7.3 Perturbations of the crystal-field system

In this section, we shall discuss various effects of the surrounding medium on a crystal-field system. The first subject to be considered is the magnetoelastic coupling to the lattice. Its contribution to the magnetic-excitation energies may be described in terms of frequency-dependent, anisotropic two-ion interactions, and we include a short account of the general effect of such terms. We next consider the coupling to the conduction electrons, which is treated in a manner which is very parallel to that used for spin-wave systems in Section 5.7. Finally, we discuss the hyperfine interaction between the angular momenta and the nuclear spins, which becomes important at the lowest temperatures, where it may induce an ordering of the moments in an otherwise undercritical singlet-ground-state system.

7.3.1 Magnetoelastic effects and two-ion anisotropy

The magnetoelastic interactions which, in the kind of system we are considering, primarily originate in the variation of the crystal-field parameters with lattice strain, produce a number of observable phenomena. The lattice parameters and the elastic constants depend on temperature and magnetic field, the crystal-field excitation energies are modified, and these excitations are coupled to the phonons. In addition, the magnetoelastic coupling allows an externally applied uniaxial strain to modify the crystal-field energies. All these magnetoelastic effects have their parallel in the ferromagnetic system discussed in Section 5.4 and, in the RPA, they may be derived by almost the same procedure as that presented there, provided that the spin-wave operators are replaced by the standard-basis operators, introduced in eqn (3.5.11).

In the paramagnetic phase in zero external field, only those strains which preserve the symmetry, i.e. the α-strains, may exhibit variations with temperature due to the magnetic coupling. The lowering of the symmetry by an applied external field may possibly introduce non-zero strains, proportional to the field, which change the symmetry of the lattice. In both circumstances, the equilibrium strains may be calculated straightforwardly within the MF approximation. As an example, we shall consider the lowest-order magnetoelastic γ-strain Hamiltonian

$$\mathcal{H}_\gamma = \sum_i \big[\tfrac{1}{2}c_\gamma(\epsilon_{\gamma 1}^2 + \epsilon_{\gamma 2}^2) - B_{\gamma 2}\big\{O_2^2(\mathbf{J}_i)\epsilon_{\gamma 1} + O_2^{-2}(\mathbf{J}_i)\epsilon_{\gamma 2}\big\}\big], \quad (7.3.1)$$

corresponding to eqn (5.4.1) with $B_{\gamma 4} = 0$. The equilibrium strain $\overline{\epsilon}_{\gamma 1}$, for instance, is determined in the presence of an external magnetic field

and external stresses by

$$\frac{1}{N}\langle\frac{\partial\mathcal{H}_\gamma}{\partial\epsilon_{\gamma 1}}\rangle = c_\gamma\overline{\epsilon}_{\gamma 1} - B_{\gamma 2}\langle O_2^2\rangle - (t_{11}-t_{22}) = 0,$$

with $\overline{\overline{t}} = (V/N)\overline{\overline{T}}$, where $\overline{\overline{T}}$ is the usual stress-tensor. Introducing the equilibrium condition into the Hamiltonian, we get

$$\mathcal{H}_\gamma(\text{sta}) = -\sum_i B_{\gamma 2}\{O_2^2(\mathbf{J}_i)\overline{\epsilon}_{\gamma 1} + O_2^{-2}(\mathbf{J}_i)\overline{\epsilon}_{\gamma 2}\} + \mathcal{H}_\gamma^0, \qquad (7.3.2a)$$

where

$$\mathcal{H}_\gamma^0 = N\big[\tfrac{1}{2}c_\gamma(\overline{\epsilon}_{\gamma 1}^2 + \overline{\epsilon}_{\gamma 2}^2) - (t_{11}-t_{22})\overline{\epsilon}_{\gamma 1} - 2t_{12}\overline{\epsilon}_{\gamma 2}\big]. \qquad (7.3.2b)$$

The thermal averages have to be calculated self-consistently, which implies that the static magnetoelastic Hamiltonian, (7.3.2), must itself be included in the total magnetic MF Hamiltonian, which determines the thermal averages such as $\langle O_2^2\rangle$ in the equilibrium equation. The magnetoelastic coupling changes the magnetic-excitation energies if the crystal is strained, because the extra crystal-field term in (7.3.2a), introduced by $\mathcal{H}_\gamma(\text{sta})$, directly modifies $\overline{\overline{\chi}}^o(\omega)$. In the $(J=1)$-model corresponding to Pr, $O_2^{\pm 2}(\mathbf{J}_i)$ couples the two doublet states, and thus the degeneracy of this level is lifted in proportion to the γ-strains.

Having included the contributions of $\mathcal{H}_\gamma(\text{sta})$ to the single-ion susceptibility, we continue by discussing the influence of the coupling between the magnetic excitations and the phonons, as determined by the dynamic part of the magnetoelastic Hamiltonian $\mathcal{H}_\gamma(\text{dyn})$, given by eqn (5.4.6) with $B_{\gamma 4} = 0$. As an example, we consider the coupling to the transverse phonons propagating in the a- or the b-direction, with the polarization vector in the basal-plane, which is derived from

$$\begin{aligned}\Delta\mathcal{H}_\gamma(\text{dyn}) &= -B_{\gamma 2}\sum_i\{O_2^{-2}(\mathbf{J}_i) - \langle O_2^{-2}\rangle\}\epsilon_i \\ &= -B_{\gamma 2}\sum_i\sum_{\nu\mu} N_{\nu\mu}a_{\nu\mu}(i)\epsilon_i, \end{aligned} \qquad (7.3.3)$$

where ϵ_i is a shorthand notation for $\epsilon_{\gamma 2}(i) - \overline{\epsilon}_{\gamma 2}$, and $N_{\nu\mu}$ is the matrix element of the Stevens operator between $<\nu|$ and $|\mu>$, cf. eqns (3.5.11–13). This Hamiltonian introduces an additional term on the l.h.s. of the equation of motion (3.5.15) for the Green function $\langle\langle a_{\nu\mu}(i)\,;\, a_{rs}(i')\rangle\rangle$:

$$\begin{aligned} B_{\gamma 2}\sum_\xi\langle\langle\{N_{\mu\xi}a_{\nu\xi}(i) - N_{\xi\nu}a_{\xi\mu}(i)\}\epsilon_i\,;\, a_{rs}(i')\rangle\rangle &\simeq \\ B_{\gamma 2}(n_\nu - n_\mu)N_{\mu\nu}\langle\langle\epsilon_i\,;\, a_{rs}(i')\rangle\rangle, \end{aligned} \qquad (7.3.4)$$

where the approximate result follows from the usual RPA decoupling introduced by eqn (3.5.16). According to eqn (5.4.25),

$$\epsilon_i = \sum_{\mathbf{k}} (ikF_{\mathbf{k}}/2)(\beta_{\mathbf{k}} + \beta^+_{-\mathbf{k}}) \exp(i\mathbf{k}\cdot\mathbf{R}_i),$$

where we assume, for simplicity, only one phonon mode. From the equations of motion determining the two Green functions $\langle\langle \beta_{\mathbf{q}} \,;\, a_{rs}(i')\rangle\rangle$ and $\langle\langle \beta^+_{-\mathbf{q}} \,;\, a_{rs}(i')\rangle\rangle$, we obtain

$$\begin{aligned}\langle\langle \beta_{\mathbf{q}} + \beta^+_{-\mathbf{q}} \,;\, a_{rs}(i')\rangle\rangle = \\ B_{\gamma 2} \sum_i \sum_{\nu\mu} (iqF_{\mathbf{q}}/2) D(\mathbf{q},\omega) e^{-i\mathbf{q}\cdot\mathbf{R}_i} N_{\nu\mu} \langle\langle a_{\nu\mu}(i) \,;\, a_{rs}(i')\rangle\rangle,\end{aligned} \tag{7.3.5}$$

where $D(\mathbf{q},\omega)$ is the phonon Green function for the mode considered:

$$D_\nu(\mathbf{q},\omega) = \frac{2\omega_{\nu\mathbf{q}}}{\hbar\big(\omega^2 - \omega^2_{\nu\mathbf{q}}\big)}. \tag{7.3.6}$$

