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Coupling between the magnetic excitations and the phonons in praseodymium

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Abstract. The dispersion relation of the magnetic excitations of the hexagonal ions in DHCP Pr and the selection rules for the linear coupling to the phonons are determined by general symmetry considerations. The magnetic excitations propagating in the symmetry directions are considered in the cases of an external magnetic field applied along an a and a b direction. The magnetic excitations are approximated by pseudo-boson excitations of the spin subspace, $J = 4$, $M_J = 0$ and ± 1, and the presence of the ions on the cubic sites is neglected.

The selection rules deduced agree with the experimental observations of Houmann' *et al.* The experimental result for the strength of the exciton–phonon interaction is used in an estimate of the effects of an applied field on the elastic constants of Pr at zero temperature. The largest effect which is predicted is a reduction of the elastic constant c_{66} by approximately 15% of its zero-field value when a field of 40 kOe is applied in the basal plane.

1. Introduction

The knowledge and the understanding of the magnetic behaviour of singlet ground state systems, of which Pr is an important example, have increased substantially during the last few years, as reviewed by Rainford (1971), Cooper (1972), and Birgeneau (1973). The experimental studies of Pr (Rainford and Houmann 1971, Houmann *et al* 1975a) have revealed that Pr is a quite complicated singlet ground state system, and that the two-ion coupling between the ions on the hexagonal sites is just below the critical value for an induced moment system (Lebech *et al* 1975, Lindgård 1975). The crystal structure of Pr is double-hexagonal close packed (DHCP) with the stacking sequence ABAC. The local symmetry of the A sites is (approximately) cubic, whereas the ions on the B and C sites experience a crystal field of hexagonal symmetry. The magnetic coupling between the two types of ions seems to be relatively weak as only the hexagonal ions appear to order magnetically in the Pr–Nd single-crystal alloys studied by Lebech *et al* (1975).

The experimental studies of the magnetic excitations of the Pr ions by inelastic neutron scattering performed by Houmann *et al*, both at zero field (1975a) and in the presence of an external field (1976), have shown that the two-ion coupling is strongly anisotropic, and that the application of a field induces interactions between the excitons and the phonons. Because of the large value of the orbital momentum of the Pr ions ($L = 5$) a strong coupling between spin space and real space is very likely to occur, and the presence of large anisotropic couplings in Pr is consistent with the observation of similar couplings in other rare-earth metals (Jensen *et al* 1975).

In § 2 we shall consider the effects of general two-ion couplings on the dispersion of the excitons in the presence of an external field applied in the basal plane. This section then serves as the basis for a systematic treatment of the exciton–phonon interaction given in § 3. Here we shall consider only the ions on the hexagonal sites which are assumed to constitute an effective spin $S = 1$ system, and we utilize a pseudo-boson description of the excitons (Grover 1965). Both approximations limit the validity of the results to zero temperature (see e.g. Buyers *et al* 1975). Finally, we consider in § 4 the static magneto-elastic effects which can be predicted from the observed behaviour of the exciton–phonon interaction at finite wavevector in Pr.

2. The dispersion of the magnetic excitations of the hexagonal ions in Pr

The ions of DHCP Pr constitute two singlet ground state systems which are only weakly coupled. The ground state of the hexagonal ions is the singlet $|M_J = 0\rangle$ state with the doublet $|M_J = \pm 1\rangle$ as the first excited state (Rainford 1971), the crystal-field splitting, Δ_h, being equal to approximately 3·2 meV (Houmann *et al* 1975a). If the tetragonal distortion of the point symmetry of the 'cubic' ions is considered to be unimportant the ground state of these ions is the Γ_1 singlet with the Γ_4 triplet as the lowest lying (dipolar) excited state at an energy of $\Delta_c \cong 8$ meV.

