

7.1 MF-RPA theory of simple model systems

The general procedure for calculating the RPA susceptibility was outlined in Section 3.5. If we consider the Hamiltonian

$$\mathcal{H} = \sum_i \mathcal{H}_J(\mathbf{J}_i) - \frac{1}{2} \sum_{ij} \mathbf{J}_i \cdot \overline{\overline{\mathcal{J}}}(ij) \cdot \mathbf{J}_j, \quad (7.1.1)$$

which includes a general two-ion coupling between the dipolar moments, and assume the system to be in the paramagnetic state, we find the RPA susceptibility to be

$$\overline{\overline{\chi}}(\mathbf{q}, \omega) = \{1 - \overline{\overline{\chi}}^o(\omega) \overline{\overline{\mathcal{J}}}(\mathbf{q})\}^{-1} \overline{\overline{\chi}}^o(\omega), \quad (7.1.2)$$

which is a simple generalization of eqn (3.5.8), as in (6.1.7). The essence of the problem therefore lies in the calculation of the non-interacting susceptibility $\overline{\overline{\chi}}^o(\omega)$, as determined by the single-ion Hamiltonian $\mathcal{H}_J(\mathbf{J}_i)$. In the case of a many-level system, where J is large, this normally requires the assistance of a computer. Analytical expressions for $\overline{\overline{\chi}}(\mathbf{q}, \omega)$ may, however, be obtained for systems where the number of crystal-field levels is small, i.e. between 2–4 states corresponding to $J = \frac{1}{2}$, 1, or $\frac{3}{2}$. Such small values of J are rare, but the analysis of these models is also

useful for systems with larger J , if the higher-lying levels are not coupled to the ground state, and are so sparsely populated that their influence is negligible. According to *Kramers' theorem*, the states are at least doubly degenerate in the absence of an external magnetic field, if $2J$ is odd. In order to construct simple models with relevant level-schemes, we may consider a *singlet-singlet* or a *singlet-triplet* configuration, instead of systems with $J = \frac{1}{2}$ or $J = \frac{3}{2}$. These models may show some unphysical features, but these do not normally obscure the essential behaviour.

The simplest level scheme is that of the singlet-singlet model. This may be realized conceptually by lifting the degeneracy of the two states with $J = \frac{1}{2}$ with a magnetic field, and then allowing only one of the components of \mathbf{J} perpendicular to the field to interact with the neighbouring ions. This is the so-called *Ising model in a transverse field*. Assuming the coupled components to be along the α -axis, we need only calculate the $\alpha\alpha$ -component of $\bar{\chi}^o(\omega)$. The lower of the two levels, at the energy E_0 , is denoted by $|0\rangle$, and the other at E_1 by $|1\rangle$. The single-ion population factors are n_0 and n_1 respectively, and the use of eqn (3.5.20) then yields

$$\chi_{\alpha\alpha}^o(\omega) = \frac{2n_{01}M_\alpha^2\Delta}{\Delta^2 - (\hbar\omega)^2}, \quad (7.1.3)$$

where $M_\alpha = |\langle 0|J_\alpha|1\rangle|$ is the numerical value of the matrix element of J_α between the two states, while the two other (elastic) matrix elements are assumed to be zero. $\Delta = E_1 - E_0$ is the energy difference, and $n_{01} = n_0 - n_1$ is the difference in population between the two states. From eqn (7.1.2), we have immediately, since only $\mathcal{J}_{\alpha\alpha}(\mathbf{q})$ is non-zero,

$$\chi_{\alpha\alpha}(\mathbf{q}, \omega) = \frac{2n_{01}M_\alpha^2\Delta}{E_{\mathbf{q}}^2 - (\hbar\omega)^2}, \quad (7.1.4a)$$

where the *dispersion relation* is

$$E_{\mathbf{q}} = [\Delta\{\Delta - 2n_{01}M_\alpha^2\mathcal{J}_{\alpha\alpha}(\mathbf{q})\}]^{1/2}. \quad (7.1.4b)$$