If this is introduced into (7.3.4), and the resulting expression is added to the l.h.s. of (3.5.18), the procedure leading to eqn (3.5.21) yields the equivalent result

$$\overline{\overline{\chi}}(\mathbf{q},\omega) - \overline{\overline{\chi}}^{\,o}(\omega)\overline{\overline{\mathcal{J}}}(\mathbf{q},\omega)\overline{\overline{\chi}}(\mathbf{q},\omega) = \overline{\overline{\chi}}^{\,o}(\omega). \tag{7.3.7}$$

However, these quantities are now four-dimensional matrices in the vector space defined by the operators J_{ix}, J_{iy}, J_{iz}, and $O_2^{-2}(\mathbf{J}_i)$, or more accurately by these operators minus their expectation values. The only extra element in $\overline{\overline{\mathcal{J}}}(\mathbf{q},\omega)$, in addition to the normal Cartesian components $\mathcal{J}_{\alpha\beta}(\mathbf{q})$, is

$$\mathcal{J}_{44}(\mathbf{q},\omega) = N\big(\frac{i}{2} qF_{\mathbf{q}} B_{\gamma 2}\big)^2 D(\mathbf{q},\omega). \tag{7.3.8}$$

The excitation energies are determined by the condition

$$\big|1 - \overline{\overline{\chi}}^{\,o}(\omega)\overline{\overline{\mathcal{J}}}(\mathbf{q},\omega)\big| = 0.$$

When $\mathbf{q}$ is along an a- or b-direction, and the external fields are applied in the basal plane, parallel or perpendicular to $\mathbf{q}$, then $\overline{\overline{\mathcal{J}}}(\mathbf{q})$ and the 3×3 Cartesian components of $\overline{\overline{\chi}}^{\,o}(\omega)$, at low frequencies, are diagonal with respect to the $(\xi\eta\zeta)$-axes. In this case, the most phonon-like pole is found at a frequency determined by

$$\big|1 - \overline{\overline{\chi}}^{\,o}(\omega)\overline{\overline{\mathcal{J}}}(\mathbf{q},\omega)\big| \Big/ \prod_\alpha \big[1 - \chi^o_{\alpha\alpha}(\omega)\mathcal{J}_{\alpha\alpha}(\mathbf{q})\big] = 1 - \Xi(\mathbf{q},\omega)\mathcal{J}_{44}(\mathbf{q},\omega) = 0, \tag{7.3.9a}$$

where $\alpha = \xi$, η, and ζ, and

$$\Xi(\mathbf{q},\omega) = \chi^o_{44}(\omega) + \sum_\alpha \frac{\chi^o_{\alpha 4}(\omega)\chi^o_{4\alpha}(\omega)\mathcal{J}_{\alpha\alpha}(\mathbf{q})}{1-\chi^o_{\alpha\alpha}(\omega)\mathcal{J}_{\alpha\alpha}(\mathbf{q})}. \qquad (7.3.9b)$$

At long wavelengths, this pole determines the velocity of the magneto-acoustic sound waves, as measured in an ultrasonic experiment, and expressing this velocity in terms of the corresponding elastic constant, we find

$$\frac{c^*_{66}}{c_{66}} = 1 - \Xi(\mathbf{q},0)B^2_{\gamma 2}/c_\gamma, \qquad (7.3.10)$$

by combining the above relation with eqns (5.4.24*b*) and (5.4.34). This result is valid when $\mathbf{q}$ is along the ξ- or η-axes, provided that the external field is applied along one of the principal axes. In the general case, it is necessary to include the coupling to the other phonon branches in eqn (7.3.7), and also to take into account possible off-diagonal terms in the Cartesian part of the matrices, but these complications may be included in the above calculations in a straightforward fashion. One question raised by (7.3.10) is whether the magneto-acoustic sound velocities, measured at non-zero frequencies, depend on possible purely-elastic contributions to the RPA susceptibilities. That these should be included in (7.3.7), at $\omega = 0$, can be seen by the argument used in deriving (3.5.22). In the preceding section, we found that the coupling between the angular momenta broadens the elastic RPA response into a diffusive peak of width 2Γ, as in (7.2.11*b*), proportional to $T^{1/2}$ at low temperatures. Unless this coupling is very weak, Γ is likely to be much larger than the applied $\hbar\omega$ in an ultrasonic experiment, in which case the total elastic contribution to $\Xi(\mathbf{q},0)$ in (7.3.10) should be included. A more detailed investigation of this question is given by, for instance, Elliott *et al.* (1972), in a paper discussing systems with Jahn–Teller-induced phase transitions.

In the paramagnetic phase without any external *magnetic* field, the susceptibility components $\chi^o_{\alpha 4}(\omega)$ all vanish in the zero frequency limit, due to the time-reversal symmetry of the system. Replacing t by $-t$ generates the transformation $\chi^o_{\alpha 4}(\omega) \to \chi^o_{\alpha^T 4^T}(-\omega)$, where the time-reversed operators are $J^T_{i\alpha} = -J_{i\alpha}$, and $O^{-2}_2(\mathbf{J}_i)^T = O^{-2}_2(\mathbf{J}_i)$. These results follows from the symmetry properties of the axial tensor operators, discussed after eqn (5.5.14), recalling that the operators are Hermitian, of rank $l = 1$ and $l = 2$ respectively. Hence, because of the time-reversal symmetry, $\chi^o_{\alpha 4}(\omega) = -\chi^o_{\alpha 4}(-\omega) = -\big(\chi^o_{\alpha 4}(\omega^*)\big)^*$, where the last result follows from (3.2.15), and we assume implicitly that all poles lie on the real axis. This quantity must therefore vanish at zero frequency, and the reactive and absorptive components are either zero or purely imaginary at non-zero frequencies. If there is no ordered moment and no

external magnetic field, the coupling between the dipolar crystal-field excitations and the long-wavelength phonons must therefore vanish by symmetry, within the present approximation, and $\Xi(\mathbf{q},0) = \chi^o_{44}(0)$ in eqn (7.3.10). In the presence of an external magnetic field, the mixed dipolar–quadrupolar susceptibility-components may become non-zero, and hence produce a direct coupling of the elastic waves and the dipolar excitations. In this case, the magnetic dipole coupling, which gives rise to a directional dependence of $\mathcal{J}_{\alpha\alpha}(\mathbf{q})$, as discussed in Section 5.5, leads to different values of c^*_{66} (as determined from the transverse sound velocity in the $b(\eta)$-direction), depending on whether the field is parallel to the ξ- or the η-axis or, if the field is fixed along one of these two axes, whether $\mathbf{q}$ is along the ξ- or the η-direction. As mentioned earlier, this anisotropy is similar to that introduced by rotational invariance, and has a comparable magnitude in paramagnetic systems (Jensen 1988b).

