MAGNETIC EXCITATIONS IN RARE EARTH Al₂ COMPOUNDS

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ABSTRACT

In the rare earth intermetallic compounds, the crystal field is often comparable to the exchange interaction between the magnetic ions. The magnetic excitations (excitons) in such systems are transitions between single-ion atomic levels, propagating through the lattice via the exchange interaction. This article reviews recent experimental and theoretical work on rare earth Al₂ compounds. The excitons in NdAl₂ and TbAl₂ have been studied by inelastic neutron scattering. The dispersion relations are analysed within the random phase approximation using a Hamiltonian including 4th and 6th order crystal field terms and an isotropic exchange interaction. The spectrum of NdAl₂ at 5 K comprises both transverse and longitudinal modes, corresponding to transitions between the ground state and excited mean-field states. The bulk magnetic properties of NdAl₂ can be understood quantitatively using the crystal field parameters derived from the analysis of the exciton spectrum. At 4 K the magnetic excitations in TbAl₂ are spin waves. At temperatures above 35 K the neutron scattering measurements show a double peak structure. This splitting of the spin wave branch is the result of an interaction between the spin-waves and excitations associated with higher-lying mean-field states, a magnon-exciton interaction.

INTRODUCTION

The magnetic properties of rare earth systems, in which the exchange energies and the crystal field nearly balance, differ substantially from those of conventional magnets. In particular, the magnetic excitations are fundamentally different from the spin-waves encountered in materials where the exchange interaction dominates the crystal field, such as the heavy rare earth elements. Instead the magnetic excitations, or magnetic excitons, can be described as transitions between single-ion states which propagate through the lattice via the exchange interactions. In the paramagnetic regime, the excitons are pure crystal field transitions which may have a q dependence due to two-ion interactions. In the ordered regime we shall see that the excitons can be thought of as transitions between mean-field states.
The elementary magnetic excitations can in principle be studied directly via inelastic neutron scattering techniques. In conventional magnets, the main effect of the crystal field is simply to create energy gaps in the spin wave spectrum, and it is difficult to get reliable information on the crystal fields from the dispersion relations. In this case a more precise determination can be obtained from single crystal magnetisation studies, or from inelastic neutron scattering or susceptibility measurements on diluted samples. For systems where crystal field and exchange energies are comparable, an analysis of the exciton spectrum may yield information on both the crystal field parameters and the wave vector dependence of the exchange interaction between the rare earth ions.

In this paper a recent study of the magnetic excitons in some REAl₂ (RE = rare earth) compounds will be reviewed. The local surroundings of the rare earth ions are cubic, which limits the number of independent crystal field parameters to two and makes these compounds suitable for detailed numerical calculations. We shall see that the crystal field creates a variety of interesting dynamical effects, and that a microscopic description of the magnetic properties can be given in terms of the crystal field and the exchange parameters derived from an analysis of the exciton spectrum.

The format of the paper is as follows. In Sec. II we set up the theory for the dispersion relations for magnetic excitons in complicated many-level systems to be used in the analysis. This RPA-theory includes not only excitations from the ground state, but also excitations out of excited states "excited state spin waves", which are important at elevated temperatures. Section III is devoted to a detailed discussion of NdAl₂ where several modes of different nature have been observed. In Sec. IV we discuss the temperature dependence of the spin wave spectrum of TbAl₂. In this compound the excited state spin waves have been directly observed through an interaction with the main spin-wave mode. Finally, Sec. V contains a general discussion.

II. THEORY OF MAGNETIC EXCITATIONS

In this section, a method will be presented for the study of collective excitations in a lattice of identical magnetic ions with discrete energy levels. The excitation spectrum will be calculated directly by considering the equations of motion of operators creating transitions between single-ion states. Using the double-time Green's function techniques, the equations of motion will be developed in the random-
phase-approximation (RPA). This theory gives a clear picture of the physical nature of the magnetic excitations in contrast to theories working in artificial pseudo-spin spaces.\textsuperscript{12}

We consider the Hamiltonian

\[ H = \sum_i V_{ci} - \sum_{ij} J_{ij} \mathbf{j}_i \cdot \mathbf{j}_j. \]  \hspace{1cm} (1)

