

INVITED REVIEW

MAGNETIC EXCITATIONS IN RARE EARTH SYSTEMS

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The observation of magnetic excitations, by means of inelastic neutron scattering, provides valuable information on the magnetic forces acting in rare-earth systems. The RPA (random-phase approximation) theory, developed into its final form in the early seventies, is now a widely used tool for analyzing the excitation spectra in systems with well-defined local moments. These excitations reflect both the dynamics of the single moments and the interactions of these moments with their surroundings.

A discussion of the information which has been obtained from studies of the magnetic excitations in the rare-earth metals is presented. The emphasis is laid on Pr-metal which has attracted much interest in recent years. Recent progress in the investigation of rare-earth intermetallic compounds, like the Laves-phase and the CsCl-type-compounds and the rare-earth pnictides, is also considered. Some aspects of the magnetic properties of the actinides can be understood in terms of a model of localized moments, and we include a discussion of USb, where the spin-wave spectrum contains direct evidence that the spins are ordered in a triple- q structure.

The magnetic excitations may be coupled to the phonons and in the metallic systems they interact with the electron–hole excitations of the conduction electrons. Therefore the sound velocities and the effective mass of the conduction electrons can be strongly affected by the spin system. Recent developments within these areas are also reviewed.

1. Introduction and general theory

In most systems the magnetic moment of a rare-earth ion may to a good approximation, be treated as a conserved entity, i.e. as a localized moment, characterized by the ground-state value of the total angular momentum, J , and the Landé factor, g , of the isolated ion. In this review we restrict ourselves to systems where this is the case, which greatly reduces the complexity of the dynamics. In metallic systems the localized spins are coupled indirectly via the exchange interaction to the conduction electrons. With a few exceptions, the orbital contribution to the total ionic momentum is large, which means that J is influenced relatively strongly by the crystalline field.

The simplest description of a rare-earth system is based on the Hamiltonian:

$$\mathcal{H} = \sum_i [V_c(\mathbf{J}_i) - g\mu_B \mathbf{J}_i \cdot \mathbf{H}] - \frac{1}{2} \sum_{i \neq j} \mathcal{J}(ij) \mathbf{J}_i \cdot \mathbf{J}_j, \quad (1)$$

where $V_c(\mathbf{J}_i)$ is the single-ion term due to the crystalline field, \mathbf{H} is the external field, $\mathcal{J}(ij)$ is the RKKY-exchange interaction, which is propor-

tional to $(g-1)^2$ and the susceptibility of the conduction electrons. The molecular-field approximation (MFA) is utilized for the determination of the static properties:

$$\mathcal{H}_{\text{MF}} = \sum_i [V_c(\mathbf{J}_i) - \{g\mu_B \mathbf{H} + \langle \mathbf{J} \rangle \mathcal{J}(\mathbf{0})\} \cdot \mathbf{J}_i], \quad (2)$$

$\mathcal{J}(\mathbf{q})$ is the Fourier transform of $\mathcal{J}(ij)$; for simplicity $\langle \mathbf{J}_i \rangle$ is assumed to be independent of the position. The MFA involves a diagonalization of eq. (2) yielding the $(2J+1)$ -eigenvalues E_p and the corresponding statevectors $|p\rangle$, together with a self-consistent calculation of the thermal expectation value

$$\langle \mathbf{J} \rangle = \sum_p \langle p | \mathbf{J} | p \rangle n_p,$$

where n_p is the population factor,

$$n_p = e^{-E_p/k_B T} / \sum_q e^{-E_q/k_B T}.$$

The dynamic response function for a single

momentum, $\chi_0(\omega)$, is then determined as:

$$\begin{aligned} \chi_0^{\alpha\beta}(\omega) &= \lim_{\epsilon \rightarrow 0^+} \left[\sum_{\substack{p,q \\ E_p \neq E_q}} \frac{\langle p | J_\alpha | q \rangle \langle q | J_\beta | p \rangle}{E_p - E_q - \omega - i\epsilon} (n_q - n_p) \right. \\ &\quad \left. + \frac{1}{k_B T} \frac{\epsilon}{\epsilon - i\omega} \left(\sum_{\substack{p,q \\ E_p = E_q}} \langle p | J_\alpha | q \rangle \langle q | J_\beta | p \rangle n_p \right. \right. \\ &\quad \left. \left. - \langle J_\alpha \rangle \langle J_\beta \rangle \right) \right]. \end{aligned} \quad (3)$$

In the random-phase approximation (RPA) the generalized susceptibility tensor is deduced to be

$$\chi(\mathbf{q}, \omega) = [1 - \chi_0(\omega) \mathcal{G}(\mathbf{q})]^{-1} \chi_0(\omega) \quad (4)$$

and the two-site correlation or scattering function, which determines the cross-section for neutron scattering is

$$\mathbf{S}(\mathbf{q}, \omega) = \frac{1}{\pi} \chi''(\mathbf{q}, \omega) / (1 - e^{-\omega/k_B T}). \quad (5)$$

The RPA-result, eq. (4), for the \mathbf{q} -dependent susceptibility was derived in the early seventies by a number of authors using either a diagrammatic expansion of the Green's functions or by a decoupling of the equations of motion; see for instance the reviews in refs. [1,2]. The different procedures are much facilitated by the use of the standard-basis operators, $|p\rangle\langle q|$. The theory has general applicability but the actual calculation of $\chi(\mathbf{q}, \omega)$ requires in most cases the assistance of a computer. Analytic expressions for $\chi(\mathbf{q}, \omega)$ are obtainable if the number of levels is small, $J = \frac{1}{2}$ or 1 and the singlet-triplet model, or in the Heisenberg limit $\mathcal{G}(\mathbf{0})J^2 \gg |V_c|$. These are also the only cases where the RPA-theory above has been improved.