The dynamic coupling between the magnetic and elastic excitations in Pr has been studied in the long-wavelength limit by Palmer and Jensen (1978), who measured the elastic constant c_{66} by ultrasonic means, as a function of temperature and magnetic field. At 4 K, it was found to be very sensitive to a field applied in the basal plane, but insensitive to a field along the c-axis, reflecting the anisotropy of the susceptibility. At non-zero fields in the basal plane, there is furthermore a considerable anisotropy, due to B^6_6. Using the crystal-field level scheme illustrated in Fig. 1.16, and a value of $B_{\gamma 2}$ consistent with that deduced from the field dependence of the magnetic excitations (Houmann *et al.* 1979), they were able to obtain a very good fit to the observed dependence of c_{66} on field, shown in Fig. 7.5, and on temperature.

The above theory is also valid at non-zero frequencies. However, if q is no longer small, we must take account of the discreteness of the lattice and replace q in (7.3.8) by a sinusoidal function of q and the lattice parameters, as in (5.4.43) in Section 5.4. Except for the change in the $\mathbf{q}$-dependence of $\mathcal{J}_{44}(\mathbf{q},\omega)$, eqn (7.3.7) still applies, and it predicts hybridization effects between the phonons and the crystal-field excitations, equivalent to those derived from the linear magnon–phonon coupling in Section 5.4. The time-reversal symmetry of the paramagnetic system in zero magnetic field does not exclude the possibility that the phonons at non-zero frequencies are coupled to the crystal-field dipolar excitations and, in the case of Pr, the doublet excitations are allowed to interact with the transverse phonons, when $\mathbf{q}$ is in the c-direction. Nevertheless, the application of a magnetic field will generally introduce new interactions via $\chi^o_{4\alpha}(\omega)$, leading to hybridization effects proportional to the field, as observed in Pr by Houmann *et al.* (1979) and interpreted by Jensen (1976a). Interactions between crystal-field excitations and

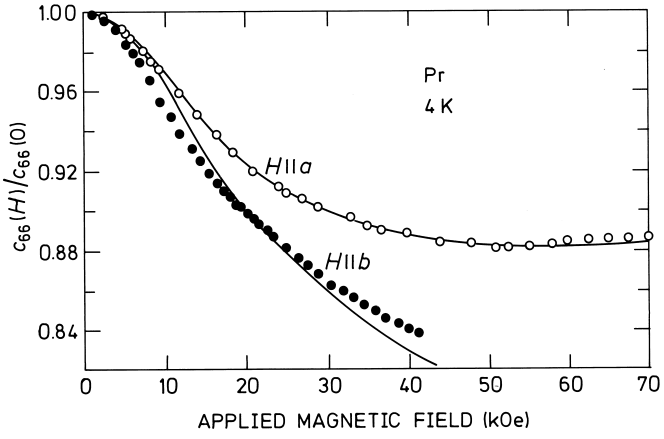

Fig. 7.5. The field dependence of the elastic constant c_{66} in Pr at 4 K, relative to the value at zero field. The elastic constant was determined from the velocity of the transverse sound waves propagating in an a-direction, and the open and closed symbols indicate the experimental results when the field was applied respectively in the a- or the perpendicular b-direction. The solid lines show the calculated field dependence.

the phonons are further discussed by Thalmeier and Fulde (1975), Fulde (1979), and Aksenov *et al.* (1981).

The coupling (5.4.50), quadratic in the magnon operators, also has its counterpart in crystal-field systems. Such interactions arise when, instead of applying the RPA decoupling in the first step, as in eqn (7.3.4), we proceed to the next step in the hierarchy of Green functions. The most important effect of these terms is to replace the crystal-field parameters by effective values, which might be somewhat temperature dependent, corresponding to an averaging of the effective crystalline field experienced by the $4f$ electrons over the finite volume spanned by the thermal vibration of the ions. As in the spin-wave case, these extra higher-order contributions do not lead to the kind of hybridization effects produced by the linear couplings. However, if the density of states of the phonons, weighted with the amplitude of the coupling to the crystal-field excitations, is particularly large at certain energies, resonance-like bound-states due to the higher-order terms may be observed in the magnetic spectrum. The *dynamic Jahn–Teller effect* observed in $CeAl_2$ (Loewenhaupt *et al.* 1979) seems to be due to these higher-order effects, according to the calculation of Thalmeier and Fulde (1982).

The expression (7.3.7) for the interaction of the crystal-field system with the phonons has essentially the same form as that derived from any

general two-ion coupling. Referring to (5.5.14), in which is introduced a general two-ion Hamiltonian in terms of the tensor operators $\widetilde{O}_{lm}(\mathbf{J}_i)$, we may write

$$\mathcal{H}_{\rm JJ} = -\frac{1}{2}\sum_{ij} \mathbf{J}_i^p \cdot \overline{\overline{\mathcal{J}}}^p(ij) \cdot \mathbf{J}_j^p, \tag{7.3.11}$$

where $\mathbf{J}^p \equiv (J_x, J_y, J_z, O_2^{-2}, \widetilde{O}_{lm}, \cdots)$ is a generalized p-dimensional moment operator, and the $\{lm\}$-set of operators comprises the tensor couplings from the original Hamiltonian, except those between the first four components. It is then immediately clear that the final RPA susceptibility is given by an expression equivalent to (7.3.7), in terms of the $p \times p$ susceptibility-matrix with $\mathcal{J}_{\alpha\beta}(\mathbf{q},\omega) = \mathcal{J}^p_{\alpha\beta}(\mathbf{q})$, except that (at long wavelengths) $\mathcal{J}_{44}(\mathbf{q},\omega) = N(iqF_{\mathbf{q}}B_{\gamma 2}/2)^2 D(\mathbf{q},\omega) + \mathcal{J}^p_{44}(\mathbf{q})$. If the frequency is not near a pole in $D(\mathbf{q},\omega)$, the effect of the coupling to the phonons on the magnetic excitations is therefore similar to that stemming from the corresponding quadrupole–quadrupole interaction. If $\mathcal{J}^p_{44}(\mathbf{0})$ is non-zero, the ultrasonic velocities are influenced by this coupling, as we now have

$$\frac{c^*_{66}}{c_{66}} = \frac{1 - \Xi(\mathbf{q},0)\mathcal{J}_{44}(\mathbf{0},0)}{1 - \Xi(\mathbf{q},0)\mathcal{J}^p_{44}(\mathbf{0})} = 1 - \frac{\Xi(\mathbf{q},0)}{1 - \Xi(\mathbf{q},0)\mathcal{J}^p_{44}(\mathbf{0})} B^2_{\gamma 2}/c_\gamma, \tag{7.3.12}$$

where the sum over α in (7.3.9b) comprises all the $(p-1)$ components for which $\alpha \neq 4$, under the same condition that $\overline{\overline{\chi}}^{\,o}(\omega)$ and $\overline{\overline{\mathcal{J}}}(\mathbf{q},\omega)$ are both diagonal for $\alpha \neq 4$. In general, $\chi^o_{4\alpha}(0)$ may be non-zero, in the paramagnetic phase in zero magnetic field, if the α-component is an even-rank tensor, and these interactions may contribute to $\Xi(\mathbf{q},0)$, whereas the odd-rank couplings are prevented from affecting the phonons in the zero-frequency limit by time-reversal symmetry.