\( V_{ci} \) is the crystal field potential on the ion at site \( i \) which may conveniently be expressed as a linear combination of Steven's operators.\textsuperscript{11} \( J_{ij} \) is the exchange integral between the ions \( i \) and \( j \). For metals the \( J_{ij} \) originates mainly from the indirect coupling via the conducting electrons, the RKKY interaction.\textsuperscript{13} However, the present theory can be extended to systems with any two-ion interaction, both in the paramagnetic and the ordered phase without introducing essential complications. In the ordered phase, the Hamiltonian is further separated into a two-ion term \( H_1 \) and a single-ion term \( H_0 \) in the following way:

\[ H = H_0 + H_1 + N J(0) \langle J^z \rangle^2 \]  \hspace{1cm} (2)

\[ H_0 = \sum_i V_{ci} - 2 J(0) \sum_i J_i^z , \] \hspace{1cm} (3)

\[ H_1 = - \sum_{ij} J_{ij} \mathbf{j}_i \cdot \mathbf{j}_j , \] \hspace{1cm} (4)

\[ \mathbf{J}_i = \mathbf{J}_i - \langle J \rangle \hat{z}_z , \quad J(0) = \sum \gamma_{ij} \] \hspace{1cm} (5)

\( H_0 \) is the molecular field Hamiltonian and \( H_1 \) is the interacting part of the Hamiltonian giving rise to dispersion of collective excitations. The statistical average \( \langle J^z \rangle \) must be calculated self-consistently. \( \hat{z}_z \) is a unit vector in the magnetization direction. The eigenstates of the single-ion Hamiltonian \( H_0 \) are denoted \( |n> \) with energies \( E_n \). To proceed further we transform the total Hamiltonian into a representation where the single-ion term is diagonal, that is to say we project any operator \( O \) onto the single-ion states \( |n> \)

\[ O_i = \sum_{mn} <n|O_i|m> \langle |n><m| \rangle , \] \hspace{1cm} (6)
The operators \(|n> <m|\) create transitions between the single ion states \(|m_i>\) and \(|n>\), are denoted as \(a_{mn}^i\). The operators \(a_{0n}^i = (|0> <n|)_i\) and \(a_{n0}^i = (|n> <0|)_i\), where \(|0>\) is the ground state, correspond to Grover's pseudoboson operators \(b_n\) and \(b_n^+\). In a singlet-singlet system these operators are identical to the pseudo-spin operators introduced by Wang and Cooper.\(^\text{15}\)

We obtain:

\[
\mathcal{H} = \sum_{in} E_n a_{mn}^i - \sum_{ij} \sum_{mn} \sum_{m'n'} i \Omega_{ij} a_{mn}^i a_{m'n'}^j,
\]

where \(\alpha\) denotes the cartesian coordinates. This transformation is, of course, exact. We now introduce the retarded double time dependent Green's functions

\[
G_{ij}^{pr,p'r'}(t) = \langle \langle a_{pr}^i(t); a_{p'r'}^j(0) \rangle \rangle
\]

as defined by Zubarev.\(^\text{16}\) \(\delta(t)\) is the unit step function. The equations of motion of the Green's functions are evaluated using the equation \(i a_{pr}^i = [a_{pr}^i, \mathcal{H}]\). For the higher order Green's functions involving operators on three different sites we apply the simplest random phase (RPA) decoupling.

RPA: \(\langle \langle a_{pr}^i(t); a_{p'r'}^j(t); a_{p''r''}^j(0) \rangle \rangle\)

\[
= \langle \langle a_{pr}^i \rangle \rangle \langle \langle a_{p'r'}^j(t); a_{p''r''}^j(0) \rangle \rangle
\]

\[+ \langle \langle a_{p'r'}^j \rangle \rangle \langle \langle a_{pr}^i(t); a_{p''r''}^j(0) \rangle \rangle. \tag{9}\]

The thermal averages \(\langle \langle a_{pr}^i \rangle \rangle\) must, in principle, be determined in a self-consistent way. However, to facilitate the calculations we insert the molecular-field values calculated from the single-ion Hamiltonian \(\mathcal{H}_0\):

\[
\langle \langle a_{pr}^i \rangle \rangle = \langle a_{pp}^i \rangle \delta_{pr} = n_p \delta_{pp} \delta_{pr} \tag{10}\]

