheless Fig. 3 shows that the excitations of the ordered phase are characterized by a single peak of considerable width. There might be some fine structure but a splitting into several modes is by no means evident. We conclude that the measurements on the spectrometer IN2 give a relevant picture of the excitations in spite of their lower resolution. Summarizing the results, one observes a single broad excitation signal of about constant strength with an average energy of about 2.7 meV and a band width of 1.0 meV. The corresponding values in the paramagnetic phase at 7.9 K were 1.6 meV for the average energy and 1.7 meV for the band width [4].

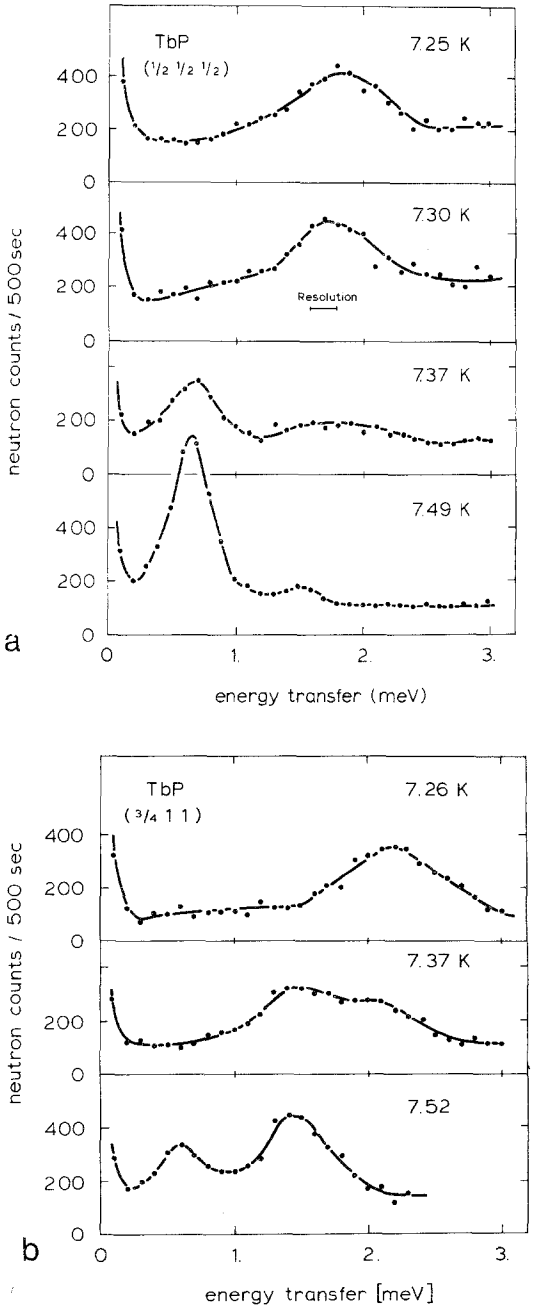

Fig. 3a and b. The scattered neutron intensities at **(a)** $\mathbf{Q}=(1/2\ 1/2\ 1/2)$ and **(b)** $\mathbf{Q}=(3/4\ 1\ 1)$ collected with $k_i=1.5\ \text{Å}^{-1}$ across the ordering temperature $T_N\simeq 7.37$ K

3. Evaluation

The excitations of the ordered phase have been evaluated in terms of a Hamiltonian which considers the crystal field and the Heisenberg exchange coupling between the Tb-moments. As usual the Hamiltonian is divided into a single-ion and an inter-ion part [3]. The single-ion part is characterized by the two parameters, x and W, of the cubic crystal field, the magnetic molecular field H_m and the quadrupolar field B_2 which describes the rhomohedral distortion of the cell below T_N. Both fields are directed along [111]. The inter-ion part contains the remaining exchange contributions and leads to a dispersion of the magnetic excitations via the Fourier transform of the exchange coupling $J(\mathbf{Q})$. We made the following assumptions.

1. The crystal field parameters x, W were chosen to be -1 and -0.0542 meV which gives a first excited state 1.625 meV above the ground state as demanded by the results of Part II. Other sets are also possible as long as the $\Gamma_1-\Gamma_4$ separation is unchanged.

2. The values of the staggered moment and the average excitation energy were used to confine roughly the molecular fields to the ranges $3<H_m<6$ Tesla and $0>B_2>-0.016$ meV. The first three excited molecular field levels will then lie between 1 and 3.5 meV.

3. The four domains have equal statistical weights as can be concluded from the intensities of equivalent magnetic Bragg reflections.