In our discussion of crystal-field excitations, we have only been concerned with the excitation spectrum derived from the time variation of the *dipole* moments. There are two reasons for this. Most importantly, the coupling between the dipolar moments expressed in eqn (7.1.1) is normally dominant in rare earth systems, so that the collective phenomena are dominated by the dipolar excitations. The other reason is that the *magnetic* response, including the magnetic susceptibility and the (magnetic) neutron scattering cross-section, is determined exclusively by the upper-left 3×3 part of $\overline{\overline{\chi}}(\mathbf{q},\omega)$, in the generalized p-dimensional vector space introduced through eqn (7.3.11). However, strong quadrupolar interactions may lead to collective effects and to an ordered phase of the quadrupole moments. The quadrupolar excitations are not directly visible in neutron-scattering experiments, but may be detected indirectly via their hybridization with the dipole excitations, in the same way as the phonons, or via their hybridization with the phonons, as measured

by the nuclear scattering of the neutrons. In a paramagnetic system in zero field, the $p \times p$ susceptibility-matrix partitions into two independent blocks, at zero frequency, the one depending only on the even-rank couplings and the other only on the odd-rank couplings. If one of the two parts of $\overline{\overline{\chi}}(\mathbf{q}, 0)$ diverges at some temperature T^*, it signals the occurrence of a second-order phase transition at this temperature. If it is the block determined by the even-rank couplings which diverges, the order parameter below T^* is associated with the quadrupole moments, assuming the lowest-rank terms to be dominant. If there is any coupling between this order parameter and one of the phonon modes, the transition is accompanied by a softening of these phonons, provided that the pure quadrupolar excitations have higher energies than the phonons at the ordering wave-vector. If this vector $\mathbf{Q}$ is zero, the corresponding elastic constant vanishes at the transition. In the case where $\mathbf{Q} \neq \mathbf{0}$, the situation corresponds to that considered in the magnetic case, and the phonon mode shows soft-mode behaviour according as there are pure elastic contributions to the (RPA) susceptibility or not. A quadrupolar phase-transition involving the phonons is usually referred to as being induced by the *Jahn–Teller* effect, and a more detailed discussion and relevant examples may be found in, for instance, Elliott *et al.* (1972). The presence of a non-zero quadrupole moment does not destroy the time-reversal symmetry, and an ordering of the dipole moments may follow only after an additional phase transition. In TmZn (Morin *et al.* 1980) an ordering of the quadrupole moments occurs below a first-order transition at $T_Q = 8.6\,\mathrm{K}$, and this phase is disrupted by the onset of ferromagnetic ordering at $T_C = 8.1\,\mathrm{K}$. In the opposite case of ordering of the dipole moments, the breaking of the time-reversal symmetry allows a direct coupling between the dipole and quadrupole moments, so that the latter are forced to order together with the dipoles, giving rise to, for example, crystal-field-induced magnetostriction effects, and the dipolar ordering will normally quench any tendency toward a purely quadrupolar-ordered phase.

In this chapter, we have formulated the various RPA results in terms of the generalized-susceptibility matrices. The results apply in paramagnetic as well as in ordered systems, so long as the order parameter is uniform throughout the crystal. They agree with the more explicit results derived previously in the case of a weakly-anisotropic ferromagnetic system. In a paramagnet or a strongly-anisotropic ferromagnet, the results above may also be given a more transparent and explicit form, but only if the number $(2J + 1)$ of different angular-momentum states can be taken as small; else the matrix-equations themselves are well-suited for solution by numerical methods. The reduction of the matrix-equations in, for instance, the $(J = 1)$-case is straightforward

and the results, corresponding to Pr in the limit $T = 0$, are given by Jensen (1976a).

In the present approximation, the sound velocities are not affected by the interaction between the dipoles, in the paramagnetic phase at zero magnetic field. However, in the vicinity of a second-order transition to a ferromagnetic phase, strong softening of the long-wavelength phonons may be observed, depending on the symmetry properties, and this behaviour cannot be explained within the RPA. We have seen that, according to eqns (5.4.15) and (5.4.38), c_{66}^* vanishes in the basal-plane ferromagnet when a field equal to the critical field H_c is applied along the hard basal-plane direction. When T_C is approached from below, H_c vanishes rapidly, resulting in a strong softening of c_{66}^* even in zero field, and it seems likely that similar behaviour should be observed when T_C is approached from above, considering that just above T_C there will be large domains of nearly constant magnetization, allowing an 'RPA' coupling between the dipole moments and the sound waves similar to that occurring in the ferromagnetic phase. Clear indications of this kind of behaviour have been seen in for example Tb (Jensen 1971b), indicating that the RPA is not even qualitatively trustworthy when the fluctuations are a dominating feature of the system.

7.3.2 Conduction-electron interactions

The *sf*-exchange Hamiltonian (5.7.6) was derived without making any special assumptions about the rare earth metal involved, and it therefore applies equally well to a metallic crystal-field system. For the weakly-anisotropic ferromagnet considered in Section 5.7, this Hamiltonian leads to a Heisenberg two-ion coupling, $\widetilde{\mathcal{J}}(\mathbf{q},\omega)$, which to a first approximation is instantaneous, and is thus effectively $\mathcal{J}(\mathbf{q}) = \widetilde{\mathcal{J}}(\mathbf{q},0) - (1/N)\sum_{q'}\widetilde{\mathcal{J}}(\mathbf{q}',0)$, as given by eqn (5.7.28). This remains true in crystal-field systems, as may be demonstrated by expanding the angular-momentum operators in (5.7.6) in terms of the standard-basis operators, and then calculating the corresponding Green functions which determine $\overline{\overline{\chi}}(\mathbf{q},\omega)$, utilizing an RPA decoupling of the coupled Green functions.

In the ordered phase, $\mathcal{J}_{zz}(\mathbf{q},\omega)$ may actually differ from the two other components of the exchange coupling, due to the polarization of the conduction electrons. However, in the paramagnetic phase in zero field, the coupling is isotropic, within the approximation made in Section 5.7. This may be seen by analysing the full expression (5.7.27) for $\widetilde{\mathcal{J}}(\mathbf{q},\omega)$, or the simpler result (5.7.26), in which the susceptibility of the conduction electrons becomes a scalar:

$$\chi_{\text{c.el.}}^{\alpha\beta}(\mathbf{q},\omega) = \tfrac{1}{2}\chi_{\text{c.el.}}^{+-}(\mathbf{q},\omega)\,\delta_{\alpha\beta}. \tag{7.3.13}$$

Here the reactive and absorptive parts of $\chi^{+-}_{\text{c.el.}}(\mathbf{q},\omega)$, still given by (5.7.26*b*), are both real and even in $\mathbf{q}$, while the reactive part is even with respect to ω, whereas the absorptive part is odd. When considering the frequency dependence of the susceptibility, we must distinguish two separate regimes, defined by the parameter

$$\vartheta = -\eta q/2k_F = (\hbar\omega/2\varepsilon_F)(k_F/q) = (2/3\nu)\mathcal{N}(\varepsilon_F)\hbar\omega(k_F/q),$$

where η is the parameter introduced in (5.7.31*c*) (with $\Delta(\text{c.el.}) = 0$). If $|\vartheta|$ is small compared to one,

$$\chi^{+-}_{\text{c.el.}}(\mathbf{q},\omega) = \mathcal{N}(\varepsilon_F)\Big\{\mathcal{F}\big(\frac{q}{2k_F}\big) + i\frac{\pi}{2}\vartheta\Big\} \qquad ; \quad |\vartheta| \ll 1, \tag{7.3.14}$$