\(n_p\) is the occupation number of level \(p\). Because of time and translational invariance in a simple Bravais lattice, we can Fourier transform our Green's functions with respect to time and space.
The doubly Fourier-transformed equations of motion turn out to be:

\[
G_{pr, p'r'}(q, \omega) (E_r - E_{p'} - \omega) \\
- \sum_{mn} G_{mn, p'r'}(q, \omega) (n_p - n_{r'}) \\
\times 2 \int (q) \sum_{\alpha} \langle m | j^\alpha | n > | r | j^\alpha | p > \\
= - \frac{1}{2\pi} (n_p - n_{r'}) \delta_{pr} \delta_{r'},
\]

(11)

The Green's functions can thus be determined by solving this coupled system of linear equations. The energies of the magnetic excitations are the poles of the Green's functions, which are the roots of the characteristic determinant of the system of equations for fixed values of \( p' \) and \( r' \). The determinant is independent of \( p' \) and \( r' \), such that the excitation frequencies are unequivocally determined.

For rare earth ions in a cubic environment, at least two of the matrix elements \( \langle n|J^+|m >, \langle n|J^-|m >, \) and \( \langle n|J^z|m > \) are zero. This means that the equations (11) determining the exciton dispersion relations can be separated into two sets of equations. One set involves matrix elements of \( J^+ \) and \( J^- \) only. The excitation branches determined by this part of the linear system of equations are denoted transverse. The other set of equations, involving matrix elements of \( J^z \) only, determines the longitudinal excitations. At zero temperature this approach is equivalent to the pseudo-Boson method introduced by Grover, and the many level spinwave theory of Buyers et al. used to interpret the exciton spectrum of TbSb.

The complex frequency dependent susceptibility can be expressed by the Green's functions:

\[
\chi^{\text{ES}}(q, \omega) = 2\pi i F.T. \delta(t) < [J^\alpha(t), J^\beta_1(0)] > \\
= -2\pi \sum_{prp'r'} G_{pr, p'r'}(q, \omega) < p | J^\alpha | r > < p' | J^\beta | r' >.
\]

(12)

F.T. denotes the Fourier transformation with respect to time and lattice. By inserting (12) into (11) we obtain
\[ \chi^\alpha_\beta(q, \omega) = \chi^\alpha_\beta(\omega) + 2 \sum_j \chi^\gamma_j \chi^\gamma_j(\omega) \] (13)

where

\[ \chi^\alpha_\beta(\omega) = \sum_{\mathbf{p} \mathbf{r}} \frac{< \mathbf{p}|j^\alpha|\mathbf{r}> < \mathbf{r}|j^\beta|\mathbf{p}> (n_p - n_r)}{E_r - E_p - \omega} \] (14)

\( \chi_0 \) is the single-ion susceptibility. Equation (13) is the usual molecular-field equation to determine the complex susceptibility. The excitations determined by Eq. (11) are thus in agreement with the excitations calculated by the method of Peschel et al.\(^{18}\)

For a neutron scattering experiment it is important to know the strength of the different lines. The cross section can be expressed as the imaginary part of the dynamic susceptibility\(^{19}\) using the fluctuation-dissipation theorem

\[ \frac{d^2 \sigma}{d \Omega d \omega} = \left( \frac{1.91 \epsilon^2 gF(k)}{2mc^2} \right)^2 \frac{ke}{ki} T \] (15)

where

\[ T = [1 - \exp(-\beta \omega)]^{-1} \sum_{\mathbf{q} \mathbf{k}} (\tilde{E}^\alpha_\beta - \tilde{k}^\alpha \tilde{k}^\beta) \text{Im} \chi^\alpha_\beta(\mathbf{k}, \omega) \] (16)

The intensities can thus be calculated from the residues of the dynamics susceptibility. For a cubic multidomain sample, the factor \((\tilde{E}^\alpha_\beta - \tilde{k}^\alpha \tilde{k}^\beta)\) must be summed over equivalent directions, which effectively removes the \( k \) dependence.