Although the coupling between the two systems may not be entirely negligible, the effects of the cubic ions on the magnetic excitations of the hexagonal ions can be included in an effective spin Hamiltonian. This is in part because $\Delta_c \gg \Delta_h$, which makes a second-order perturbative decoupling of the excitations of the two systems a fair approximation, as shown in the Appendix. Further, all the symmetry operations of the hexagonal ions (HCP structure) leave the system of the cubic ions invariant.

Henceforth we neglect the presence of the ions on the cubic sites, and the general spin Hamiltonian is expanded in products of Racah operators (Buckmaster *et al* 1972, Lindgård and Danielsen 1974):

$$\tilde{O}_{l,m}(J_i)\tilde{O}_{l',m'}(J_j)$$

where J_i is the total moment of the ith ion. Because of time reversal symmetry only terms for which $l + l'$ is even may appear. The spin Hamiltonian is reduced if the crystal-field levels for which $|M_J| > 1$ are neglected, so that

$$\sum_{M=-1,0,1} |M\rangle\langle M| = 1; \qquad |M\rangle = |J = 4, M_J = M\rangle$$

which corresponds to an effective spin $S = 1$ system. Owing to this approximation we have

$$\tilde{O}_{l,m} = \sum_{p=-1}^{1} \sum_{q=-1}^{1} \langle p|\tilde{O}_{l,m}|q\rangle |p\rangle\langle q|. \tag{1}$$

In accordance with the correspondance to an $S = 1$ system an arbitrary Racah operator, $\tilde{O}_{l,m}$ (formally l ranges from 1–8 when $J = 4$), either vanishes identically (when $|m| > 2$ and l is even or when $|m| > 1$ and l is odd) or is equal to a constant times $\tilde{O}_{2,m}$ or $\tilde{O}_{1,m}$ according to whether l is even or odd. When projected on the subspace defined by (1) the general spin Hamiltonian is fully described in terms of the nine linear independent

operators $\tilde{O}_{l,m}$, $l = 0, 1, 2$ ($\tilde{O}_{0,0}$ is the identity operator):

$$\mathscr{H} = \sum_i \sum_{m=-2}^{2} V_m \tilde{O}_{2,m}(J_i) + \tfrac{1}{2} \sum_{i \neq j} \sum_{l=1}^{2} \sum_{m=0}^{l} \sum_{m'=-l}^{l} [K^l_{mm'}(i,j)\tilde{O}_{l,m}(J_i)\tilde{O}_{l,m'}(J_j) + (-1)^{m+m'} K^l_{mm'}(i,j)^* \tilde{O}_{l,-m}(J_i)\tilde{O}_{l,-m'}(J_j)]. \tag{2}$$

The effective parameter $K^l_{mm'}(i,j)$ includes the possible contributions of couplings $\tilde{O}_{l',m}(J_i)\tilde{O}_{l'',m'}(J_j)$, l' or $l'' \geqslant 3$, for which l' and l'' have the same parity as l. In (2) we shall refer to a coordinate system with the x, y, and z axis along the a, b and c direction

The calculations are facilitated by the following transformation of the wavefunctions:

$$\begin{aligned} |0) &= |0\rangle \\ |1) &= \frac{1}{\sqrt{2}}(|+1\rangle + |-1\rangle) \\ |2) &= \frac{-\mathrm{i}}{\sqrt{2}}(|+1\rangle - |-1\rangle). \end{aligned} \tag{3}$$

Using the symmetry properties of the matrix elements of the Racah operators it is easily shown that

$$(p|\tilde{O}_{l,m}|q) = (-1)^{l+m}(q|\tilde{O}_{l,m}|p). \tag{4}$$

Defining the 3×3 matrix $\tilde{\tilde{O}}_{l,m}$ as the one for which the element of the $(p+1)$th row and the $(q+1)$th column is $(p|\tilde{O}_{l,m}|q)$ we have as examples