These excitations are actually spin waves in this case of extreme axial anisotropy, but they have all the characteristics of crystal-field excitations. The energies are centred around Δ , the energy-splitting between the two levels, and the bandwidth of the excitation energies, due to the two-ion interaction, is proportional to the square of the matrix element, and to the population difference, between them. These factors also determine the neutron-scattering intensities which, from (3.2.18) and (4.2.3), are proportional to

$$\begin{aligned} \mathcal{S}_d^{\alpha\alpha}(\mathbf{q}, \omega) &= \frac{1}{1 - e^{-\beta\hbar\omega}} \frac{n_{01}M_\alpha^2\Delta}{E_{\mathbf{q}}} \{\delta(\hbar\omega - E_{\mathbf{q}}) - \delta(\hbar\omega + E_{\mathbf{q}})\} \\ &\simeq M_\alpha^2 \frac{\Delta}{E_{\mathbf{q}}} \{n_0\delta(\hbar\omega - E_{\mathbf{q}}) + n_1\delta(\hbar\omega + E_{\mathbf{q}})\}. \end{aligned} \quad (7.1.5)$$

The approximate expression is obtained by using $\hbar\omega \simeq \pm\Delta$ in the temperature denominator.

The above results are only valid as long as the excitation energies remain positive for all \mathbf{q} . The mode of lowest energy is found at the wave-vector \mathbf{Q} at which $\mathcal{J}_{\alpha\alpha}(\mathbf{q})$ has its maximum. Introducing the critical parameter

$$R(T) = 1 - \frac{\chi_{\alpha\alpha}^o(0)}{\chi_{\alpha\alpha}(\mathbf{Q}, 0)}, \quad (7.1.6a)$$

which, in the present approximation, depends on T through n_{01} :

$$R(T) = 1 - (E_{\mathbf{Q}}/\Delta)^2 = n_{01}R_0 \quad ; \quad R_0 = \frac{2M_{\alpha}^2\mathcal{J}_{\alpha\alpha}(\mathbf{Q})}{\Delta}, \quad (7.1.6b)$$

we find that the excitation energies are all positive as long as $R(T) < 1$. This parameter increases monotonically when the temperature is lowered and, if the zero-temperature value R_0 is greater than one, the energy $E_{\mathbf{Q}}$ of the *soft mode* vanishes at a temperature $T = T_N$ (or T_C if $\mathbf{Q} = \mathbf{0}$) determined by $R(T_N) = 1$. Correspondingly, the susceptibility $\chi_{\alpha\alpha}(\mathbf{Q}, 0)$ becomes infinite at this temperature. This indicates that the system undergoes a second-order phase transition, from a paramagnetic phase to one which has the same symmetry as the soft mode. In this case, this means that $\langle J_{\alpha i} \rangle = \langle J_{\alpha} \rangle \cos(\mathbf{Q} \cdot \mathbf{R}_i + \varphi)$, where the MF equations have a non-zero solution for $\langle J_{\alpha} \rangle$ below, but not above, T_N .

We shall assume ferromagnetic ordering with $\mathbf{Q} = \mathbf{0}$. For the Ising model in a transverse field, the development of a ferromagnetic moment below T_C corresponds to a rotation of the moments away from the direction of the 'transverse field'. The MF Hamiltonian in the ($|0\rangle$ $|1\rangle$)-basis is

$$\mathcal{H}_{\text{MF}}(i) = \begin{pmatrix} E_0 & -\delta \\ -\delta & E_1 \end{pmatrix} \quad ; \quad \delta = M_{\alpha}\mathcal{J}_{\alpha\alpha}(\mathbf{0})\langle J_{\alpha} \rangle. \quad (7.1.7)$$