There are two improvements of the theory which are desirable. Firstly, an obvious shortcoming is that the dipole-excitations appearing in $\mathbf{S}(\mathbf{q}, \omega)$ are δ -functions in ω . Secondly, the theory is not self-consistent, since the presence of two-site corre-

lation modifies the single-ion averages, n_p . These corrections should in principle be obtainable by summing $\mathbf{S}(\mathbf{q}, \omega)$, and the similar correlation functions for the standard-basis operators, over \mathbf{q} and ω . However, in most cases they depend on the particular choice of the RPA-correlation functions and cannot be trusted [3,4]. The RPA-theory above has been stringently refined for $J = 1$ in the easy-axis case by Yang and Wang [3], and in the paramagnetic easy-planar case by Bak [5] and Jensen [4]. The $J = \frac{1}{2}$ Ising model has been analysed thoroughly by Stinchcombe [6]. High-temperature-series expansion results are available in these cases and for the singlet-triplet model; see the review by Wang [7] and the recent paper of Johnson and Wang [8]. We shall also mention the correlated-effective-field method of Lines [9], where effects due to two-site correlation are introduced in a simple phenomenological, but physically reasonable, way. The theory is of general utility, and it predicts the static properties of many systems more accurately than the MFA. A comparison with the more refined theories indicates that the method of Lines is most acceptable in the weak-anisotropy limit.

The simple RPA-theory, eqs. (2)–(4), is straightforwardly extended to cases where the Hamiltonian, eq. (1), includes additional interactions. The presence of general two-ion couplings in eq. (1) may be expressed using a compact matrix-notation. We introduce the generalized p -dimensional momentum operator: $\mathbf{J}^p \equiv (J_x, J_y, J_z, \tilde{O}_{lm}, \tilde{O}_{l'm'}, \dots)$ where \tilde{O}_{lm} are Racah operators of rank higher than 1, and $p \geq 3$. A general two-ion Hamiltonian may then be written in terms of a $p \times p$ coupling-matrix:

$$\mathcal{H}_{II} = -\frac{1}{2} \sum_{i \neq j} \mathbf{J}_i^p \mathcal{G}(ij) \mathbf{J}_j^p. \quad (6)$$

Introducing $p \times p$ susceptibility-matrices the RPA-result may be expressed as above except that $\mathcal{G}(\mathbf{q})$ in eqs. (2) and (4) is replaced by $\frac{1}{2}[\mathcal{G}(\mathbf{q}) + \mathcal{G}^\dagger(\mathbf{q})]$. The magnetic response is then determined by the upper left 3×3 matrix of $\chi(\mathbf{q}, \omega)$. The RPA-theory may also be extended (see for instance ref. [2]) to cases where the magnetic excitations are coupled to the phonons, the electron-hole pair excitations of the conduction electron, the

nuclear magnetic moments, or magnetic impurities.

The inelastic neutron scattering cross-section is proportional to (the magnetic part of) $\mathbf{S}(\mathbf{q}, \omega)$. The information obtained by studies of the excitation spectrum is usually not sufficient for a determination of the different terms in the Hamiltonian. In general one has to combine these results with various studies of the bulk properties (magnetization, magnetostriction, heat capacity) and their dependence on the thermodynamical variables (magnetic field, stress, temperature). In the following sections we shall discuss a number of specific examples. Extensive reviews of magnetic excitations in rare-earth systems have been published [1,2,10–13]; see also a number of the invited contributions in ref. [14]. We will attempt to include some of the essential features of these reviews and to emphasize recent developments. We concentrate on the rare-earth metals and intermetallic compounds, in which systems dispersive effects are important.

2. The heavy-rare-earth metals

The magnetic excitations, i.e. the spin waves, in the low-temperature phases of the heavy rare-earth metals Gd, Tb, Dy, Ho and Er are fairly well described, both experimentally and, on a phenomenological basis, theoretically; see the reviews [1, 10–12]. Because $L=0$ for the Gd^{+3} -ion the crystal-field anisotropy vanishes to leading order and Gd-metal is very close to a Heisenberg system. Gd is ferromagnetically ordered below 293 K. Because V_c can be neglected the RPA-theory is considerably simplified, and the lack of self-consistency in eq. (4) is remedied in a straightforward manner, in which case the theory becomes identical to the elementary RPA-spinwave theory.

Cable et al. [15] have studied the temperature dependence of the magnetic excitation spectrum of Gd close to T_c . The stiffness constant of the spin waves in the long-wavelength limit is observed to vanish at T_c in a way which is consistent with hydrodynamic scaling theory. For spin-waves at large q -values the linewidths show a pronounced broadening close to T_c , but the peaks persist at

non-zero energies above T_c up to about $1.2T_c$.