$$\tilde{\tilde{O}}_{1,0} = \begin{Bmatrix} 0 & 0 & 0 \\ 0 & 0 & -\mathrm{i} \\ 0 & \mathrm{i} & 0 \end{Bmatrix} \quad \tilde{\tilde{O}}_{1,\pm 1} = \begin{Bmatrix} 0 & \mp\tfrac{1}{2}\alpha & -\mathrm{i}\tfrac{1}{2}\alpha \\ \mp\tfrac{1}{2}\alpha & 0 & 0 \\ -\mathrm{i}\tfrac{1}{2}\alpha & 0 & 0 \end{Bmatrix} \tag{5}$$

where we define

$$\alpha = [J(J+1)]^{1/2} = \sqrt{20}.$$

The Fourier transforms of the coupling parameters in (2) are defined as

$$\begin{aligned} K^l_{mm'}(\boldsymbol{q}) &= \sum_{j \text{ same sublattice as } i} K^l_{mm'}(i,j) \exp[\mathrm{i}\boldsymbol{q}.(\boldsymbol{R}_i - \boldsymbol{R}_j)] \\ \tilde{K}^l_{mm'}(\boldsymbol{q}) &= \sum_{j \text{ other sublattice from } i} K^l_{mm'}(i,j) \exp[\mathrm{i}\boldsymbol{q}.(\boldsymbol{R}_i - \boldsymbol{R}_j)] \end{aligned} \tag{6}$$

as usual in the case of an HCP structure (two ions per unit cell). At zero temperature all the ions are in their ground state which in the molecular-field approximation is given by the wavefunction $|0)$. The application of an external field along the x direction as described by the Zeeman Hamiltonian

$$\mathscr{H}_Z = -\boldsymbol{h}.\sum_i (\boldsymbol{J}_x)_i; \qquad \boldsymbol{h} = g\mu_B \boldsymbol{H} \tag{7}$$

admixes the two wavefunctions $|0)$ and $|1)$:

$$\begin{aligned} |0') &= \cos\theta|0) + \sin\theta|1) \\ |1') &= \cos\theta|1) - \sin\theta|0) \\ |2') &= |2) \end{aligned} \tag{8}$$

where $|0'\rangle$ is the modified wavefunction of the ground state. In the molecular-field approximation the amount of admixture, θ, is determined by (at zero temperature):

$$\{\Delta + \tfrac{9}{2}\sin^2\theta[K^2_{00}(0) + \tilde{K}^2_{00}(0)] + 2\beta^2\sin^2\theta[K^2_{2-2}(0) + \tilde{K}^2_{2-2}(0)]\}\tan 2\theta$$
$$= \sqrt{2}\alpha h + \alpha^2\sin 2\theta[K^1_{1-1}(0) + \tilde{K}^1_{1-1}(0)] \tag{9a}$$

where $\beta = \alpha^2\sqrt{6}/8 = 5\sqrt{6}/2$ and $\Delta = \Delta_h$ is the crystal-field splitting determined by (2) as

$$\Delta = \tfrac{3}{2}V_0 - \tfrac{9}{2}\alpha^2[K^2_{00}(0) + \tilde{K}^2_{00}(0)]. \tag{9b}$$

Defining the exchange constant

$$\lambda(0) = \frac{\alpha^2}{\Delta}[K^1_{1-1}(0) + \tilde{K}^1_{1-1}(0)] \tag{10}$$

then the condition for a ferromagnetic ordering of the induced moments

$$\langle 0'|J_x|0'\rangle = \frac{\alpha}{\sqrt{2}}\sin 2\theta \tag{11}$$

is at zero field $\lambda(0) \geqslant 1$. If terms in (9) proportional to $\sin^2\theta$ are neglected we recognize the usual molecular-field result

$$\tan 2\theta = \sqrt{2}\alpha h/\Delta + \lambda(0)\sin 2\theta.$$

In the following treatment of the excitations of the ground state determined by the equations (8) and (9) we shall utilize the pseudo-boson technique of Grover (1965) and define the excitation operators

$$a_i = |0'\rangle_i\langle 1'|_i; \qquad b_i = |0'\rangle_i\langle 2'|_i \tag{12}$$

of the ith ion, and we shall adopt the convention

$$|1'\rangle_i\langle 1'|_i = a_i^\dagger a_i \text{ etc,}$$

which by the use of the closure assumption leads to

$$|0'\rangle_i\langle 0'|_i = 1 - a_i^\dagger a_i - b_i^\dagger b_i.$$

In the derivation of the exciton spectrum we assume a_i and b_i to be orthogonal boson operators and we neglect terms in (2) which are not independent of or quadratic in the boson operators. Both approximations imply that the results derived are valid only in the limit of zero temperature.