Introducing the new eigenstates

$$\begin{aligned} |0'\rangle &= \cos\theta|0\rangle + \sin\theta|1\rangle \\ |1'\rangle &= \cos\theta|1\rangle - \sin\theta|0\rangle, \end{aligned} \quad (7.1.8a)$$

we find that the coupling parameter δ , due to the molecular field, gives rise to a non-zero moment $\langle 0'|J_{\alpha}|0'\rangle = M_{\alpha}\sin 2\theta$ in the ground state. Because it is a singlet, the ground state $|0\rangle$ in the paramagnetic phase is necessarily 'non-magnetic', in zero field. This condition does not apply in the ordered phase, so the nomenclature *induced-moment* system is frequently used. In the ordered phase, the splitting between the two singlets is $\Delta/\cos 2\theta$, and $\langle J_{\alpha} \rangle = n_{01}M_{\alpha}\sin 2\theta$ (where n_0 and n_1 are now

the population factors of the new eigenstates). The condition that \mathcal{H}_{MF} should be diagonal in the new basis requires that

$$\cos 2\theta = \frac{1}{n_{01}R_0}, \quad (7.1.8b)$$

which only has a solution if $n_{01}R_0 \geq 1$, in accordance with the critical condition $R(T_C) = 1$. The MF susceptibility is

$$\chi_{\alpha\alpha}^o(\omega) = \frac{2n_{01}M_\alpha^2\Delta \cos 2\theta}{(\Delta/\cos 2\theta)^2 - (\hbar\omega)^2} + \beta(n_0 + n_1 - n_{01}^2)M_\alpha^2 \sin^2 2\theta \delta_{\omega 0}, \quad (7.1.9)$$

revealing that there are now two kinds of excitation. The first is a continuation of the paramagnetic inelastic branch, with the dispersion relation

$$E_{\mathbf{q}}^2 = \frac{\Delta}{\cos 2\theta} \left(\frac{\Delta}{\cos 2\theta} - 2n_{01}M_\alpha^2 \mathcal{J}(\mathbf{q}) \cos^2 2\theta \right), \quad (7.1.10)$$

which is again positive at all wave-vectors, consistent with the stability of the ordered phase. $E_{\mathbf{Q}}$ therefore vanishes when T approaches T_C from above or below, and this kind of second-order phase transition is frequently known as a *soft-mode transition*. In addition to the inelastic mode, there appears a diffusive mode which, within the RPA, is purely elastic. The diffusive mode, but not the inelastic branch, has a parallel in the spectrum of the longitudinal fluctuations of a Heisenberg ferromagnet, described by eqn (3.5.27), since the spectrum analysed here is longitudinal relative to the polarization of the spontaneously ordered moment.

The behaviour discussed above is typical for a system where the crystal-field ground state is a singlet. The most characteristic feature of such a system is that the two-ion coupling must exceed a certain threshold value, relative to the crystal-field splitting, in order to force the system into a magnetically-ordered state at low temperatures. In this case, the condition is that the ratio R_0 must be greater than one. The general (MF) condition is that $\chi_{\alpha\alpha}^o(0)\mathcal{J}_{\alpha\alpha}(\mathbf{Q}) > 1$, for at least one of the α -components, where $\chi_{\alpha\alpha}^o(0)$ is the paramagnetic susceptibility at zero temperature. This condition is a consequence of the fact that the single-ion susceptibility remains finite in the zero-temperature limit, if the ground state is non-degenerate. If the ground state is degenerate, on the other hand, one or more components of the static single-ion susceptibility contains an elastic contribution proportional to $1/k_B T$, and its divergence in the $T = 0$ limit results in an ordering of the moments, within the MF approximation, no matter how weak the two-ion coupling. Fluctuations not included in the MF theory modify the critical

condition for $\mathcal{J}(\mathbf{Q})$, but the qualitative behaviour is unchanged. It is therefore possible to realize a system in which the moments are relatively strongly coupled to each other, but which remains paramagnetic at low temperatures, i.e. a crystal-field system in which cooperative effects are important. Perhaps the best example is elemental Pr, which is only slightly undercritical, with $R_0 \simeq 0.92$, and therefore exhibits a rich variety of unusual magnetic phenomena.