where the correction to the real part, of the order ϑ^2, may be neglected. This is the same result as obtained in the ordered phase, eqns (5.7.32) and (5.7.36), when the small frequency-dependent term in the former is neglected. When $|\vartheta|$ becomes larger than 1 (or $q > 2k_F$), the imaginary part vanishes, as shown in the calculations leading to (5.7.36), and the real part becomes strongly dependent on ω, vanishing for large values of ϑ as $\vartheta^{-2} \propto \omega^{-2}$. If $\hbar\omega = 1$–$10\,\text{meV}$, then $\vartheta = (10^{-4} - 10^{-3})k_F/q$ in the rare earth metals, so that the corrections to (7.3.14) are only important in the immediate neighbourhood of $q = 0$. The physical origin of this particular effect is that the susceptibility of the free-electron gas is purely elastic in the limit $q = 0$, and it does not therefore respond to a uniform magnetic field varying with a non-zero frequency. In the polarized case, the contributions to the transverse susceptibility are all inelastic at long wavelengths, so this retardation effect does not occur when the polarization gap $\Delta(\text{c.el.})$ is large compared to $|\hbar\omega|$. The exchange coupling, in the limit $q = 0$, includes both the elastic and inelastic contributions, as in (5.7.26*c*), and the abnormal behaviour of the elastic term may be observable in paramagnetic microwave-resonance experiments, where the anomalies should be quenched by a magnetic field. On the other hand, it may not be possible to study such an isolated feature in $\mathbf{q}$-space by inelastic neutron-scattering experiments. Leaving aside the small-q regime, we have therefore that the effective exchange-coupling is

$$\mathcal{J}(\mathbf{q},\omega) = \mathcal{J}(\mathbf{q}) + i\zeta(\mathbf{q})\hbar\omega, \tag{7.3.15}$$

where $\zeta(\mathbf{q})$ is given by (5.7.37*b*), and $\mathcal{J}(\mathbf{q})$ is the reduced zero-frequency coupling given above, or by (5.7.28).

In the case of the weakly-anisotropic ferromagnet, the frequency dependence of the exchange coupling affects the spin-wave excitations

in the same way as results when $\mathcal{J}(\mathbf{q})$ is replaced by $\mathcal{J}(\mathbf{q},\omega)$ in the usual RPA expression for the susceptibility, i.e.

$$\overline{\overline{\chi}}(\mathbf{q},\omega) = \left\{1 - \overline{\overline{\chi}}^{o}(\omega)\mathcal{J}(\mathbf{q},\omega)\right\}^{-1}\overline{\overline{\chi}}^{o}(\omega). \tag{7.3.16}$$

In order to establish that this procedure is valid in general, to leading order in $1/Z$, we must appeal to the $1/Z$-expansion discussed in Section 7.2. It is clear that the usual RPA decoupling (3.5.16), $a_{\nu\xi}(i)a_{\nu'\mu'}(j) \simeq \langle a_{\nu\xi}(i)\rangle a_{\nu'\mu'}(j) + a_{\nu\xi}(i)\langle a_{\nu'\mu'}(j)\rangle$, is not a good approximation if $i = j$, and in (3.5.15) it is only applied in cases where $i \neq j$, as $\mathcal{J}(ii) = 0$ by definition. Here, however, $\mathcal{J}(\mathbf{q},\omega)$ does contain a coupling of one ion with itself, since $\mathcal{J}(ii,\omega) = i\zeta_0\hbar\omega$, where

$$\zeta_0 = \frac{1}{N}\sum_{\mathbf{q}}\zeta(\mathbf{q}) = 2\pi\langle|j(\mathbf{q})|^2\rangle\mathcal{N}^2(\varepsilon_F), \tag{7.3.17}$$

as is obtained by replacing $|j(\mathbf{q})|$ in (5.7.37b) by a constant averaged value in the integral determining ζ_0. This indicates that it is also necessary to rely on the RPA decoupling when $i = j$, in order to obtain the result (7.3.16) when ζ_0 is not zero. On the other hand, the RPA decoupling may work just as well if only the time arguments of the two operators are different, which is the case as $\mathcal{J}(ii, t = 0) = 0$ independently of ζ_0. Only when $t = 0$, is $a_{\nu\xi}(i,t)a_{\nu'\mu'}(i,0)$ equal to $a_{\nu\mu'}(i,0)\delta_{\xi\nu'}$, in direct conflict with the RPA decoupling. This indicates that it may not be necessary to consider separately the effects of $\zeta(\mathbf{q}) - \zeta_0$ and of ζ_0. This point is treated more precisely by the $1/Z$-expansion procedure developed in Section 7.2. Since $\mathcal{J}(\mathbf{q},\omega)$ replaces $\mathcal{J}(\mathbf{q})$, it makes no difference whether $\mathcal{J}(\mathbf{q},\omega)$ is frequency-dependent or not, nor whether $\mathcal{J}(ii,\omega) \neq 0$, and this procedure leads immediately to the result (7.3.16), in the zeroth order of $1/Z$. If $\mathcal{J}(\mathbf{q},\omega)$ contains a constant term, resulting from $\mathcal{J}(ii,t) \propto \delta(t)$, it is removed automatically in the next order in $1/Z$, according to the discussion following eqn (7.2.9). The argument for subtracting explicitly any constant contribution to $\mathcal{J}(\mathbf{q},\omega)$, in eqn (7.3.16), is then that this procedure minimizes the importance of the $1/Z$ and higher-order contributions. The modifications of the $1/Z$ contributions are readily obtained by substituting $\mathcal{J}(\mathbf{q},\omega)$ for $\mathcal{J}(\mathbf{q})$ in the expression (7.2.7c), which determines $K(\omega)$, i.e.

$$\widetilde{K}(\omega) = K(\omega) + \frac{1}{N}\sum_{\mathbf{q}} i\zeta(\mathbf{q})\hbar\omega G(\mathbf{q},\omega)/G(\omega) = K(\omega) + i\langle\zeta(\omega)\rangle\hbar\omega, \tag{7.3.18a}$$

and the self-energy is then obtained as

$$\Sigma(\mathbf{q},\omega) = i\zeta(\mathbf{q})\hbar\omega + \widetilde{\Sigma}(\omega), \tag{7.3.18b}$$

where $\widetilde{\Sigma}(\omega)$ is the previous function with $K(\omega)$ replaced by $\widetilde{K}(\omega)$. The most interesting effects of the scattering of the magnetic excitations against the electron-hole pair excitations of the conduction electrons derive from the first term in the self-energy, which already appears in the 'RPA' in (7.3.16). The lifetime of the excitations becomes **q**-dependent and remains finite in the zero-temperature limit, whereas the imaginary part of $\Sigma(\omega)$, and therefore also of $\widetilde{\Sigma}(\omega)$, vanishes exponentially at low temperatures, in the order $1/Z$. The importance of the higher-order contributions associated with this scattering mechanism, as compared to those of the intrinsic processes, i.e. the relative magnitudes of $\langle\zeta(\omega)\rangle\hbar\omega$ and $K(\omega)$, may depend on the system considered, but in Pr, for example, $\mathrm{Im}\big[K(\omega)\big]$ is much the dominant term at frequencies lying within the excitonic band. Hence, $\langle\zeta(\omega)\rangle$ may be neglected in $\widetilde{K}(\omega)$ at temperatures where the linewidths are still somewhat smaller than the overall bandwidth.