We shall consider only the excitations propagating along the highly symmetric x, y and z directions, in which cases a number of the Fourier transformed coupling parameters, (6), vanish identically. For instance, only terms for which $m + m'$ are even may contribute to the excitations propagating in the basal plane, and the three-fold axis implies that the excitons propagating along the c direction only depend on terms in (2) for which $m + m' = 0$ or 3. We shall not give many more details but only sketch the procedure used in the derivation of the dispersion relations. The spin Hamiltonian is reduced effectively by the symmetry operations of the space group. The presence of two ions per unit cell is accounted for by defining two equivalent sets of excitation operators, (12), each associated with one of the two sublattices. The expansion of the Racah operators, (1), in terms of the (transformed) excitation operators is introduced in (2) and the equations of motion are derived using the boson commutation relations. The dynamics of the system are characterized by four different kinds of excitation

operators implying that the dispersion relation in general consists of four different branches $E_{\nu,\kappa}(\boldsymbol{q})$, $\nu = 1, 2$ and $\kappa = 1, 2$. The excitation energies are expressed as

$$E_{\nu,\kappa}(\boldsymbol{q}) = \{[A_{\nu,\kappa}(\boldsymbol{q}) + B_{\nu,\kappa}(\boldsymbol{q})][A_{\nu,\kappa}(\boldsymbol{q}) - B_{\nu,\kappa}(\boldsymbol{q})]\}^{1/2} \tag{13}$$

where $A_{\nu,\kappa}(\boldsymbol{q}) \pm B_{\nu,\kappa}(\boldsymbol{q})$ are defined in terms of a new set of parameters

$$A_{\nu,\kappa}(\boldsymbol{q}) \pm B_{\nu,\kappa}(\boldsymbol{q}) = \Delta_\nu - \mathscr{K}_\nu^{\pm}(\boldsymbol{q})(\pm)(-1)^\kappa |\tilde{\mathscr{K}}_\nu^{\pm}(\boldsymbol{q})|. \tag{14}$$

The index κ defines the mode $E_{\nu,\kappa}(\boldsymbol{q})$ to be either acoustic or optical according to whether κ is equal to 1 or 2. The other index ν defines the mode to be an x mode ($\nu = 1$) or a y mode ($\nu = 2$). In the presence of an external field we shall refer to these modes as the longitudinal or the transverse mode (x and y mode respectively when the field is along the x direction). For the excitons propagating along the y direction (ΓM) we derive

$$\Delta_1 = \Delta_{\|} = \{\Delta + \tfrac{9}{2}\sin^2\theta[K_{00}^2(0) + \tilde{K}_{00}^2(0)] + 2\beta^2 \sin^2\theta[K_{2-2}^2(0) + \tilde{K}_{2-2}^2(0)]\}/\cos 2\theta \tag{15a}$$

and

$$\Delta_2 = \Delta_\perp = \cos^2\theta\Delta_1 - 4\beta^2 \sin^2\theta[K_{2-2}^2(0) + \tilde{K}_{2-2}^2(0)]. \tag{15b}$$