Pr crystallizes in the double hexagonal-close-packed (dhcp) structure, illustrated in Fig. 1.3, with the stacking sequence ABAC along the c -axis. This implies that there are two non-equivalent types of site of different symmetry in the crystal. The ions in A layers are in an approximately cubic environment, with nearest neighbours close to the fcc configuration, while those in the B and C layers experience a crystal field of hexagonal symmetry and form together an hcp structure. The tripositive Pr ion, with two $4f$ electrons, is a *non-Kramers* ion ($S = 1$, $L = 5$, and $J = 4$ for the ground-state multiplet) allowing the occurrence of singlet crystal-field states. Experimental observations, particularly of neutron scattering, have revealed that both kinds of site in fact have a singlet as the ground state. The lowest states of the *hexagonal* ions are the singlet $|J_\zeta = 0\rangle$ followed by the doublet $|J_\zeta = \pm 1\rangle$, with an energy difference of $\Delta_h \simeq 3.5$ meV, as illustrated in Fig. 1.16. If the distortion of the point symmetry of the *cubic* ions, due to the non-ideal c/a ratio, is neglected, their ground state is the Γ_1 -singlet, with the Γ_4 -triplet lying $\Delta_c \simeq 8.4$ meV above it. A complete survey of the classification and energies of crystal-field states in cubic surroundings has been given by Lea, Leask, and Wolf (1962). The possibility that the Γ_4 state is split into a singlet and a doublet, due to the deviation from cubic symmetry, has not yet been investigated experimentally. At temperatures well below 40 K (~ 3.5 meV), only the two ground states are populated significantly, and Pr may be considered to be a coupled singlet-doublet and singlet-triplet system. Furthermore, the difference between Δ_h and Δ_c is so large, compared to the two-ion interactions, that the excitation spectrum can be divided into two parts, related respectively to the crystal-field transitions on each kinds of ion. The weak coupling of the two components may be accounted for by second-order perturbation theory (Jensen 1976a), leading to an effective decoupling, with the two-ion parameters replaced by slightly different, effective values. Hence, at low temperature, Pr may be treated as a combination of a singlet-doublet system on an hcp lattice and a singlet-triplet system on a simple hexagonal lattice. Of these, the singlet-doublet system is much the more important because of the smaller value of the crystal-field splitting. The singlet-doublet scheme corresponds to an effective $J = 1$ and, if the two doublet states are defined to be $|1_S\rangle = (|+1\rangle + |-1\rangle)/\sqrt{2}$

and $|1_a\rangle = (|+1\rangle - |-1\rangle)/\sqrt{2}i$, the only non-zero matrix elements of \mathbf{J} are $\langle 1_a|J_\zeta|1_s\rangle = i$ and $\langle 0|J_\xi|1_s\rangle = \langle 0|J_\eta|1_a\rangle = \sqrt{J(J+1)/2}$, plus their Hermitian conjugates. In Pr, the matrix element of J_ζ is a factor of $\sqrt{10}$ smaller than the other matrix elements. This means that the transformation of the ($J = 4$) ion of Pr to an effective $J = 1$ system introduces a scaling of the two-ion couplings $\mathcal{J}_{\xi\xi}(\mathbf{q})$ and $\mathcal{J}_{\eta\eta}(\mathbf{q})$ by a factor of 10, compared to $\mathcal{J}_{\zeta\zeta}(\mathbf{q})$, and the latter may therefore be neglected to a first approximation. Hence the ($J = 1$) XY -model is an appropriate low-temperature description of the hexagonal ions in Pr.