In Pr, the effect of the conduction electrons on the linewidths at low temperatures only becomes visible due to the strong increase in the value of $\zeta(\mathbf{q})$ in the limit of small q, where it is approximately proportional to $1/q$. Houmann *et al.* (1979) were thus able to observe the remarkable broadening of the acoustic modes illustrated in Fig. 7.6, as q was reduced at 6 K. The width at $q = 0.2$ Å is only slightly greater than the experimental resolution, but the peak has become very broad by 0.05 Å, and it has almost vanished into the background at $q = 0$, even though the integrated intensity is expected to increase as the energy decreases. This behaviour is in sharp contrast to that observed in Tb where, as shown in Fig. 5.13 on page 269, the width at small q is greatly reduced by the spin-splitting of the Fermi surface, in accordance with eqn (5.7.37). Since the spin-splitting of the Pr Fermi surface becomes very substantial in a large field, as illustrated in Fig. 1.10, the scattering of the long-wavelength magnetic excitations by the conduction electrons should be quenched by the application of a field. A careful study of this phenomenon would allow a detailed investigation of the interaction between the conduction electrons and the $4f$ moments.

The modification of $\widetilde{K}(\omega)$ also contributes to the broadening of the diffusive peak and, instead of (7.2.11), the result for $J = 1$ is now

$$G(\omega) = G(0)\frac{i\Gamma_1\hbar\omega - \Gamma^2}{(\hbar\omega + i\Gamma)^2}, \tag{7.3.19a}$$

with

$$\Gamma_1 = 2\langle\zeta(0)\rangle/\beta \qquad \text{and} \quad \Gamma = \Gamma_1 + \sqrt{2K(0)/\beta}. \tag{7.3.19b}$$

The term linear in $\langle\zeta(0)\rangle$, introduced in (7.2.10), predicts Lorentzian broadening, if $K(0)$ is neglected. The intrinsic contribution may also

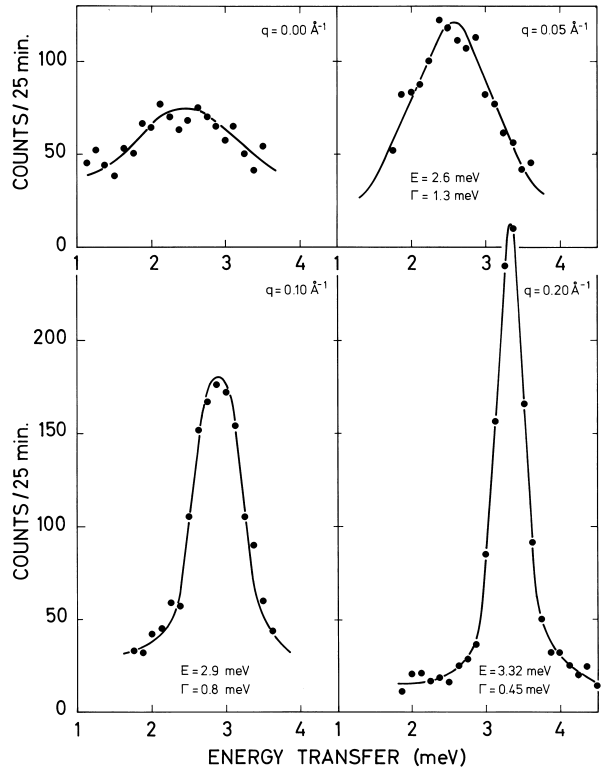

Fig. 7.6. Neutron-scattering spectra from the acoustic branch of the magnetic excitations propagating along the c-axis on the hexagonal sites of Pr at 6 K. The observed values of Γ, the full width at half maximum, increase rapidly as q decreases, due to scattering by the conduction electrons, and at $q = 0$ it is difficult to distinguish the peak from the background. The experimental energy resolution is about 0.35 meV.

here dominate at most temperatures, but it is clear that this cannot hold true in the high-temperature limit, where Γ_1 increases proportionally to T, whereas $K(0)/\beta$ approaches a constant value. So, in the high-temperature limit, (7.3.19) leads to the *Korringa law* (Korringa 1950) for the linewidth:

$$G(\mathbf{q},\omega) \simeq G(\omega) \simeq G(0)\frac{i\Gamma_1}{\hbar\omega + i\Gamma_1}, \qquad \text{with}$$
$$\Gamma_1 = 2\langle\zeta(0)\rangle k_B T = 4\pi\langle|j(\mathbf{q})|^2\rangle\mathcal{N}^2(\varepsilon_F)k_B T, \tag{7.3.20}$$

since $\langle\zeta(0)\rangle = \zeta_0$ in this limit. We argued above that $\langle\zeta(\omega)\rangle$ could be neglected, in comparison with the intrinsic effects, at relatively low

temperatures but, in the high-temperature limit, $\langle\zeta(\omega)\rangle$ is the dominant term. Becker *et al.* (1977) have deduced the influence of the electron-hole-pair scattering on the crystal-field excitations, with an accuracy which corresponds to the results obtained here to first order in $1/Z$, using an operator-projection technique. They performed their calculations for an arbitrary value of J, but without including the intrinsic damping effects which, as pointed out above, may be more important, except in the high-temperature limit.

The effects of the *sf*-exchange Hamiltonian on the effective mass and the heat capacity of the conduction electrons in a crystal-field system may be derived in an equivalent way to that used for the spin-wave system. The mass-enhancement, $m^*/m = 1 + \lambda_{\rm CF}$, is deduced to be given by (White and Fulde 1981; Fulde and Jensen 1983):

$$\begin{aligned}\lambda_{\rm CF} &= \mathcal{N}(\varepsilon_F)\frac{1}{2k_F^2}\int_0^{2k_F} dq \int \frac{d\Omega_{\mathbf{q}}}{4\pi} q|j(\mathbf{q})|^2 \sum_\alpha \chi_{\alpha\alpha}(\mathbf{q},\omega\to 0)\\ &= \frac{1}{N}\sum_{\mathbf{q}} \frac{\zeta(\mathbf{q})}{2\pi\mathcal{N}(\varepsilon_F)} \sum_\alpha \chi_{\alpha\alpha}(\mathbf{q},\omega\to 0),\end{aligned} \tag{7.3.21a}$$

and is a generalization of eqn (5.7.50), valid in the paramagnetic phase. The term $\chi_{\alpha\alpha}(\mathbf{q},\omega\to 0)$ is the zero-frequency susceptibility, omitting possible elastic contributions, assuming the broadening effects to be small. At non-zero temperatures, it is found that excitations with energies small compared to k_BT do not contribute to the mass-enhancement, and therefore, even in the low-temperature limit considered here, the purely elastic terms in $\chi_{\alpha\alpha}(\mathbf{q},\omega)$ do not influence the effective mass. This is also one of the arguments which justifies the neglect to leading order of the effect on m^* of the longitudinal fluctuations in a ferromagnet, which appear in $\chi_{zz}(\mathbf{q},\omega)$. In contrast, the elastic part of the susceptibility should be included in eqn (5.7.57), when the magnetic effects on the resistivity are derived in the general case, as in Section 5.7. In systems like Pr, with long-range interactions, the dispersive effects due to the $\mathbf{q}$-dependence of $\overline{\overline{\chi}}(\mathbf{q},\omega)$ are essentially averaged out, when summed over $\mathbf{q}$. In this case, we may, to a good approximation, replace $\overline{\overline{\chi}}(\mathbf{q},\omega)$ in sums over $\mathbf{q}$ by its MF value $\overline{\overline{\chi}}^{\,o}(\omega)$. The correction to the MF value of the low-temperature heat capacity in Pr, for example, is minute (Jensen 1982b). In the eqns (7.3.18–20) above, this means that, to a good approximation, $\langle\zeta(\omega)\rangle \simeq \frac{1}{N}\sum_{\mathbf{q}}\zeta(\mathbf{q}) = \zeta_0$ even at low temperatures, and that the mass-enhancement parameter is

$$\lambda_{\rm CF} \simeq \frac{\zeta_0}{2\pi\mathcal{N}(\varepsilon_F)} \sum_\alpha \chi^o_{\alpha\alpha}(\omega\to 0). \tag{7.3.21b}$$