At low temperatures Tb and Dy are ferromagnets with their moments perpendicular to the c -axis, and Ho and Er are ordered in conical structures. In these metals the crystal-field is important. Due to the anisotropy the magnitudes of the ordered moments at $T=0$ are slightly reduced from their maximum values by about 0.5–1.0%. The elementary spin-wave theory, which assumes equally spaced $|J_z = M\rangle$ -levels, has been generalized to account for the off-diagonal coupling of these levels which is introduced by V_c ; see refs. [16,17] and references therein. These calculations utilize essentially e/J as the expansion parameter, where e is the ratio between the anisotropy and exchange energies, $V_c/\mathcal{J}(\mathbf{0})J^2$. Numerical calculations [12,18] performed on models corresponding to Tb ($e/J \approx 0.06$) and Er ($e/J \approx 0.15$) at $T=0$ showed that the generalized spin-wave theory [17] agrees in all essential features with eq. (4) which involves an exact treatment of the MF-Hamiltonian. The importance of the anisotropy is expected to be reduced at elevated temperatures; see also the discussion of the spin waves in ErFe_2 [19]. In comparison with the general RPA-theory, eq. (4), the spin-wave theory has the advantage of being much more transparent, both with respect to the extraction of relevant parameters and when considering various perturbations.

As discussed in some reviews [1,12] there is indirect evidence that anisotropic two-ion couplings in Tb and Er at low temperatures contribute to the dispersion nearly as much as the Heisenberg interaction. In Tb these anisotropic contributions are isolated by studying the field-dependence of the spin waves propagating in the c -direction [20]. A number of the effects in Tb, which are consistently explained in terms of anisotropic two-ion couplings, differ distinctly from the minor single-ion anisotropy effects neglected in the spin-wave theory. Although the analysis of the spin-wave dispersion in the c -direction of Er [21] indicates that the two-ion anisotropy is relatively more pronounced in this metal, the interpretation is subject to larger uncertainties than in the case of Tb. The experimental dispersion relation [22] can be reproduced in an acceptable way without the incorporation of anisotropic two-ion couplings [23], but this

interpretation requires a constant anisotropy term of 35 meV, which is almost a factor of two larger than that deduced [24] from magnetization measurements, and the intensity-ratio between the $+q$ and $-q$ spin-wave branches of the cone differs from the experimental value by a factor of about three in the interval $\pi/c < q < 2\pi/c$. Both these discrepancies are removed when anisotropic two-ion couplings are introduced [21].

Large couplings between the lattice and the angular momentum system have been detected in most of the rare-earth metals; again Gd-metal is an exception. For example, the spin waves and the phonons have been observed to be hybridized in Tb, Dy and Er, and these crystals are distorted appreciably in their ordered phases. The velocity of the transverse sound waves in Tb with both propagation and polarization vectors in the basal plane have recently been studied [25]. If we consider the transverse sound waves propagating parallel to a field applied along the hard a -axis in the basal plane of Tb, the RPA-theory predicts that the velocity of these waves should vanish at the second-order transition (below T_c) from a phase where the magnetization is parallel to the field to a phase which has a moment perpendicular to the field. The upper marginal dimensionality [26] for this transition is $d^* = 2$, corresponding to a structural phase transition in a cubic crystal with c_{66} being the soft elastic constant, except that in the case of the magnetic transition the long-range dipole coupling further depresses the importance of the critical fluctuations by lifting the degeneracy between the transverse waves propagating parallel or perpendicular to the field (this argument was not given correctly in the original paper [25]). With the coupling parameters determined by magnetostriction measurements, the RPA-theory gave a reasonable account of the ultrasonic experiments, in which c_{66} was observed to be reduced by as much as 50%. Due to experimental difficulties and/or intrinsic damping effects the transmitted sound waves could not be detected in the close neighbourhood of the transition.

The interaction between the spin waves and the electron-hole pair excitations of the conduction electrons has been studied in the ferromagnetic phase of Tb. The scattering of the magnons by the

conduction electrons has been observed directly as giving rise to a non-zero linewidth of the magnons, $\Delta\omega/\omega \approx 0.05$, in the low-temperature limit [27]. The q -dependence of the width reflects the splitting of the polarized electron bands, increasing quite abruptly around 0.25 \AA^{-1} . As shown in fig. 1 the simple free-electron model accounts qualitatively for the observed q -dependence and agrees within a factor of two corresponding to the uncertainties involved in the model, with the absolute magnitude of the effect. This seems also to be the case for the electrical resistivity of ferromagnetic Tb, which has been measured and calculated in the temperature range 1.5–50 K by Hessel Andersen and Smith [28]. In the calculation the band splitting $\Delta = \epsilon_+(\mathbf{k}) - \epsilon_-(\mathbf{k})$, is neglected, which approximation seems to be quite generally accepted. In a consistent use of the free-electron model the magnetic resistivity-integral is dominated at low temperatures by umklapp-scattering processes and the small-angle scattering is absent because the exchange-splitting introduces a cut-off at $q_{\min} = k_F^+ - k_F^- \approx \frac{1}{2}(\Delta/\epsilon_F)k_F$. In this model the linewidth of the magnons in fig. 1 for $q < q_{\min} \approx 0.25 \text{ \AA}^{-1}$ is correspondingly due to processes for which the scattering vector is larger than a reciprocal lattice vector but smaller than $2k_F \approx 2.8 \text{ \AA}^{-1}$. Without the cut-off the linewidth would diverge like $1/q$ in

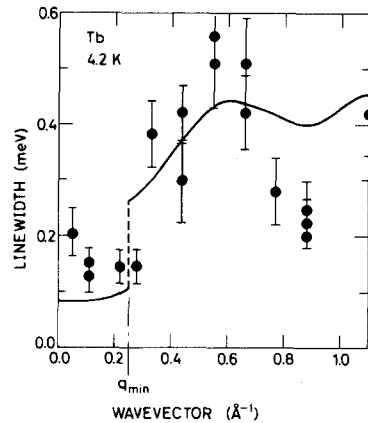


Fig. 1. The linewidths of the magnons propagating in the c -direction of Tb at 4.2 K. The experimental results are from ref. [27]. The solid line shows the result of a free-electron-model calculation, which includes umklapp-scattering processes ($2k_F = 2.8 \text{ \AA}^{-1}$) and q_{\min} is the smallest scattering vector allowed due to the exchange splitting of the bands.

the long wavelength limit. Although, the free electron model is very crude, the apparent success of the model in fig. 1 indicates that the resistivity calculations should include the cut-off and the umklapp-contributions in order to give a reasonable account of the strongly polarized ferromagnets Gd, Tb or Dy.