4. Since no evident mode splitting was observed and since the dispersion is quite smooth, the exchange $J(Q)$ was assumed to be isotropic and given by the contributions J_1 and J_2 of the first and second nearest neighbours only.

5. The mixing of magnetic dipole and electric quadrupole excitations was neglected (see below).

In calculating the dispersion relation we followed closely Ref. 3. The best description of the experimental results was achieved with molecular fields along a line in the H_m, B_2-plane which extends from about (3.5 Tesla, $-12\,\mu$eV) to about (4.5 Tesla, $-6\,\mu$eV); the group of the first three excited molecular field states which originate from the Γ_4-state, is then about 2.5 meV, the next higher states are above 4 meV as can be seen in Fig. 4. Because of these moderate fields the selection rules of the cubic paramagnetic phase are still approximately valid. Thus the strongest magnetic excitations are those to the first three excited levels; magnetic transitions to higher states were found to have practically no influence. The quadrupole matrix elements to the first three levels are still small, the quadrupole transitions to the higher states can also be neglected, since the corresponding excitations are too far off in energy in order to lead to a mixing with the strong magnetic modes. Consequently the only relevant states of molecular field level scheme are the first excited states $|a\rangle$, $|b\rangle$, and $|c\rangle$ which are connected with te ground state $|0\rangle$ via the dipole elements $\langle a|J_z|0\rangle = M_a$, $\langle b|J_+|0\rangle = M_b$ and $\langle c|J_-|0\rangle = M_c$. The energies of the first three excited states are found to be nearly degenerate with $E_a = E_b = E_c = 2.7$ meV and the transition matrix elements are $M_a = 2 \pm 0.2$, $M_b = 4.3 \pm 0.5$ and $M_c = 2.9 \pm 0.3$ with a resulting magnetic moment of $7.1 \pm 0.1\, u_B$. The values for exchange parameters are $J_1 = 5 \pm 1\,\mu$eV and $J_2 = -7 \pm 1\,\mu$eV. H_m, B_2, J_1 and J_2 were derived by fitting the averaged excitation energy $\bar{\omega}(\mathbf{Q})$ to the data of Fig. 2 with

$$\bar{\omega}(\mathbf{Q}) = \frac{\sum_{d=1}^{4} \sum_{s=1}^{4} \omega_{s,d}(\mathbf{Q})\, I_{s,d}(\mathbf{Q})}{\sum_{d=1}^{4} \sum_{s=1}^{4} I_{s,d}(\mathbf{Q})} \tag{3}$$

where $\omega_{s,d}(\mathbf{Q})$ and $I_{s,d}(\mathbf{Q})$ are the excitation energy and the intensity of the s^{th} mode in the domain d. The first four branches of the Brillouin zone of the [111] domain as calculated with the parameters of the best fit are shown in Fig. 5. The two transverse modes (solid lines) originate from $J_{\mp}$-transitions to the states $|b\rangle$ and $|c\rangle$ and are strongly hybridized, the longitudinal mode (dashed line) represents the propagating J_z-transition to the state $|a\rangle$. It is split into an acoustic and an optical branch. Only one of these longitudinal branches carries intensity depending whether the Brillouin zone contains a magnetic or a nuclear Bragg point. Thus at a given $\mathbf{Q}$, each domain contributes only three rather than four modes to the average of (3). The number of distinct excitation energies is further reduced by coincidences of modes of identical polarization from different domains. In practice the average is dominated by a small number of excitations whose energies and intensities are

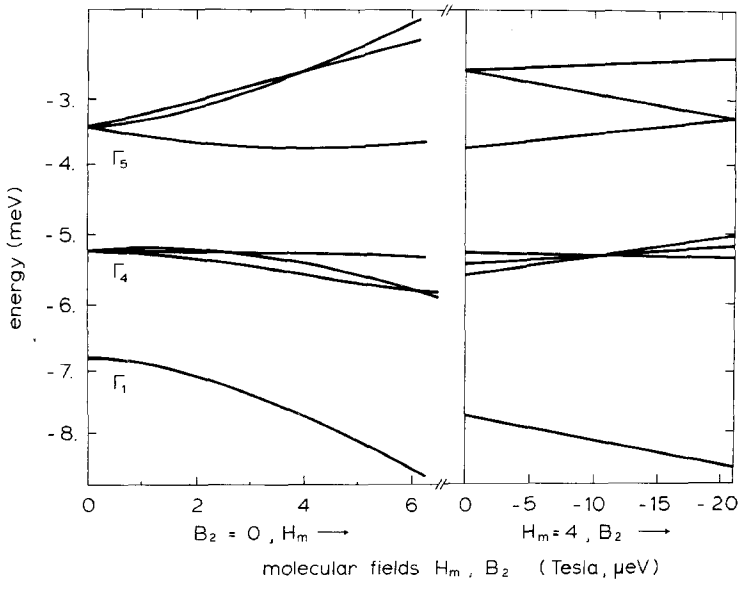

Fig. 4. The splitting of the lowest three crystal field levels of Tb^{3+} in TbP in the presence of the magnetic and rhombohedral molecular fields