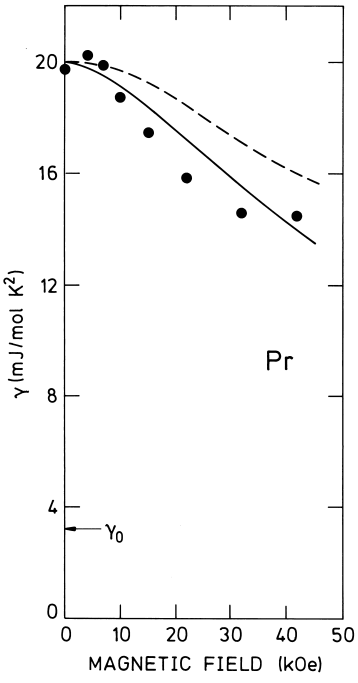

Fig. 7.7. The field dependence of the coefficient γ of the linear electronic heat capacity of Pr at low temperatures. The experimental results of Forgan (1981) are compared with a theory including the renormalization of the mass, due to the interaction of the conduction electrons with the magnetic excitations, and also taking into account the phonon enhancement and the dependence of the Fermi level on magnetic field. The dashed line shows the results of the theory when the change of the Fermi energy with field is neglected.

The mass-enhancement due to the crystal-field excitations is reflected directly in the effective mass measured in the de Haas–van Alphen effect, and in the linear term in the low-temperature electronic specific heat, analogously to the spin-wave system. The former effect has been studied by Wulff *et al.* (1988), who find that the theory of Fulde and Jensen (1983) accounts very well for the field dependence of the masses of several orbits, using the same values of the sf-exchange integral I, about 0.1 eV, as reproduce the variation of the orbit areas discussed in Section 1.3. The substantial field dependence of the electronic heat capacity, measured by Forgan (1981), is shown in Fig. 7.7, and compared with values calculated from eqn (7.3.21*b*), taking into account the field dependence of the electronic state density at the Fermi level, calculated by Skriver (private communication), and the phonon enhancement (Skriver and Mertig 1990). At higher temperatures, the imaginary part of $\mathcal{J}(\mathbf{q},\omega)$ in (7.3.16) gives rise to the same contribution to the magnetic heat capacity as the extra term in (5.7.52) in the spin-wave case, with $\zeta(\mathbf{q})\sum_\alpha \chi_{\alpha\alpha}(\mathbf{q},\omega\to 0)$ replacing $2\Gamma_{\mathbf{q}}/E_{\mathbf{q}}^2$. This contribution should be added to the non-linear corrections to the total low-temperature heat capacity calculated by Fulde and Jensen (1983).

7.3.3 Coupling to the nuclear spins

The hyperfine coupling to the nuclear spins normally has a negligible influence on the properties of the electronic magnetic moments. However, in the special case of a crystal-field system with a singlet ground-state, where the two-ion coupling is smaller than the threshold value for magnetic ordering, this minute coupling may become of decisive importance. Under these circumstances, the hyperfine interaction may induce a cooperative ordering of the combined system of the electronic and nuclear magnetic moments at very low temperatures. The Hamiltonian describing the hyperfine interaction in a rare earth ion has been comprehensively discussed by Bleaney (1972) and McCausland and Mackenzie (1979), and the leading-order term is

$$\mathcal{H}_{\rm hf} = A\,\mathbf{I}\cdot\mathbf{J}, \tag{7.3.22}$$

where $\mathbf{I}$ is the nuclear spin. For the isotope of Pr with mass number 141, which has a natural abundance of 100%, $I = 5/2$ and $A = 52.5\,\mathrm{mK} = 4.5$ μeV. This coupling modifies the MF susceptibility $\overline{\overline{\chi}}^{o}(\omega)$ of the single ion, and since A is small, we may derive this modification by second-order perturbation theory. In order to simplify the calculations, we assume that the MF ground-state of the electronic system is a singlet, and that k_BT is much smaller than the energy of the lowest excited J-state, so that any occupation of the higher-lying J-states can be neglected. Considering first a singlet–singlet system, with a splitting between the two states $|0>$ and $|1>$ of $\Delta \gg |A|$, where only $M_z = <0|\,J_z\,|1>$ is non-zero, and denoting the combined electronic and nuclear states by $|0, m_I>$ and $|1, m_I>$, where $I_z|p, m_I> = m_I|p, m_I>$, we find that the only non-zero matrix elements of $\mathcal{H}_{\rm hf}$ are

$$<0, m_I|\,\mathcal{H}_{\rm hf}\,|1, m_I> = <1, m_I|\,\mathcal{H}_{\rm hf}\,|0, m_I> = m_I M_z A,$$

yielding the following modifications of the state vectors:

$$\begin{cases} |0', m_I> = |0, m_I> -(m_I M_z A/\Delta)|1, m_I> \\ |1', m_I> = |1, m_I> +(m_I M_z A/\Delta)|0, m_I>, \end{cases}$$

to leading order. If we neglect the shifts in energy of the different levels, due to the hyperfine coupling, and the change of the inelastic matrix element,

$$<0', m_I|\,J_z\,|1', m_I> = M_z\{1 - (m_I M_z A/\Delta)^2\} \simeq M_z,$$

the susceptibility is only modified by the non-zero matrix-element,

$$<0', m_I|\,J_z\,|0', m_I> = -2m_I M_z^2 A/\Delta,$$

within the $(2I+1)$-ground state manifold, i.e.

$$\delta\chi^{o}_{zz}(\omega) = \beta\frac{1}{2I+1}\sum_{m_I}\big(2m_I M_z^2 A/\Delta\big)^2\delta_{\omega 0} = \beta\tfrac{1}{3}I(I{+}1)A^2(2M_z^2/\Delta)^2\delta_{\omega 0}. \tag{7.3.23}$$

This result may be straightforwardly generalized to an arbitrary level scheme, including non-zero matrix elements of the other **J**-components, as the different contributions are additive. The susceptibility may then be written

$$\chi^{o}_{\alpha\beta}(\omega) = \chi^{J}_{\alpha\beta}(\omega) + A^2\sum_{\gamma\gamma'}\chi^{J}_{\alpha\gamma}(\omega)\chi^{I}_{\gamma\gamma'}(\omega)\chi^{J}_{\gamma'\beta}(\omega), \tag{7.3.24}$$

to leading order in A, which is valid as long as the general assumptions made above are satisfied. $\chi^{J}_{\alpha\beta}(\omega)$ is the MF susceptibility for the electronic system alone, when the extra term $\delta\mathcal{H}_J(\mathrm{MF}) = A\langle\mathbf{I}\rangle{\cdot}\mathbf{J}$ is included in its MF Hamiltonian. In order to derive the effective MF Hamiltonian $\mathcal{H}_I(\mathrm{MF})$, determining the susceptibility of the nuclear spins $\chi^{I}_{\alpha\beta}(\omega)$, we must consider the possibility, neglected above, that $\mathcal{H}_{\mathrm{hf}}$ may lift the $(2I+1)$-fold degeneracy of the ground-state manifold. Calculating the energies of the ground-state levels, in the presence of an external field, by second-order perturbation theory, we find straightforwardly that the equivalent Hamiltonian, describing the splitting of these levels, is

$$\mathcal{H}_I(\mathrm{MF}) = -g_N\mu_N\mathbf{H}\cdot\mathbf{I} + A\big\{\langle\mathbf{J}\rangle + A\langle\mathbf{I}\rangle\cdot\overline{\overline{\chi}}^{J}(0)\big\}\cdot\mathbf{I} - \tfrac{1}{2}A^2\mathbf{I}\cdot\overline{\overline{\chi}}^{J}(0)\cdot\mathbf{I}. \tag{7.3.25a}$$