3. The light-rare-earth metals

The two light-rare-earth metals, Pr and Nd, have been studied extensively in recent years. These metals crystallize in the dhcp-structure with four ions per unit cell. The point symmetry is hexagonal for the two sites and nearly cubic for the other two. Nd orders at 19.9 K in a longitudinally polarized antiferromagnetically modulated structure. At T_N the modulation vector, \mathbf{Q} , is 0.144 in reduced units and is directed along the \mathbf{b} -axis in the basal plane [29]. Based on renormalization group arguments [30] it is suggested that the actual magnetic structure is a superposition of the three “single- \mathbf{Q} ” domains, corresponding to the three possible directions of \mathbf{Q} , the so-called triple- \mathbf{Q} structure [31]. Slightly below T_N , at ~ 19.3 K, there is another phase transition where the direction of \mathbf{Q} starts to deviate from the \mathbf{b} -axis. The neutron diffraction work on Nd has recently been reviewed by Lebeck [29]. In spite of several attempts [32] no well-defined magnetic excitations have been observed in Nd, neither above nor below T_N , nor when the moments are aligned ferromagnetically in an external field, with the exception of the report of Sinha [1], that there are some signs of two crystal-field excitations of the cubic ions at high energies (see note (1) added in proof).

In Pr, where $J = 4$, the hexagonal and cubic ions constitute two non-magnetic singlet-ground-state systems. The two systems are only weakly coupled, but the two-ion interaction between the hexagonal ions is just below the threshold at which an ordering similar to the one observed in Nd becomes energetically favourable at low temperatures. The studies of the magnetic excitation spectrum in Pr both as a function of temperature [33] and of magnetic field [34] have led to a very

detailed understanding of the magnetic properties of Pr; see also the review [13]. The ground state of the hexagonal ions is the $|0\rangle$ -singlet, z being along the c -axis, and the crystal-field splitting between this level and the dipolar excited $|\pm 1\rangle$ doublet is (3.52 ± 0.1) meV. The ground state of the cubic ions is close to being the Γ_1 -singlet, with the Γ_4 -triplet lying at (8.4 ± 0.1) meV above the ground state. The possibility that the Γ_4 -triplet is split into a singlet and a doublet, due to the deviation from cubic point symmetry, has not yet been investigated experimentally.

A molecular-field model, which includes all the crystal-field levels of the Pr-ions, has been developed [34]. This model accounts for the field and temperature dependences of the excitation energies and for the bulk properties at low temperatures. At elevated temperatures the model predicts correctly the magnetic specific heat [4], but the calculated bulk-susceptibilities do not agree satisfactory with experiments. Lebeck and Rainford [35] have recently separated the contributions of the hexagonal and cubic ions to the c -axis susceptibility. The hexagonal contribution vanishes at low temperatures, and the model predicts that this contribution starts to be significant above 10 K, whereas the experiments show that this does not happen before the temperature exceeds ~ 20 K. The failure of the molecular-field model at these low temperatures is somewhat surprising. The high temperature discrepancies might be due to the temperature dependence of the magnetoelastic, α -strain, contribution to the axial anisotropy. The magnitude of this magnetoelastic coupling can be estimated from the magnetostriction measurements [36]. We have found that this effect only leads to minor improvements of the model, the most noticeable being the removal of the low-temperature difference, of about 40 kOe [34], between the calculated and the observed field of 320 kOe for the transition occurring when the field is applied along the c -direction. Another possibility is that the two-site correlation effects might give rise to important modifications. However, we found to leading order that the presence of correlation only introduces small adjustments of the “effective” MFA-susceptibilities [4].

In fig. 2 is shown the dispersion relations for

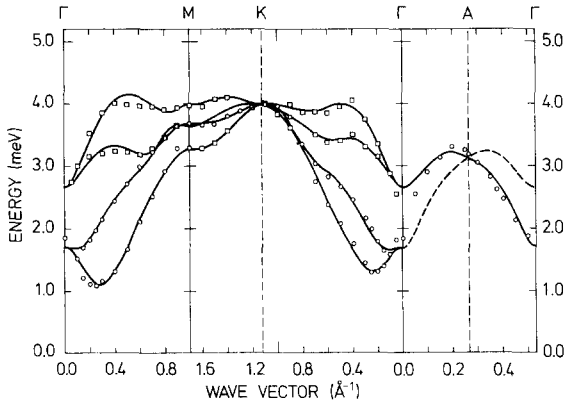


Fig. 2. Dispersion relations for the magnetic excitations propagating on the hexagonal sites of Pr at 6.4 K. The squares and circles denote the experimental results for the acoustic and optical modes, respectively. The lower of the optical and acoustic branches are the excitations polarized (predominantly) parallel to the wavevector and the upper ones are the transverse modes (after ref. [34]).