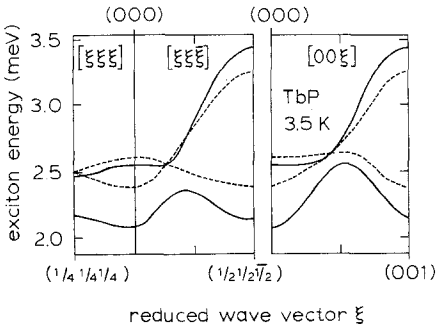

Fig. 5. The theoretical dispersion of the lowest magnetic excitations for the first Brillouin zone of the [111]-domain. The solid lines give the strongly hybridized $J_{\pm}$-excitations, the dashed lines the acoustic and optic branch of the J_z-excitation

shown by vertical bars in Fig. 1. However, even in the high resolution scans of Fig. 3 it was not possible to resolve these modes. The large line widths may be taken as an indication that several modes contribute to the observed neutron groups. The averaged mode is calculated to have a constant strength independent of **Q** in agreement with the experiment.

4. Discussion

TbP was already well characterized by the first and second part of this work. The present third part contributes a more precise determination of the molecular fields in the ordered phase than it was possible to obtain from the measurements of the spontaneous magnetization and the molecular field calculations of Part I. The exchange and quadrupolar coupling coefficients derived in I yields the first three excited molecular field states at energies $E_a = 2.3$ meV and $E_b = E_c = 3.1$ meV which corresponds to fields H_m and B_2 of about 3 Tesla and $-19\,\mu$eV. A splitting between the J_z and the $J_{\pm}$ excitations of that order would have been visible in the inelastic neutron experiment.

The values of the isotropic exchange coupling to the first and second neighbours $12J_1 = (60 \pm 12)\,\mu$eV and $6J_2 = (-42 \pm 6)\,\mu$eV agree reasonably well with a best fit of the corresponding isotropic coefficients of $66\,\mu$eV and $-53\,\mu$eV [6] which were derived from the dispersion of the $\Gamma_1 - \Gamma_4$ exciton in the paramagnetic phase. However, it is clear that the measurements of [4] above T_N allowed for a much more accurate and detailed insight into the exchange coupling of TbP than the present study below T_N. In particular the present results are insufficient to show the anisotropic nature of $J(\mathbf{Q})$. The following reasons might explain this shortcoming:

i) Quite generally the magnetic excitations of a slightly over-critical non-magnetic ground state system have a larger ratio of band width to mean excitation energy just above T_N than below i.e., the dispersion of the excitation which reflects the exchange coupling is more pronounced above T_N. This feature is most easily seen from the expression for the excitation of a singlet-singlet system with a level splitting Δ [1]

$$\omega(\mathbf{Q}) = \Delta[1 - J(\mathbf{Q}) M^2 (n_0 - n_1)/\Delta]^{1/2} \tag{4}$$

where $\Delta(T < T_N) > \Delta(T > T_N)$ and $M^2(T < T_N) < M^2(T > T_N)$ because of the action of the molecular field in the ordered phase.

ii) The ordered phase introduces additional parameters which complicate the evaluation of the data. In the special case of TbP the paramagnetic phase is characterized by one single ion parameter, the splitting between the crystal field states Γ_1 and Γ_4. Below T_N the two additional molecular fields H_m and B_2 have to be added. The lifting of the degeneracies of the crystal field states by the molecular fields leads to a large number of excitations and the assignment of the modes is less straightforward than in the paramagnetic regime. In practice it might be difficult to discriminate this effect from the action of an anisotropic coupling. Finally the possible formation of domains introduces a high degree of uncertainty and rules out an analysis of the polarization of the modes. In TbP the information on the excitations is further obscured by an accidental coincidence of the first three excited molecular field states.

The superiority of the data of the paramagnetic phase is best demonstrated by the fact that the most detailed information on the magnetic interactions in crystal field dominated systems was obtained from the study of the parmagnetic excitations in the singlet ground state systems Pr-metal [8], PrSb [7] and TbP [4, 6].

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