An explicit field dependence of the crystal-field splittings, is removed by the use of the equilibrium condition (9). The $\boldsymbol{q}$-dependent energy parameters of the longitudinal mode are

$$\mathscr{K}_1^-(\boldsymbol{q}) = \tfrac{3}{4}\alpha^2[K_{1-1}^2(\boldsymbol{q}) + K_{11}^2(\boldsymbol{q})] \tag{16a}$$

and

$$\mathscr{K}_1^+(\boldsymbol{q}) = \alpha^2 \cos^2 2\theta[K_{1-1}^1(\boldsymbol{q}) - K_{11}^1(\boldsymbol{q})] - \sin^2 2\theta\{\tfrac{9}{4}K_{00}^2(\boldsymbol{q}) + \tfrac{9}{2}\beta K_{20}^2(\boldsymbol{q}) + \beta^2[K_{2-2}^2(\boldsymbol{q}) + K_{22}^2(\boldsymbol{q})]\} \tag{16b}$$

where we use $K_{20}^2(\boldsymbol{q}) = K_{02}^2(\boldsymbol{q}) = K_{0-2}^2(\boldsymbol{q})$. The dispersion of the transverse mode is determined by

$$\mathscr{K}_2^-(\boldsymbol{q}) = \tfrac{3}{4}\alpha^2 \cos^2\theta[K_{1-1}^2(\boldsymbol{q}) - K_{11}^2(\boldsymbol{q})] - 4\sin^2\theta\, K_{00}^1(\boldsymbol{q}) \tag{17a}$$

and

$$\mathscr{K}_2^+(\boldsymbol{q}) = \alpha^2 \cos^2\theta[K_{1-1}^1(\boldsymbol{q}) + K_{11}^1(\boldsymbol{q})] - 4\beta^2 \sin^2\theta[K_{2-2}^2(\boldsymbol{q}) - K_{22}^2(\boldsymbol{q})]. \tag{17b}$$

The expression for $\tilde{\mathscr{K}}^{\pm}(q)$ is obtained from $\mathscr{K}^{\pm}(\boldsymbol{q})$ by replacing $K_{mm'}^l(\boldsymbol{q})$ in (16) and (17) by $\tilde{K}_{mm'}^l(\boldsymbol{q})$. The dispersion relations deduced above are only strictly valid for the excitons propagating along the *y direction* (the ambiguity of the sign in front of $(-1)^\kappa$ in equation (14) is removed by a consideration of the modes in the long-wavelength limit). Subject to slight modifications we can use the same expressions for the dispersion of modes propagating in the two other symmetry directions. In the case of the excitons propagating along the *x direction* (ΓK) the right-hand side of (14) is to be replaced by

$$\Delta_\nu - \mathrm{Re}\{\mathscr{K}_\nu^{\pm}(\boldsymbol{q}) - (-1)^\kappa \tilde{\mathscr{K}}_\nu^{\pm}(\boldsymbol{q})\}.$$

The imaginary part, $\mathrm{Im}\{\mathscr{K}_\nu^{\pm}(\boldsymbol{q}) - (-1)^\kappa \tilde{\mathscr{K}}_\nu^{\pm}(\boldsymbol{q})\}$, gives rise to an interaction between the acoustic x mode, $E_{1,1}(\boldsymbol{q})$, and the optical y mode, $E_{2,2}(\boldsymbol{q})$, and the equivalent coupling of $E_{1,2}(\boldsymbol{q})$ and $E_{2,1}(\boldsymbol{q})$, which will prevent the dispersion relations of the coupled modes

from crossing each other. $\mathrm{Im}\{\mathscr{K}_{\nu}^{\pm}(\boldsymbol{q})\}$, which is zero when $\boldsymbol{q}$ is parallel to the y axis, may be nonzero when $\boldsymbol{q}$ is along the x direction only in the presence of antisymmetric two-ion couplings (within a sublattice). When $\boldsymbol{q}$ is parallel to the *z direction* (ΓA) (and at zero wavevector) the dispersion relations are simplified by the vanishing of the coupling parameters $K^{l}_{mm'}(\boldsymbol{q})$ in (16) and (17) for which $m + m' \neq 0$. In equation (14) $(\pm)(-1)^{\kappa}|\tilde{\mathscr{K}}^{\pm}(\boldsymbol{q})|$ is replaced by $+(-1)^{\kappa}\tilde{\mathscr{K}}^{\pm}(\boldsymbol{q})$ implying the usefulness of the double-zone representation. In the presence of the external field this representation is not exact as $K^{2}_{21}(\boldsymbol{q}) = -K^{2}_{21}(-\boldsymbol{q})$ introduces an acoustic–optical coupling between $E_{\nu,1}(\boldsymbol{q})$ and $E_{\nu,2}(\boldsymbol{q})$ proportional to $\sin 2\theta$. However, in spite of this coupling, the modes remain doubly degenerate at the Brillouin zone boundary (A). At zero field the x and y modes are degenerate and the double-zone representation is valid.