the singlet-doublet excitations propagating on the hexagonal sites of Pr at 6.4 K. At wavevectors with a component perpendicular to the c -axis the double degeneracies of the acoustic and the optical branches are lifted. This result provides unambiguous evidence for the presence of two-ion anisotropy in Pr, which is of the same order of magnitude as the isotropic interaction. It is worth noting that the symmetry of this anisotropic coupling differs from those deduced to be contributing to the c -axis dispersion in Tb or in Er, but is the same as those lifting the acoustic-optical degeneracy of the spin waves at the K-point in Tb, which splitting amounts to about 0.4 meV [37]. Now K is a point of high symmetry, which for instance implies that the excitations in Pr should be doubly degenerate, and the observed four-fold degeneracy must be accidental. In Tb, the symmetry only allows the coupling between the two hcp-sublattices to contribute to the splitting at K. Instead, we expect that anisotropic couplings of the type observed in Pr should have more influence around M, by giving rise to energy differences of the order of 2 meV between spin waves at a given q but propagating in the different magnetic domains.

The excitation of lowest energy in Pr is the longitudinal optical mode with a reduced wavevector of 0.13 along ΓM . This is the incipient soft

mode which would determine the magnetic structure appearing at a second-order phase transition. The magnetic structure expected in Pr coincides with the one observed in Nd, suggesting similar two-ion couplings in the two metals. In fig. 3 is shown the temperature dependence of some magnetic excitations in Pr. The dashed curves are the predictions of the molecular-field model discussed above, and the solid lines are the results when correlation effects are included [4]. The lowest mode in fig. 3 is the incipient soft mode. If we define R_T as the ratio between the actual exchange coupling and the value which would drive the system critical at the temperature T , ($R_{T_N} \equiv 1$) then the RPA-value of $1 - R_T$ is the square of the ratio between the energy of the incipient soft mode and the crystal-field splitting of 3.52 meV, that is $R_{T=0} \approx 0.92$ in Pr. The magnetoelastic γ -strain coupling, which might distort the hexagonal sym-

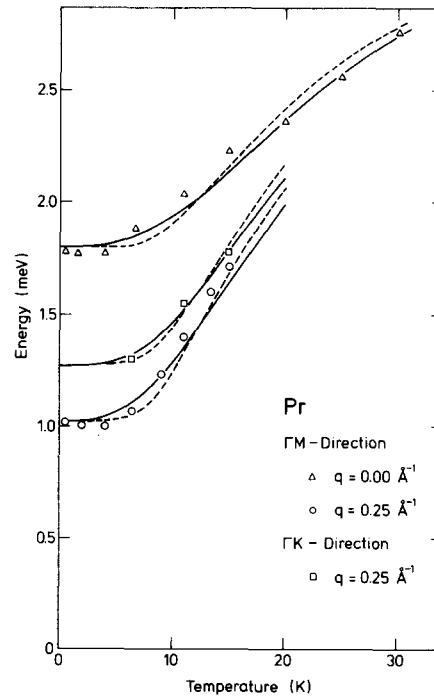


Fig. 3. The excitation energies at three different q -vectors in Pr as functions of T . The lowest lying mode in the figure is the incipient soft mode. The dashed lines are the results deduced using the MF-model of Houmann et al. [34]. The solid lines show the results of the self-consistent RPA-theory applied to the same model (after ref. [4]).

metry of the basal plane, is well established in Pr, both by its effects on the magnetic spectrum [34], from sound velocity measurements [38], and from magnetostriction experiments [36]. Because of this coupling the application of a uniaxial pressure in the a -direction splits the crystal-field $|\pm 1\rangle$ doublet and decreases the energy of the incipient soft mode. The RPA-theory predicts a second-order soft-mode transition at a pressure of ~ 0.7 kbar in the low temperature limit [34, 38]. The occurrence of this transition was verified experimentally by McEwen et al. [39], who also observed a large reduction of the energies of the longitudinal optical modes with wavevectors close to the critical one. More extensive and accurate measurements have later shown [40] that the transition occurs at approximately half the pressure predicted above. At sufficiently low temperatures, below ~ 0.5 K, the hyperfine interaction between the ionic and nuclear spins becomes important, as discussed by Murao [41]. The zero-frequency contribution of this coupling to the magnetic susceptibility implies that the system eventually orders without the application of an external pressure. This transition has been studied in a neutron diffraction experiment by McEwen and Stirling [42], and in agreement with heat capacity [43] and resistivity [44] measurements there are indications that the phase transition occurs in the temperature interval 50–200 mK. The interpretation of the experimental data is obscured by the presence of a quasielastic peak with maximum intensity near the critical q , but of large width in q -space [39,42,45,46]. The peak appears around 10 K and the intensity increases steadily with decreasing temperatures. Around 5 K the maximum intensity is about one fourth of the inelastic intensity of the incipient soft mode. Below ~ 1 K a much sharper peak develops on top of the broad one. Careful investigations [46] show that the narrow peak still has a finite width in q -space, and that a Bragg-peak, showing long-range magnetic ordering, does not appear until ~ 60 mK. Around 40 mK the ordered moment is about $0.4\mu_B$ /hexagonal ion and is still increasing [46]. The quasielastic peak-intensity around 5 K is 20–40 times larger than the estimated elastic contributions due to the couplings to the nuclear spins or to the electron-hole pair

excitations of the conduction electron. The experimental value of R_0 ranges from the RPA-value of 0.92 to 0.96. These values are derived from the specific heat [43] and the pressure experiments [40], respectively. The excess scattering intensity of the quasielastic peak above 1 K (which was overestimated by a factor ≈ 4 in ref. [4]) indicates that R_0 is slightly larger than the RPA-value, namely $R_0 \approx 0.935$, which corresponds to $T_N \approx 60$ mK in agreement with the observation in ref. [46].