The unit cell of the rare earth \( \text{Al}_2 \) compounds contains two magnetic ions. The spectrum will therefore consist of both acoustic and optical modes. The theory can easily be extended to this case. One simply has to replace \( \gamma(q) \) by \( \gamma(q) + |\gamma(q)|^2 \) for the acoustic branches and by \( \gamma(q) - |\gamma(q)|^2 \) for the optical branches in the equations determining the energies and neutron intensities. \( \gamma(q) \) is the Fourier transform within one sublattice, and \( \gamma'(q) \) is the Fourier transform between the two sublattices. However, the magnetic structure factor \( 1 + \cos(\pi \cdot q) \), must be taken into account.\(^{19}\) The plus sign is valid for the acoustic modes, the minus sign for the optical modes. This factor makes it possible to distinguish between optical and acoustic modes. \( \phi \) is a phase angle given by \( \exp(i \phi) = \gamma'(q)/|\gamma'(q)| \).
NdAl$_2$ is an example of a magnetic system in which the crystal field and exchange energies are of the same order of magnitude. NdAl$_2$ orders in a simple ferromagnetic structure for $T < 65K$ with magnetic moments pointing along $<100>$ directions. The magnetic moment at 4.2K is $2.5\mu_B + 0.1\mu_B$, which is significantly lower than the free ion value $3.28\mu_B$ of the $^4I_9/2$ ground state multiplet of the Nd$^{3+}$ ion. The crystal field is thus strong enough to produce considerable quenching, and we expect it therefore to have strong effects on the magnetic exciton spectrum.

An inelastic neutron scattering study of the excitons in the ordered state has recently been reported by Houmann, Bak, Purwins and Walker. The experiment was performed on a triple axis spectrometer at Riso. The experimental results for momentum transfer in the $<110>$ direction are given in Fig. 1.

Two well-resolved low-lying branches were observed, one acoustic and one optical. It was not possible to resolve the acoustic branch below $q = 0.2\text{Å}^{-1}$. However, the feature of the spectrum which makes it fundamentally different from an ordinary spin wave spectrum is the existence of a band of scattered neutron intensity at higher energies $\sim 10-15$ meV. This part of the spectrum is completely resolved into two peaks only near the zone boundary, with intensities corresponding to the low-lying branches. Near the zone centre, one acoustic branch with a marked wave vector dependence is clearly resolved. The optical branches could not be traced separately in this energy region for experimental reasons. The existence of three well-defined excitons at the zone boundary, where optical and acoustic modes are degenerate, implies six modes for a general point in the Brillouin zone. We shall now see that the features of this spectrum can be understood using the theory described in Sec. II.

For the cubic symmetry appropriate to the rare earth Al$_2$ compounds, the most general crystal field Hamiltonian describing any single ion interactions inside a manifold of given $J$ is simply

$$V_{ci} = B_4^{0} [0^0_{4i} + 5 0^4_{4i}] + B_6^{0} [0^0_{6i} - 21 0^4_{6i}]$$  \hspace{1cm} (17)$$

The coordinate axes have been chosen along the cube edges. In the analysis we shall assume that the Hamiltonian can be written on the form (1) with this crystal field potential. All anisotropic and higher order exchange interactions have thus been omitted together with magnetoelastic effects. The exciton
Fig. 1. (a) Dispersion relations for magnetic excitations in NdAl$_2$ for momentum transfer in the <110> direction. The lines are the results of the analysis described in the text. (b) $\gamma(q)$ and $\gamma'(q)$ deduced from the fit. TA: Transverse acoustic modes; TO: Transverse optical branches; LA: Longitudinal acoustic branch; LO: Longitudinal optical branch. Data taken from Ref. 9.
spectrum was calculated for a wide range of parameters $B_4$ and $B_6$. The mean-field constant $\langle 0 | \mathcal{H}_0 | 0 \rangle$ was determined to yield a Curie temperature of 65K in agreement with experiment. $\mathcal{H}_0$ was diagonalized self-consistently to yield single-ion wavefunctions and energies, and the exciton energies were computed directly from Eq. (11). All ten single ion levels were taken into account. The exchange interactions $\mathcal{H}_0(q) + \mathcal{H}_0^*(q')$ can be determined for $q \neq 0$ by fitting the dispersion relations calculated by this procedure to the two low-lying well-defined optical and acoustic branches. By means of an iteration process following these lines, $B_4$ and $B_6$ were determined as the parameters giving the best agreement with the upper branches. Generally spoken, one can say that the lower branches give information on the exchange interactions, and the positions of the upper branches yield information on the crystal field parameters. Once the lower branches are calculated, the dispersion of the upper branches is fixed without further fitting of the exchange. It turns out that the analysis can be performed in an unique way because of the small number of independent crystal field parameters. The resulting values of the crystal field parameters obtained in this way are $B_4 = -1.0 \times 10^{-3}$ meV and $B_6 = 4.0 \times 10^{-5}$ meV. The theoretical spectrum consists of six strong modes for a wide range of parameters; however, even relative small deviations ($\sim 15\%$) from the best values will shift the positions of the exciton branches severely and destroy any agreement with experiment. Thus Houmann et al. have shown that an analysis of the magnetic excitons in the ferromagnetic regime for systems with large crystal field may give detailed information on both the exchange interaction and the crystal field parameters.