The dispersion relations derived above are entirely general in so far as the excitations can be approximated by boson excitations of an effective spin $S = 1$ system. The dispersion relations derived previously (Lindgård and Houmann 1971, Rainford 1971) do not include the effects of the terms $K^{l}_{mm'}(\boldsymbol{q})$ for which $l = 2$. Here we find that $K^{2}_{1\pm1}(\boldsymbol{q})$ causes a $\boldsymbol{q}$ dependence of $A_{\nu,\kappa}(\boldsymbol{q}) - B_{\nu,\kappa}(\boldsymbol{q})$ (without contributing to the molecular-field equilibrium condition (9)), and that the application of an external field introduces contributions from two-ion couplings which do not affect the dispersion at zero field. The simple random-phase result for the temperature dependence of the exciton energies (Houmann *et al* 1975a) is easily generalized to include the quadrupole contributions $K^{2}_{1\pm1}(\boldsymbol{q})$. Both these terms and $K^{1}_{1\pm1}(\boldsymbol{q})$ are multiplied by the temperature renormalization factor $R(T)$ defined by Houmann *et al* (1975a).

If the external field is applied along the y direction then the mixing of the wavefunctions $|0)$ and $|2)$, as given by (8) when interchanging 1 and 2, is determined by the same equilibrium equation, (9), as before. The dispersion relations in this case of the x-transverse mode ($\nu = 1$) and the y-longitudinal mode ($\nu = 2$) are given by the expressions above using the following prescription: the index ν of the right hand side of equation (14) is replaced by ν' where $\nu' = 1$ when $\nu = 2$ and vice versa. $K^{l}_{mm'}(\boldsymbol{q})$ in the equations (16) and (17) are replaced by $(-1)^{(m+m')/2}K^{l}_{mm'}(\boldsymbol{q})$. The acoustic–optical coupling of the excitons propagating in the c direction is now between the modes $E_{1,1}(\boldsymbol{q})$ and $E_{2,2}(\boldsymbol{q})$ and between $E_{2,1}(\boldsymbol{q})$ and $E_{1,2}(\boldsymbol{q})$.

The response of the system when applying the field along the c direction is very small. In this case the field mixes the wavefunctions $|1)$ and $|2)$ implying that the x and y modes can no longer be eigen-excitations of the system.

3. Exciton–phonon interaction

The apparent importance of two-ion magnetic anisotropy in Pr suggests the presence of a strong coupling between the excitations of the spin system and of the lattice, as has been observed in the magnetic heavy rare-earth metals (with the exception of Gd). Although the heavy rare-earths are characterized as being spin-wave systems at low temperatures, these systems (especially the basal-plane ferromagnets Tb and Dy) have many features in common with the one formed by the hexagonal ions in Pr. We shall therefore employ an almost identical method in the following account of the exciton–phonon interaction in Pr as that used in the treatment of the magnon–phonon interaction in Tb (Jensen 1971, Jensen and Houmann 1975).