This result can be interpreted as expressing the ability of **J** to follow instantaneously any changes of **I**. The molecular field due to $\langle\mathbf{J}\rangle$ is subtracted from the response to **I**, which then instead gives rise to the last quadrupolar term. This quadrupolar contribution is the only effect which is missing in a simple RPA decoupling of the interactions introduced through $\mathcal{H}_{\mathrm{hf}}$. If $\overline{\overline{\chi}}^{J}(0)$ is not a scalar, the last term gives rise to a quadrupole-splitting of the ground-state manifold, and the zero-frequency susceptibility is then, to leading order in this term,

$$\chi^{I}_{\alpha\alpha}(0) = \frac{1}{3}I(I+1)\beta\Big[1 + \tfrac{1}{15}A^2\beta(I+\tfrac{3}{2})(I-\tfrac{1}{2})\big\{3\chi^{J}_{\alpha\alpha}(0) - \sum_{\gamma}\chi^{J}_{\gamma\gamma}(0)\big\}\Big] \tag{7.3.25b}$$

if $\overline{\overline{\chi}}^{J}(0)$ is diagonal. The results above were first obtained and analysed by Murao (1971, 1975, 1979), except that he replaced $\chi^{J}_{\alpha\alpha}(0)$ in (7.3.25) by $(1/N)\sum_{\mathbf{q}}\chi^{J}_{\alpha\alpha}(\mathbf{q},0)$ which, according to the above interpretation, is to be expected in order $1/Z$. For the hexagonal ions in Pr-metal, $A\chi^{J}_{\alpha\alpha}(0) = 0.026$ for the two basal-plane components, but is

zero for the *cc*-component, which implies that the induced quadrupolar-interaction is a factor of about seven larger than the intrinsic value of the electric-quadrupole hyperfine-interaction for the ion $(<0|\,\mathcal{H}_Q\,|0>= (5/7)P_\parallel(I_\xi^2 + I_\eta^2)$, with $P_\parallel = -0.128\,\mathrm{mK}$, using the notation of Bleaney (1972)). In any case, the quadrupole contribution to (7.3.25*b*) only makes a 1.5% correction at the transition temperature $T_N \approx 50\,\mathrm{mK}$ in Pr. The induced quadrupole interaction, due to the highly anisotropic fluctuations of the electronic moments, may be important in nuclear-magnetic-resonance (NMR) experiments. The most important effect in NMR is, however, the strong enhancement of the Zeeman splitting between the nuclear levels by the hyperfine coupling. Introducing $\mathcal{H}_I(\mathrm{MF}) = -g_N\mu_N\mathbf{H}_I^{\mathrm{eff}}\cdot\mathbf{I}$ in (7.3.25*a*), we find an enhancement

$$|H_I^{\mathrm{eff}}/H| \simeq |1 - (g\mu_B/g_N\mu_N)A\chi_{zz}(\mathbf{0},0)|, \tag{7.3.26}$$

which, for the hexagonal ions in Pr, gives a factor of about 40 in the low-temperature limit, when the field is applied in the basal-plane, but unity if H is along the *c*-axis. In addition to the hyperfine interactions considered above, the nuclear spins may also interact directly with the conduction electrons, leading to an extra *Knight shift* and Korringa broadening of the NMR-levels. The most important NMR-linewidth effect is, however, due to the fluctuations of the localized electronic moment. If $J = 1$, corresponding to Pr, these fluctuations lead to a Lorentzian broadening, so that $\chi^I_{\xi\xi}(0) \to \chi^I_{\xi\xi}(0)\big[i\Gamma_N/(\hbar\omega + i\Gamma_N)\big]$, with

$$\Gamma_N = 10(n_0n_1/n_{01})M_\xi^2\mathrm{Im}\big[\widetilde{K}(\omega = \Delta/\hbar)\big],$$

to first order in $1/Z$. In the case of Pr, this gives $\Gamma_N \simeq \exp(-\beta\Delta)\times 1.0$ meV (Jensen *et al.* 1987).

The magnetization and the neutron-scattering cross-section are determined in the RPA by the usual susceptibility expression (7.1.2), with $\overline{\overline{\chi}}^{\,o}(\omega)$ now given by (7.3.24), provided that we neglect the contributions of the small nuclear moments. This means that, even though the electronic system has a singlet ground-state, the hyperfine interaction induces an elastic contribution, and assuming the electronic system to be undercritical, so that $R(0) < 1$ in (7.1.6), we obtain in the low temperature limit, where $k_BT \ll \Delta$,

$$\chi_{\xi\xi}(\mathbf{q},0) = \frac{\Delta^2\big\{1 + A^2\chi^J(0)\chi^I(0)\big\}}{E_{\mathbf{q}}^2 - (\Delta^2 - E_{\mathbf{q}}^2)A^2\chi^J(0)\chi^I(0)}\chi^J(0), \tag{7.3.27}$$

where $\chi^J(0) = 2M_\xi^2/\Delta$, and $E_{\mathbf{q}}$ is given by (7.1.4*b*), with $n_{01} = 1$. If we introduce the nuclear spin susceptibility, neglecting the quadrupolar contribution, into this expression, it predicts a second-order phase

transition, at a temperature determined by

$$k_B T_N = \tfrac{1}{3} I(I+1) A^2 \chi^J(0) \frac{\Delta^2 - E_{\mathbf{Q}}^2}{E_{\mathbf{Q}}^2} = \tfrac{1}{3} I(I+1) A^2 \chi^J(0) \frac{R_0}{1-R_0}, \tag{7.3.28}$$

to a modulated phase described by the wave-vector $\mathbf{Q}$ at which $\mathcal{J}(\mathbf{q})$ has its maximum value, where R_0 is the critical parameter defined by eqn (7.1.6). With $\Delta = 3.52\,\mathrm{meV}$ and $E_{\mathbf{Q}} = 1.0\,\mathrm{meV}$ for the hexagonal excitations in Pr, the electronic system is just undercritical, with a critical ratio $R_0 \simeq 0.92$. This means that the importance of the hyperfine interaction is much enhanced, and eqn (7.3.28) predicts $T_N = 45\,\mathrm{mK}$ for the cooperative ordering of the nuclear and electronic moments in Pr. The transition is no longer accompanied by a soft mode, but there is rather an elastic peak, with a scattering intensity given by

$$\mathcal{S}_d^{\xi\xi}(\mathbf{q}, \omega \approx 0) = \tfrac{1}{3} I(I+1) A^2 \frac{(2M_\xi^2/E_{\mathbf{q}})^2}{1 - \chi^J(0)\{1 + A^2 \chi^J(0) \chi^I(0)\} \mathcal{J}(\mathbf{q})} \, \delta(\hbar\omega), \tag{7.3.29}$$

in the paramagnetic phase, which diverges at $\mathbf{q} = \mathbf{Q}$ when T approaches T_N, analogously to the behaviour of the singlet–triplet case described by (7.1.13).