Figure 2 shows the single-ion level scheme as a function of the molecular field. The crystal-field-only scheme has a doublet, $\Gamma_6$, as the ground state and two quartets, $\Gamma_8^{(1)}$ and $\Gamma_8^{(2)}$, as excited states. The magnetic moment associated with the $\Gamma_6$ state is $1.33 \mu_B$. In the exchange field, the degeneracies of these states are lifted and the excited levels are admixed into the ground state. The magnetic moment of the mean-field ground state is $2.6 \mu_B$ in agreement with the value $2.5 \mu_B$ determined by neutron diffraction. The quenching of the free ion moment of $3.28 \mu_B$ can thus be explained as a pure crystal field effect.

We denote the mean field states $|1\rangle$, $|2\rangle$, ..., $|10\rangle$ according to increasing energy. The most important matrix elements creating excitations between the levels at low temperature are
Fig. 2 Single-ion level scheme of NdAl₂ as a function of molecular field. The vertical line indicates the actual field obtained by the self consistent diagonalisation of $\mu_0$. (Ref. 9)
The first two matrix elements give rise to two optical and two acoustic transverse modes, and the third matrix element creates two longitudinal branches. The two lowest exciton branches originate mainly from the $J^\pm$ coupling between the two states associated with the $\Gamma_6$ crystal field state. Since the corresponding wavefunctions are approximately $|J,J>\text{ and } |J,J-1>$, these modes correspond to the spin waves in magnetic systems with strong exchange interaction. The remaining four branches of longitudinal and transverse character are associated mainly with transitions between the ground state and excited states originating from the $\Gamma_6(1)$ quartet. Matrix elements between the ground state and higher lying states are much smaller, and consequently the excitons associated with these states are not observable.

$<2|J^-|1> = 3.25$, $<5|J^+|1> = 2.28$, $<6|J^z|1> = -1.71$

The magnetic excitons in NdAl$_2$ can thus be understood within the framework of the RPA theory using a Hamiltonian including crystal field and isotropic Heisenberg exchange interaction terms. Further measurements are suggested to obtain more detailed experimental information. In particular one may hope to measure the dispersion of the crystal field transitions in the paramagnetic regime and thus determine the crystal field and exchange-parameters in an independent way. Furthermore a better resolution of the upper exciton branches should be possible. The smearing out of these modes seems to indicate that linewidth considerations are important.
We now discuss the macroscopic magnetic properties of NdAl$_2$. We assume that the Nd$^{3+}$ ion in an externally applied magnetic field, $\mathbf{H}$, can be described by the single ion Hamiltonian

$$\mathcal{H}_0 = B_4 \left( O^0_4 + 5 O^4_4 \right) + B_6 \left( O^0_6 - 21 O^4_6 \right) - g\mu_B (\mathbf{H} + \mathbf{H}_{MF}) \cdot \mathbf{j}$$

The mean field, $\mathbf{H}_{MF}$, obeys the self consistency condition

$$\mathbf{H}_{MF} = g\mu_B \langle \mathbf{j} \rangle, \quad \lambda = \frac{2 \left( \mathcal{V}(0) + \mathcal{O}(0) \right)}{g^2 \mu_B^2} \quad (19)$$

The crystal field parameters $B_4$ and $B_6$ and the mean-field constant $\lambda$ were determined from the analysis of the exciton experiment. We are then in possession of all the parameters necessary to calculate the bulk magnetic properties of NdAl$_2$. This gives us an opportunity of testing the reliability of the crystal field parameters derived by Houmann et al.