Both the crystal-field and the two-ion coupling parameters in (2) depend on the relative positions of the ions, $\boldsymbol{R}_i - \boldsymbol{R}_j$, and to first order in the Cartesian components

of the displacement, $\delta R_\alpha(ij)$, the coupling between the spin system and the lattice is expressed by

$$\mathscr{H}_{s-l} = \sum_{i \neq j} \sum_{\alpha} \sum_{l,l'=0}^{2} \sum_{m,m'} \delta R_\alpha(ij) D^{l'm'}_{lm,\alpha}(ij) \tilde{O}_{l,m}(J_i) \tilde{O}_{l',m'}(J_j) + \text{hermitian conjugate} \qquad (18)$$

where $D^{l'm'}_{lm,\alpha}(ij)$ are phenomenological coupling parameters. As in (2) $l + l'$ is even owing to time reversal symmetry, and single-ion terms are included as those for which either l or l' is zero. The Cartesian 1, 2 and 3 axes are chosen to be along the x, y and z direction respectively. In (18) we have utilized the $S = 1$ basis, (1), by considering only terms for which l and l' are both smaller than 3.

In the treatment of the magnetic excitations of the hexagonal ions in Pr we could, in principle, neglect the presence of the ions on the cubic sites. In a determination of the selection rules for the coupling between these excitations and the phonons we may still make use of this assumption. This simplification is possible because the cubic sites are the centres of inversion symmetry of the total crystal. The selection rules of the coupling to one of the 2×3-phonon branches of the HCP lattice are the same as those to the two equivalent ones (with respect to the displacement vectors of the hexagonal ions) of the $2 \times 2 \times 3$-phonon branches of the real crystal. We shall add that when $\boldsymbol{q}$ is along the x or y directions one of the optical phonon modes is not coupled to the hexagonal lattice or to the hexagonal excitons.

The procedure used in the derivation of the selection rules for the exciton–phonon interaction in Pr is the same as used by Jensen and Houmann (1975) in the case of Tb. The number of non-vanishing coupling parameters in the spin-lattice Hamiltonian, (18), is reduced by symmetry operations (corresponding to those of the HCP lattice). The spin part is expanded in the excitation operators introduced in the preceding section. Only the direct coupling of the excitons and the phonons is of interest in the present context, and all terms in (18) which are not linear in the exciton operators are neglected. The components of the displacement vector are expanded in terms of normal phonon coordinates. The selection rules deduced in this way are given in table 1. The excitations propagating in the highly symmetric x, y and z directions are considered in both the cases of a field applied along the x and the y direction. Because of the approximate description of the magnetic excitations, the selection rules are valid only in the limit of zero temperature. We remark that the selection rules for the coupling between the transverse excitons (y modes in case the field is applied along the x axis) and the phonons are the same as those deduced for the magnon–phonon interaction in a basal plane ferromagnet (Cracknell 1974, Jensen and Houmann 1975).

At zero field only the transverse phonons which have their wavevector or their polarization vector parallel with the c axis are allowed to couple to the excitons. There were no indications of these couplings in the neutron scattering experiments by Houmann *et al* (1975a). By the application of a field in the basal plane it is possible to induce other kinds of exciton–phonon interactions. Such couplings, which are marked by H_x or H_y in the table, should appear as energy gaps at the crossing points of the unperturbed exciton and phonon dispersion relations, and these energy gaps should be proportional to $\sin\theta$ (plus possible corrections of the order of $\sin^3\theta$). This kind of field induced exciton–phonon coupling was observed by Houmann *et al* (1976) in their studies of the field dependence of the exciton spectrum in Pr. Some of their experimental results are shown in figure 1 (here the wavevector is parallel to the y axis and the field is applied

along the x direction). In this configuration the experiments revealed a strong, field dependent interaction between the EA_y exciton mode and the TA_x phonon mode (the labelling of the modes is the one introduced in the caption to table 1). A coupling between the EO_y and the TA_x modes is also evident, whereas the possible coupling of the EA_x and the LA modes is only weakly indicated. Although the polarization vector of the transverse phonon mode which couples to the excitons was not determined in the neutron experiment the energy difference between the TA_x and TA_z modes (10% as determined by Greiner *et al* (1973) in the long-wavelength limit) is sufficiently large to allow the specification above of the phonon mode. Houmann *et al* also observed that the EA_x–TA_y