The RPA theory of the XY -model, in the singlet–doublet case, is nearly identical to that developed above for the Ising model in a transverse field. One difference is that $n_0 + n_1 + n_2 = n_0 + 2n_1 = 1$, instead of $n_0 + n_1 = 1$, but since this condition has not been used explicitly (the population of any additional higher-lying levels is neglected), it may be considered as accounted for. The other modification of the above results is that there are now two components of $\bar{\chi}(\mathbf{q}, \omega)$ which are important: $\chi_{xx}^o(\omega) = \chi_{yy}^o(\omega)$ are given by the same expression as $\chi_{\alpha\alpha}^o(\omega)$ in eqn (7.1.3) (with $M_\alpha = 1$ when $J = 1$), whereas $\chi_{xy}^o(\omega) \equiv 0$ (the (xyz) -axes are assumed to coincide with the $(\xi\eta\zeta)$ -axes). This means that, for a Bravais lattice, there are two poles at positive energies in the RPA susceptibility (7.1.2) at each \mathbf{q} -vector. As long as $\mathcal{J}_{xy}(\mathbf{q}) = 0$, one of the modes describes a time variation of J_x alone, and the other J_y alone, and their dispersion relations are both given by eqn (7.1.4b), with α set equal to x or y . It is interesting to compare this result with the spin-wave case. Although the magnetic response is there also determined by a 2×2 matrix equation, it only leads to one (spin-wave) pole at positive energies, independently of whether the two-ion coupling is isotropic. The cancellation of one of the poles is due to the specific properties of $\chi_{xy}^o(\omega)$ in (5.1.3), produced by the molecular field (or the broken time-reversal symmetry) in the ordered phase. In the case considered above, the two modes may of course be degenerate, but only if $\mathcal{J}_{xx}(\mathbf{q})$ is equal to $\mathcal{J}_{yy}(\mathbf{q})$. In an hcp system, such a degeneracy is bound to occur, by symmetry, if \mathbf{q} is parallel to the c -axis. If the degeneracy is lifted by anisotropic two-ion couplings, which is possible in any other direction in \mathbf{q} -space, the x - and y -modes mix unless \mathbf{q} is parallel to a b -axis. The validity of the results derived above is not restricted to the situation where the doublet lies above the singlet. If the XY -model is taken literally, all the results apply equally well if Δ , and hence also n_{01} , is negative. However, if the z -components are coupled to some extent, as in Pr, the importance of this interaction is much reduced at low temperature if Δ is positive. In this case the zz -response, which is purely elastic,

$$\chi_{zz}(\mathbf{q}, \omega) \simeq \chi_{zz}^o(\omega) = 2\beta n_1 \delta_{\omega 0}$$

is frozen out exponentially in the low-temperature limit.

As shown in Fig. 7.1, the dispersion relations for the magnetic excitations on the hexagonal sites in Pr, measured by Houmann *et al.* (1979), illustrate many of the characteristic features of the ($J = 1$) XY -model. As mentioned above, when \mathbf{q} is along ΓM , the excitations are pure x - or y -modes. The hexagonal ions constitute an hcp structure, so there are an optical and an acoustic mode for each polarization. The excitation energies (7.1.4) are then generalized analogously to eqn (5.1.9), and since $\mathcal{J}_2(\mathbf{0})$ is negative in this case, the lower two branches are the optical modes. From intensity measurements of the type illustrated in Fig. 4.2, it may readily be deduced that the lowest branch is the longitudinal optical y -mode. The experimental dispersion relations show clearly that $\mathcal{J}_{xx}(\mathbf{q})$ and $\mathcal{J}_{yy}(\mathbf{q})$ have very different dependences on wave-vector, and that the anisotropic component is a substantial fraction of the two-ion coupling.