The magnetisation as a function of an external magnetic field in high symmetry directions can be calculated by solving Eqs. (18) and (19). When the magnetic field is in the $<100>$ direction, the magnetic moment remains in this direction, and the problem is reduced to one dimension. When the external magnetic field is applied along other symmetry directions, the analysis is more complicated. In this case we solve the equations self-consistently in the plane given by the direction of the magnetic field and the $<100>$ direction, implicitly assuming that the magnetic moment is confined to this plane. The computations can be carried out using an iteration method. This procedure allows us to calculate $\mathbf{M}$ in an external magnetic field without introducing new phenomenological, temperature-dependent anisotropy parameters.

Theoretical single-crystal magnetisation curves are shown in Fig. 3 together with experimental points at 4.2 and 20K measured by Cock, Roeland, Purwins, Walker and Furrer. To facilitate the detailed comparison with experiment and to avoid confusing the drawing, we have normalised the experimental points to agree with the theoretical zero field magnetisation at 4K. This involves an enhancement of the observed points by 5%. The normalised experimental points are seen to be in detailed agreement with theory. The kinks on the theoretical magnetisation curves indicate the critical magnetic fields where the magnetisation vector
Fig. 3 The magnetisation as a function of the external magnetic field in the three main symmetry directions. The moments shown are the components along the applied magnetic field. The measured points have been augmented by 5% to normalise to the calculated zero field moment at 4K. Data taken from Refs. 23 and 25.
is aligned along the field. At 4.2K the kink occurs at 100 kOe. The 5% discrepancy is certainly within what could be expected from a mean-field theory without any fitting parameters, further it is well within the uncertainties associated with the determination of the crystal field parameters and the mean-field constant from the exciton experiment. The measurements thus provide strong support for the crystal field parameters extracted from the exciton dispersion curves.

The present data give no justification for changing the simple crystal field model of NdAl₂ by introducing additional effects, such as anisotropic exchange interactions or magnetoelastic effects. It seems rather unlikely that a consistent picture could be obtained, if such effects were important.

IV. OBSERVATION OF EXCITED STATE SPIN WAVES IN TbAl₂

It has been pointed out by Peschel, Klenin and Fulde,¹⁸ that in the paramagnetic regime magnetic excitations from the ground state of a lattice of rare earth ions can interact with excitations out of excited magnetic states with very low population, provided that the energies of the non-interacting excitations are comparable. This interaction leads to a splitting of the ground state exciton mode, which in principle can be observed by inelastic neutron scattering. In this section we shall discuss the system TbAl₂, where a splitting of the same nature has been directly observed in the ordered phase by Purwins, Houmann, Bak and Walker.¹⁰ This was the first observation and theoretical interpretation of an interaction of this kind.

TbAl₂ orders ferromagnetically below 105K with magnetic moments in the < 111 > direction. The Curie temperature is high compared with other REAl₂ compounds. Accordingly the quenching of the low temperature spontaneous magnetic moment is very small, and the magnetic excitations are ordinary spin waves with an energy gap at q = 0 due to crystal field effects.²¹ However, we shall see that when the temperature is raised, the excitation spectrum behaves in a most unusual way.

The neutron scattering experiment on the temperature dependence of the spin-waves was performed on a triple axis spectrometer at the DR 3 reactor at Riso. Some typical experimental results are shown in Fig. 4. At 4.2K a well-defined magnon peak at 1.58 meV is observed. As the temperature is raised to about 35K, a new peak arises in the neutron spectrum with lower energy than the original magnon peak. The intensity of the new peak increases
Fig. 4. Typical neutron spectra for TbAl$_2$ as a function of temperature (Ref. 10).
with increasing temperature while the intensity of the upper peak decreases. Above 60K the low-energy peak, which has taken over most of the intensity, disappears into the background. Figure 5 shows the experimental points for all measured wave vector transfers and temperatures. We shall interpret this double peak structure as an interaction between the magnon mode and a magnetic exciton, an "excited state spin wave" originating from a transitions between some higher-lying excited magnetic states.