The introduction of magnetic impurities in Pr may enhance the low temperature susceptibility and thereby increase T_N to a more accessible range. The excitation spectrum in Pr + 5% Nd has been studied, both in the paramagnetic and in the ordered phase. The spectrum showed clear evidence for a crystal-field level of the Nd-ions on the hexagonal sites lying around 1.4 meV. A CPA-calculation [47] has been performed in this case and the linewidth of the excitations just above T_N was found to be enhanced by a factor of about two due to the Nd-impurities, in fair agreement with the observations. A similar investigation of Pr + 2.5%Nd is in progress, and neutron diffraction measurements [46] have revealed that many of the features of pure Pr are also present in this alloy system.

The linewidth of the magnetic excitations in pure Pr between 1–30 K is mostly due to single-site fluctuations, as considered by Bak [5]. The scattering against the electron-hole pair excitations of the conduction electrons, which has been treated by Becker et al. [48], is found to be of importance for the acoustic modes in the long-wavelength and low-temperature limits [34]. Forgan [49] has measured the heat capacity of Pr between 1 and 6 K in magnetic fields of 0–4 T applied in the basal plane. The linear electronic term γT was found to be a factor of four larger than the value $\gamma_0 = 5.0$ mJ/mol K² expected from band calculations; see for instance the review by Harmon [50]. Further, γ was found to be reduced by 25% at maximum field; see fig. 4. White and Fulde [51] have explained both the mass-enhancement effects as being due to the coupling of the conduction electrons with the magnetic excitations. The estimation of the effect in Pr made by White and Fulde may be improved, utilizing that the dispersion of the magnetic excita-

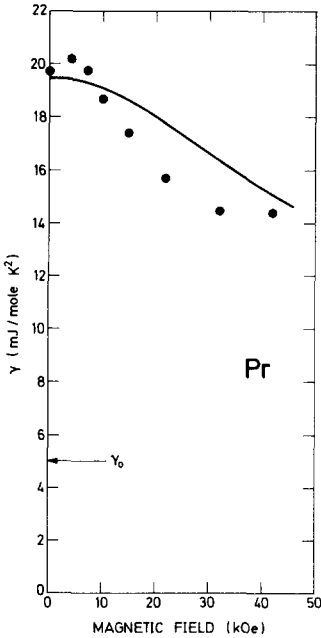


Fig. 4. The linear electronic term, γT , in the heat capacity of Pr. γ is shown as a function of a magnetic field applied in the basal plane. The experimental results have been obtained by Forgan [49]. The solid line is the result of the calculation using eq. (7) (after ref. [52]) based on the theory of White and Fulde [51].

tions in Pr only introduces minor correlation effects around 1 K [4]. Within an estimated error of less than 10% we can replace $\chi(\mathbf{q}, \omega = 0)$ in the integral over \mathbf{q} -space occurring in the mass-enhancement factor, eq. (8) in ref. [51], by the non-interacting value $\chi_0(\omega = 0)$, see eqs (3)–(4) above, or when using the notations of ref. [51]:

$$\gamma = \gamma_0 \left[1 + (g-1)^2 J_{sf}^2 N(0) \times \sum_{\alpha} \frac{1}{2} \{ \chi_{0,\text{cub}}^{\alpha\alpha}(0) + \chi_{0,\text{hex}}^{\alpha\alpha}(0) \} \right]. \quad (7)$$

The solid line in fig. 4 [52] shows the behaviour predicted by eq. (7) using $\gamma_0 = 5.0$ mJ/mol K², corresponding to $N(0) = 1.06$ eV⁻¹ per atom and spin, and $J_{sf} = 0.092$ eV. This value of J_{sf} agrees with that deduced from the polarization of the conduction electrons in Gd.

4. Intermetallic rare earth compounds

The rare-earth *monopnictides* crystallize in the NaCl-structure. In these compounds dispersive magnetic excitations have been observed in TbSb [53], PrSb [54], and in TbP [55,56]. These cubic systems all have the Γ_1 -singlet as the ground state. The exchange coupling in TbSb and in TbP exceeds slightly the critical value, and they order in the type II-antiferromagnetic structure at 15.1 and 7.4 K, respectively. The phase transition in TbP is of first order. PrSb is undercritical but the application of a hydrostatic pressure larger than about 30 kbar reduces the Γ_1 – Γ_4 splitting so much that a transition to a type I-antiferromagnet occurs [54]. The paramagnetic excitation at the modulation vector of the ordered phase in PrSb is not expected to become completely soft at the phase transition, because of the elastic contributions of the Γ_4 - and Γ_5 - triplets to $\chi_0(\omega = 0)$, i.e. the second term in eq. (3). In fig. 5 are shown the experimental results for PrSb [54] compared with the RPA-behaviour expected for the critical mode when $T_N = 18$ K. The agreement is convincing, but this is not the case below T_N where the calculated mode lies about a factor of two higher than the observed one. This