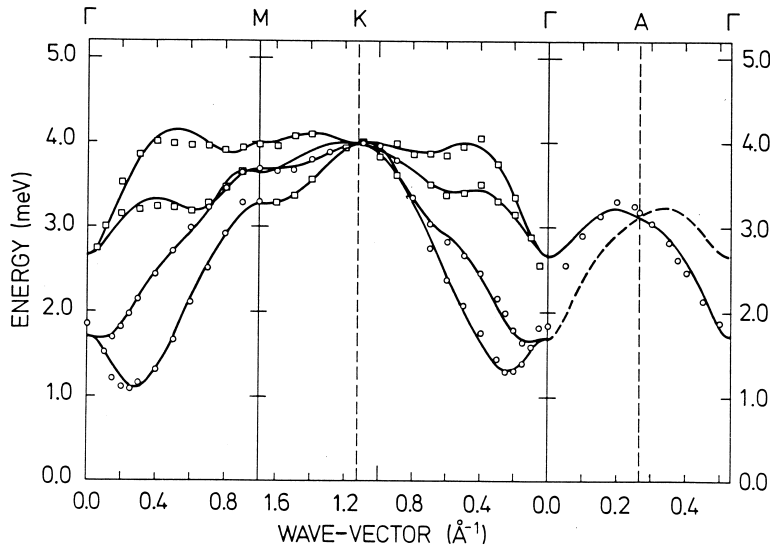


Fig. 7.1. Dispersion relations for the magnetic excitations propagating on the hexagonal sites of Pr at 6K. In the basal plane, the squares and circles denote the experimental results for the acoustic and optical modes respectively. The double degeneracy of these excitations is lifted by anisotropic exchange, and the lower and upper branches correspond respectively to polarizations predominantly parallel and transverse to the wave-vector. The double-zone representation is used for the ΓA direction, along which the two transverse excitations are degenerate by symmetry, and therefore form a single branch.

The singlet–triplet model, relevant in the case of cubic symmetry and, with some modifications, also for the cubic ions in Pr, introduces one new feature; each component of the single-ion susceptibility includes a mixture of an elastic and an inelastic response. In surroundings with cubic symmetry, $\bar{\chi}^o(\omega)$ is proportional to the unit tensor, and the diagonal component is

$$\chi^o(\omega) = \frac{2n_{01}M_1^2\Delta}{\Delta^2 - (\hbar\omega)^2} + 2\beta n_1 M_2^2 \delta_{\omega 0}, \quad (7.1.11)$$

where now $n_0 + 3n_1 = 1$. This result follows from the circumstance that J_x , for instance, has a matrix element between the singlet state and one of the triplet states, and a matrix element between the two other triplet states, the numerical values of which are denoted by M_1 and M_2 respectively. In the $\Gamma_1 - \Gamma_4$ case with $J = 4$, corresponding to Pr, $M_1 = \sqrt{20/3}$ and $M_2 = 1/2$. The inelastic $\chi(\mathbf{q}, \omega \neq 0)$ is equivalent to (7.1.4) for the singlet–singlet system, but with M_α replaced by M_1 . Because of the elastic contribution, the critical condition $R(T_N) = 1$ is now determined from

$$R(T) = (2n_{01}M_1^2 + 2\beta\Delta n_1 M_2^2) \frac{\mathcal{J}_{\alpha\alpha}(\mathbf{Q})}{\Delta}. \quad (7.1.12)$$

The inelastic neutron-scattering spectrum is also determined by eqn (7.1.4) with $M_\alpha = M_1$ and $\alpha = x, y, \text{ or } z$, when the off-diagonal coupling is neglected. The only difference is that there may now be three different branches, depending on the polarization. In addition to the inelastic excitations, the spectrum also includes a diffusive, elastic mode. In order to determine its contribution to the scattering function, $\delta_{\omega 0}$ in (7.1.11) may be replaced by $\delta^2 / \{\delta^2 - (\hbar\omega)^2\}$, and if the limit $\delta \rightarrow 0$ is taken at the end, the result is found to be:

$$\begin{aligned} \mathcal{S}_d^{\alpha\alpha}(\mathbf{q}, \omega \approx 0) &= \frac{\chi^o(0) - \chi^o(\omega \rightarrow 0)}{\beta\{1 - \chi^o(\omega \rightarrow 0)\mathcal{J}_{\alpha\alpha}(\mathbf{q})\}\{1 - \chi^o(0)\mathcal{J}_{\alpha\alpha}(\mathbf{q})\}} \delta(\hbar\omega) \\ &= 2n_1 M_2^2 \left(\frac{\Delta}{E_{\mathbf{q}}}\right)^2 \frac{\chi_{\alpha\alpha}(\mathbf{q}, 0)}{\chi^o(0)} \delta(\hbar\omega). \end{aligned} \quad (7.1.13)$$