The strong interactions between the magnetic ions and the corresponding small quenching of the magnetic moment implies that the eigenfunctions of the magnetic ions are simple $|J,M_J>$ states. The $J_j^- J_j^+$ part of the isotropic exchange interaction between the ions $i$ and $j$ has large matrix elements between neighbouring levels, whereas the matrix elements of $J^2$ can be ignored. Only transverse magnetic excitations (like spinwaves) are expected in this case. The crystal field part of the Hamiltonian acts as a perturbation shifting the mean-field levels without changing the wavefunctions substantially. The shift between the two lowest lying levels determines the energy gap associated with the low-temperature spin-waves. In general the temperature dependence of the lowest excited levels combined with a change in population of the mean field levels gives rise to the temperature-renormalisation of the spin wave energies and the energy gap. However, if the energy difference between two succeeding excited levels becomes comparable to the spin wave energy, the coupling between the corresponding excited state magnon (exciton) and the spin waves via the two-ion matrix elements of the exchange interaction becomes important, i.e., an interaction between the modes takes place. This resonance gives rise to a mixing of the magnon mode and the exciton mode, and hence to the observed anti-crossing effects, analogous to the magnon-phonon interaction, causing similar splittings of the magnon branches. However, in the latter case, the phonon represents a transition from the boson ground state of the lattice at low temperatures, and therefore the interaction can be observed even at 0 K. In the actual case the excited states corresponding to the exciton mode are not populated at low temperature, and consequently there will be no interactions. However, when the temperature increases, the excited states become populated, and the interaction becomes possible.

The qualitative physical picture described here can be confirmed quantitatively using the Green’s function theory described in Sec. II. The Hamilton-
Fig. 5. Temperature dependence of the magnetic excitation energies in TbAl$_2$. Full and dotted lines: theory. Points: experiment. The left hand side of the figure shows the single ion states of Tb$^{3+}$ at 4K. Data taken from Ref. 10.
ian for the Tb ions is written as the sum of crystalline field terms and isotropic exchange terms on the form (1) with

\[ V_{ci} = -\frac{2}{3} B_4 \left[ o_4^0 - 20 (2)^{\frac{1}{2}} o_4^3 \right] + \frac{16}{9} B_6 \left[ o_6^0 + \frac{35}{4} (2)^{\frac{1}{2}} o_6^3 + \frac{77}{8} o_6^6 \right] \] (20)

This potential is essentially the same as the potential (17) which was used to describe NdAl\(_2\). However, the quantisation axis is chosen along the direction of magnetisation (<111>).

\( J_0 \) is diagonalised self-consistently as a function of temperature to yield mean-field eigenfunctions and energies to serve as a basis for calculating the exciton spectrum. The calculations of the acoustic modes determined by \( \sqrt{\text{eff}}(q) = \sqrt{r}(q) + \sqrt{p}(q) \) are carried out for a wide range of crystal parameters \( B_4 \) and \( B_6 \) in the same way as for NdAl\(_2\). The macroscopic magnetic properties calculated on the basis of these parameters must be in qualitative agreement with the experimental facts, that the easy direction of magnetisation is the <111> direction, the Curie temperature is 105K, the low temperature magnetic moment is near to the free ion value \( 9\mu_B \), and the spin wave energy gap at 4K is 1.6 meV. These conditions impose severe restrictions on the parameters. There is only very little freedom left to vary the two parameters to explain the detailed behaviour of the excitation spectrum as a function of temperature.