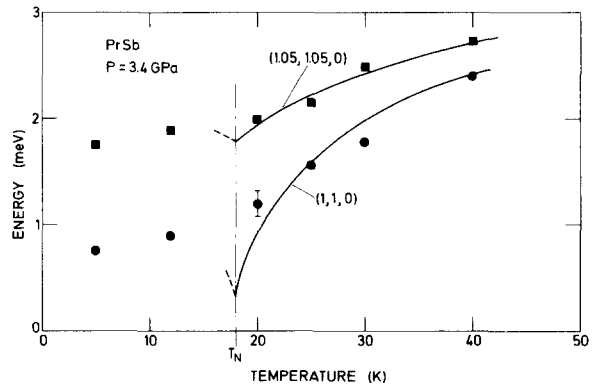


Fig. 5. The temperature dependence of the magnetic excitations in PrSb when a hydrostatic pressure of ~ 3.4 GPa is applied. McWhan et al. [54] found that $T_N = (18 \pm 1)$ K at this pressure, and the figure shows their experimental results for the critical mode (1, 1, 0) and for a mode with a slightly different wavevector (1.05, 1.05, 0). The full lines show the dependences predicted by the RPA in the paramagnetic phase. The result for the critical mode is determined alone by T_N and the crystal-field level scheme proposed in ref. [54].

discrepancy might be due to the magnetoelastic couplings which are important for the formation of the ordered structure. TbP is less critical than PrSb because of the onset of a first-order transition, and the RPA-theory correctly predicts the energy and the scattering intensity of the excitations in the paramagnetic phase, even in the close neighbourhood of T_N [55]. The RPA-theory is not directly affected by the presence of anisotropic two-ion interactions which lift the threefold degeneracy of the Γ_1 - Γ_4 excitations at non-zero q . In both TbP and PrSb [54–56] the excitations split into two branches along the (100) and (110) directions, and the splittings are of the same order of magnitude as the width of the excitation bands. The excitations are still threefold degenerate along (111) within the experimental resolution. A general two-ion interaction, in the form of a Cartesian tensor $\mathcal{J}_{\alpha\beta}(ij)$, predicts two and three branches in the (111) and (110) directions, respectively. In order to reproduce the observed degeneracies along (110) and (111) it is necessary to assume the tensor interactions to be diagonal when the Cartesian axes are along the three (100) directions [56]. This is not the case for the magnetic dipole coupling, which is diagonal only if the z -axis is chosen locally to be along the bond axis. However, the further splittings produced by the magnetic dipole coupling are estimated to be too small to be resolved experimentally [56]. In HoSb [57], the splitting at L in the (111) direction is determined indirectly, and it is found to be a factor of 2–3 smaller than that produced by the magnetic dipole coupling alone.

In comparison with the elements the exchange coupling in these metallic compounds is relatively weak and of short range, and the magnetoelastic couplings and additional two-ion quadrupolar interactions might be comparable in strength with the exchange interaction. Structural phase transitions have not yet been observed in the pnictides, but the quadrupole couplings have important consequences for the magnetic properties; see for instance the discussions of the $\text{Ho}_c\text{Y}_{1-c}\text{Sb}$ system [57] and the Tb-pnictides [58]. In the cubic crystals the dipole and the quadrupole excitations do not mix with each other in the paramagnetic phase. Close to a second-order transition, however, this might

not be strictly true. The critical fluctuations may induce non-linear couplings, which violate the RPA-selection rules related to the static system. For instance, the elastic constants might occasionally be influenced by the magnetic fluctuations just above a magnetic transition, as is suggested to be the case in HoSb [57].

The coupling between the magnetic excitations and the conduction electrons has been studied in a number of the pnictides by measuring the electrical resistivity as a function of temperature; see the review of Hessel Andersen [59]. The most extensive work is that carried out on the $\text{Tb}_c\text{Y}_{1-c}\text{Sb}$ system [60]. The magnetic contributions were isolated experimentally and analysed in terms of the RPA-theory for the magnetic excitations both in the paramagnetic and the antiferromagnetically ordered phase. Satisfactory agreement was obtained for the entire range of concentration c by use of only two common parameters, k_F and the electron-ion exchange constant.

Many of the systems discussed in this review order in periodic magnetic structures. One of the more delicate questions is whether the modulated structure is described by a single wavevector or by a superposition of several symmetrically disposed wavevectors. Neutron-diffraction measurements cannot distinguish between a multi- q structure and a system made up of a corresponding distribution of single- q domains; see for instance ref [29]. In this context it is of interest to discuss USb, where it has been possible to settle the question by an examination of the magnetic excitations [61]. Actually, USb is one of the few actinides where reasonably well-defined magnetic excitations have been observed [62]. It crystallizes in the NaCl-structure and orders antiferromagnetically at 240 K in a structure which, in the single- q picture, is of type-I with the moments oriented parallel to q in a (100)-direction. At low temperatures the moments are large and near their saturation value. However, in spite of the large value of the moments the excitation spectrum consists of two branches, one of which appears to be longitudinally polarized [62]. An analysis [61] shows that these two features, which are in contrast to the behaviour of a normal spin-wave system, are both explained if the system is assumed to be ordered in the triple- q

structure, in which case they are simple consequences of the non-collinear arrangement of the moments, pointing in the different (111)-directions. Furthermore, as shown in fig. 6, all other details of the spectrum are satisfactorily described in this model using only three parameters, the values of which are compatible with the other properties of USb.