The two-ion coupling is assumed to be diagonal, and $\chi^o(\omega \rightarrow 0)$ is the static susceptibility without the elastic contribution. The scattering function at $\mathbf{q} = \mathbf{Q}$, integrated over small energies, diverges when T approaches T_N , as it also does in the singlet–singlet system. In the latter case, and in the singlet–doublet system, the divergence is related to the softening of the inelastic mode ($E_{\mathbf{Q}} \rightarrow 0$ when $T \rightarrow T_N$), as in eqn (7.1.5). In the singlet–triplet system, it is the intensity of the

elastic, diffusive mode which diverges, whereas the intensity of the inelastic mode stays finite and its energy is still non-zero at the transition. Within the simple MF-RPA theory, the critical behaviour has changed, because of the elastic term in the crystal-field susceptibility, so that the transition is no longer accompanied by a soft mode. The energy of the inelastic mode at $\mathbf{q} = \mathbf{Q}$, when T is close to T_N , depends on Δ and on how large the elastic term is at the transition. If this elastic contribution is small, the energy of the inelastic mode may be so small that it becomes overdamped because of the influence of the critical fluctuations, and therefore indistinguishable from the divergent diffusive peak. However, if the inelastic mode is sufficiently separated in frequency from the low-frequency critical fluctuations, it may persist as a reasonably well-defined excitation even near the phase transition.

The dhcp structure of Pr has four atoms per unit cell, so there are four branches of the dispersion relation for each polarization. If the hexagonal and cubic sites are decoupled, these decompose into two sets, each comprising two modes, which may be described as acoustic and optical, propagating on the sites of a particular symmetry. The complementary excitations to those of Fig. 7.1 propagate on the cubic sites, and their dispersion relations, also studied by Houmann *et al.* (1979), are illustrated in Fig. 7.2. If the hexagonal sites are ignored, the cubic sites lie on a simple hexagonal lattice, so that a double zone may be

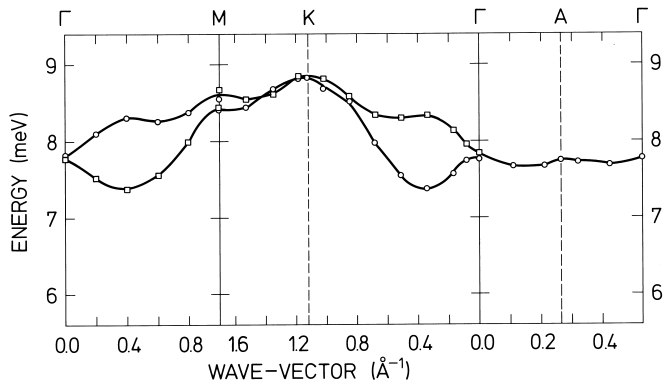


Fig. 7.2. Dispersion relations for the excitations propagating on the cubic sites of Pr at 6 K, plotted in the Brillouin zone of the dhcp structure. The upper and lower branches in the basal plane are respectively the acoustic and optical modes. The polarization vector of these excitations is perpendicular to the c -axis. In contrast to Fig. 7.1, no splitting of these branches by anisotropic two-ion coupling is observed, within the experimental resolution of about 0.5 meV.

used. However, it is both more convenient and, in general, more correct to use the true Brillouin zone for the dhcp structure, as in Fig. 7.2. The excitations in this figure are polarized in the plane, and may also be described by (7.1.4), with parameters appropriate to the cubic sites. The z -modes were not observed in these experiments, on account of the neutron scans employed. The dispersion is much smaller than that on the hexagonal sites and, in particular, it is negligible in the c -direction, indicating very weak coupling between planes of cubic ions normal to this axis. Again in contrast to the hexagonal ions, the splitting between modes of different polarization is not resolved, demonstrating that the anisotropy in the two-ion coupling is smaller.