The excitation energies are the roots of the secular determinant of (11), including transitions between all 13 levels. The roots of the diagonal elements of the characteristic matrix of Eqs. (11),

\[ \omega_{\text{diag}}(q) = E_r - E_p - 2(n_p - n_r) \sqrt{r}(q) \sum_{\alpha} |<r|j^\alpha|p>|^2 \] (21)

are the non-interacting excitation frequencies. For a simple ferromagnet this term yields the low-temperature spin wave theory, if \( |r> \) and \( |p> \) are chosen as the two lower states. The dispersion of the excited states is small because of the Boltzmann factors \( n_p \) and \( n_r \). The off-diagonal elements due to two-ion interactions give rise to perturbations of the non-interacting energies. According to general perturbation theory, the energy shifts are largest, when the corresponding diagonal coefficients approach each other. This effect can thus be described as a resonance (or interaction) between two exciton modes. The best agreement with experiment was obtained using the parameters \( B_4 = 7.0 \cdot 10^{-4} \) meV and \( B_6 = 2.15 \cdot 10^{-6} \) meV.
The calculated energies of the mode with observable neutron intensities are given in Fig. 5 together with the single ion level scheme at 4K. The parameters used in the calculation give $T_c = 105\text{K}$ and nearly pure $J^z$ single ion states. We therefore denote these states by the corresponding $J^z$ quantum numbers. $B_4$ is of the same order of magnitude as the parameter used to describe magnetisation data of TbAl$_2$. However, a large discrepancy exists for the parameter $B_6$, although the theoretical magnetisation curves calculated on the basis of the present parameters are in fair agreement with experiment.

At low temperatures the calculation shows only one acoustic excitation branch, which can be interpreted as an ordinary magnon branch with an energy gap, since it is mainly due to a $|J > \rightarrow |J-1 >$ transition. As the temperature is raised the upper states become slightly populated. The renormalised magnon energy approaches and crosses the energy difference between the excited states $|2 >$ and $|1 >$, so that an interaction between the $|2 > \rightarrow |1 >$ excited state spin waves and the main magnon mode can take place. In the temperature range where the measurements were carried out, the population of the excited states corresponding to the bare exciton is very small. Consequently the neutron scattering cross section for the exciton is at least two orders of magnitude smaller than that for the magnon. The excited states can thus only be observed through the magnon-exciton interaction. The experimental ratios between the intensities of the low-lying and the high-lying excitation is roughly 1 to 4 at 35K and 1 to 1 at 45K, compared with the theoretical prediction (Eq. 16) of 1 to 5.2 and 1 to 1.3 respectively.

We conclude that interactions between magnetic excitations may occur if the energies of two modes are comparable, and this resonance may be directly measured by inelastic neutron scattering. The anticrossing effects that were observed in TbAl$_2$ may well occur in other rare earth compounds. Recently Holden and Buyers have suggested that the weak temperature dependence of the magnetic excitons in Pr$_3$Tl$_3$ originates from a mode-mode interaction of the same nature.

V. DISCUSSION

The analysis of the magnetic excitations in TbAl$_2$ and, in particular, in NdAl$_2$, has given detailed information on the fundamental microscopic magnetic interactions in rare earth intermetallic compounds. The exciton spectra can be reproduced using a simple Hamiltonian including two crystal
field parameters and an isotropic RKKY-like exchange interaction. Since the analysis yields numerical values of the parameters $B_4$ and $B_6$, it is interesting to see how these parameters are related to parameters obtained for other REAl$_2$ compounds and by means of other kinds of measurements. Such a comparison has been performed by Purwins et al. Assuming a simple effective point charge model, like the one successfully applied to the rare earth monopnictides by Birgeneau et al., the parameters for the whole series of REAl$_2$ compounds are found to be identical within 30%, when scaling with the appropriate reduced matrix elements are taken into account. This indicates that the effective charge distributions around the magnetic ions are independent of the particular rare earth constituent.

Finally we shall mention, that besides influencing the magnetic properties, the crystal field levels may play a crucial role in determining the superconducting properties of diluted magnetic systems. The nonmagnetic compound LaAl$_2$ is superconducting below 3.3K. As the simple crystal field model seems to be valid also for RE$_x$La$_{(1-x)}$Al$_2$ compounds, the effects on the superconducting properties may be calculated using the crystal field parameters derived from neutron inelastic scattering and magnetisation work. Measurements of $T_c$ as a function of Tb concentration in LaAl$_2$ clearly demonstrate the influence of the crystal field levels.
REFERENCES

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