A number of *rare-earth intermetallic compounds with the CsCl structure* have been investigated in recent years. The dispersion relation of the magnetic excitations has been studied experimentally in the ordered phases of HoZn [63], ErCu [64], TbZn [65] and TmZn [66]. The different couplings in these compounds compare in order of magnitude with those observed in the pnictides. In TmZn the quadrupole interactions are strong enough to induce a structurally ordered phase by a first-order transition at $T_Q = 8.6$ K; see ref. [66] and references therein. The quadrupolar phase is disrupted by the onset of ferromagnetic ordering at $T_c = 8.1$ K. In $\text{Tm}_{0.9}\text{Lu}_{0.1}\text{Zn}$ the dilution of Tm with

Lu causes a small decrease of T_Q to 5.8 K, whereas the exchange coupling becomes too weak to induce magnetic ordering in the quadrupolar phase, where the ground state is a singlet. This extension of the range of the quadrupolar phase has made it possible to study the dipole excitations in this phase (Morin et al. [67]). They observed modifications of the spectrum due to the effect of the molecular quadrupole-field, but they did not observe dispersive effects directly related to two-ion quadrupole interactions.

Inelastic neutron scattering has been performed on several of the heavy-rare-earth iron and cobalt *Laves-phase compounds*, RFe_2 and RCO_2 . This work has recently been reviewed by Koon and Rhyne [68]. The structure is specified by the position of six atoms, and the unit cell contains only two inequivalent sites, one for the transition metal and one for the rare-earth. The iron compounds order magnetically at high temperatures, ~ 600 K, whereas the transition temperatures for the RCO_2 -compounds are much lower. The ground-state excitation spectrum observed in these compounds consists generally of three branches, a low-lying acoustic mode, a flat dispersionless mode resulting from the rare-earth ions, and a highly dispersive upper mode resembling the spin-wave mode in the itinerant system of the pure transition metals. The latter mode is only observed in the iron compounds, and the remaining three optical modes are expected to lie at high energies which are not readily accessible in the scattering experiments. Koon and Rhyne [68] have developed a six-sublattice RPA-model, corresponding to eqs. (1)–(4), in which the itinerant 3d-spin system is described in terms of localized quasi-spins proportional to the moment assigned to the transition-metal ions. This simplified model for the 3d-spin system is found to offer an excellent description of the observed spectra, which include both groundstate excitations and transitions between higher levels of the rare-earth ions. The only failure of the model is that the predicted highly dispersive Co–Co mode is unobservable in HoCo_2 and ErCo_2 (see note (2) added in proof). The analysis of the spectra shows that the dominant exchange coupling in the Laves-phase compounds is between the transition-metal spins with a significantly weaker coupling of

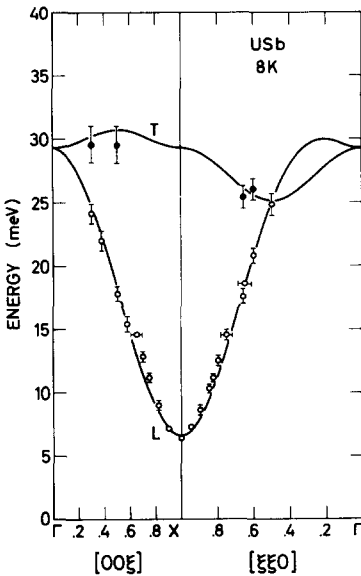


Fig. 6. The spin-wave spectrum in USb at 8 K. The experimental results are taken from Lander and Stirling [62]. The full lines show the spin-wave dispersion relations predicted in the case of a triple- q structure, after ref. [61]. The polarization of the spin-waves is perpendicular to the moments, but parallel or perpendicular to the wavevector for the L- and T-modes, respectively.

the 3d and rare-earth moments, and the coupling between the rare-earth ions themselves is found to be vanishingly small. Clausen et al. [19] have continued the study of the temperature dependence of the spin waves in ErFe_2 . Further, the two Ho-compounds, $\text{Ho}_2\text{Co}_{17}$ and $\text{Ho}_2\text{Fe}_{17}$, have recently been investigated experimentally by Clausen and Lebeck [69,70]. The crystallographic structure of these compounds is more complex than the Laves-phase compounds, e.g. there are two inequivalent rare-earth sites, with hexagonal symmetry, per unit cell. In spite of these complications the excitation spectra are found to be qualitatively similar to those of the Laves-phase compounds. One of the interesting features is that the two crystallographically different rare-earth sites are magnetically equivalent.

5. Conclusion

One general feature of the rare-earth systems discussed in this review, is that their excitation spectra are described rather satisfactorily in terms of the RPA-theory. This seems to hold true independently of the relative magnitudes of the exchange interaction and the quadrupole or crystal-field terms. The effective RPA-parameters of a given system are expected to stay constant only within a limited range of temperatures and fields. However, with a few exceptions it is difficult to isolate genuine correlation effects because the knowledge of the Hamiltonian may be comparatively incomplete. Close to second-order phase transitions, or in systems of lower dimensionality than three, other phenomena, which differ qualitatively from the predictions of the RPA-theory, may occur, as for instance is the case in the low temperature limit of Pr.

Another general characteristic of the rare-earth systems is the multitude of different couplings which have been observed. This accentuates the possibility that the Hamiltonian may include terms not normally encountered. Specifically we may note that anisotropic two-ion couplings have been detected in the various rare-earth systems almost every time they can be manifested by lifting accidental degeneracies in the spectra. One of the

possible mechanisms for producing anisotropic two-ion couplings has been discussed in detail by Cooper and Siemann [71] in the case of Ce-compounds.

Notes added in proof

(1) In a paper presented at this conference McEwen et al. [72] report the observation of magnetic excitations in Nd-metal. The neutron scattering intensity is weak, but the experiment indicates the presence of reasonably well-defined excitations both above and below T_N .

(2) The itinerant-like Co-Co mode in the cobalt Laves-phase compound HoCo_2 has now been detected by Castets et al. [73]. The mode is found to lie almost a factor of two higher in energy than predicted by the simple RPA-theory [68].

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