Table 1. The selection rules for the linear coupling between the magnetic excitations and the phonons propagating on the hexagonal ions of Pr. The results are given for the modes propagating along the x, y and z directions (ΓK, ΓM and ΓA) corresponding to the tables 1(*a*), 1(*b*) and 1(*c*) respectively. The different modes are labelled in accordance with their characters at small wavevectors considering the crystal to be an HCP lattice. EA_x denotes the acoustic exciton polarized along the x axis, $E_{11}(\boldsymbol{q})$, etc. The subscript of TA (TO) defines the direction of the polarization vector of the acoustic (optical) transverse phonons (the eigenvectors of the modes propagating in the x (*a*) direction labelled LA and TO_y may be of a mixed character, and similar for LO and TA_y). 0 marks the interactions which may be present at zero field, whereas $H_x(H_y)$ designates a coupling proportional to the field applied along the x (y) direction ($H^2_{x,y}$ are couplings proportional to the field squared). In the DHCP crystal of Pr there are twice as many phonon branches as appearing in the table. One set of the nine optical branches and the acoustic phonons will behave in accordance with the acoustic phonons appearing in the table. The two other sets of the optical branches correspond to the optical phonons in the table.

(*a*)	EA_x	EA_y	EO_x	EO_y
LA	H_x	H_y	H_y	H_x
TA_y	H_y	H_x	H_x	H_y
TA_z		0	0	
LO	H_y	H_x	H_x	H_y
TO_y	H_x	H_y	H_y	H_x
TO_z	0			0

(*b*)	EA_x	EA_y	EO_x	EO_y
LA	H_x	H_y	H_x	H_y
TA_x	H_y	H_x	H_y	H_x
TA_z	0		0	
LO	H_x	H_y	H_x	H_y
TO_x	H_y	H_x	H_y	H_x
TO_z	0		0	

(*c*)	EA_x	EA_y	EO_x	EO_y
LA	H_x	H_y	$H^2_{x,y}$	
TA_x		0	H_y	H_x
TA_y	0		H_x	H_y
LO	$H^2_{x,y}$		H_x	H_y
TO_x	H_y	H_x		0
TO_y	H_x	H_y	0	

coupling of the modes propagating in the x direction in a field applied along the y direction is just as strong as the equivalent EA_y–TA_x interaction in figure 1. No coupling appeared between the magnetic and elastic excitations propagating in the c direction.

The amplitude of the exciton–phonon coupling at finite wavevector (reasonably close to Γ) may be utilized for a prediction of the magnitude of magnetoelastic effects (at zero wavevector). The magnetostriction coefficients are directly related to the linear parts of the $\boldsymbol{q}$ dependences of the couplings between the acoustic magnetic and elastic excitations in the long-wavelength limit. These relations are most easily obtained considering only the single-ion part of the magnetoelastic Hamiltonian which then includes the long-wavelength contributions of two-ion couplings in an effective fashion:

$$\mathcal{H}_{\text{me}} = -\tfrac{1}{2}\sum_i \{[B^{(1)}_{20}\epsilon^{\alpha,1} + B^{(2)}_{20}\epsilon^{\alpha,2}]2\tilde{O}_{2,0}(J_i) + B_{21}[\epsilon^{\epsilon}\tilde{O}_{2,-1}(J_i) - (\epsilon^{\epsilon})^*\tilde{O}_{2,1}(J_i)] + B_{22}[\epsilon^{\gamma}\tilde{O}_{2,-2}(J_i) + (\epsilon^{\gamma})^*\tilde{O}_{2,2}(J_i)]\}. \tag{19}$$

The Cartesian strains, ϵ_{ij}, are defined in the usual way in terms of the elastic displacements, $\boldsymbol{u}(\boldsymbol{x}, t)$:

$$\epsilon_{ij} = \tfrac{1}{2}[\partial u_i/\partial x_j + \partial u_j/\partial x_i] \tag{20a}$$

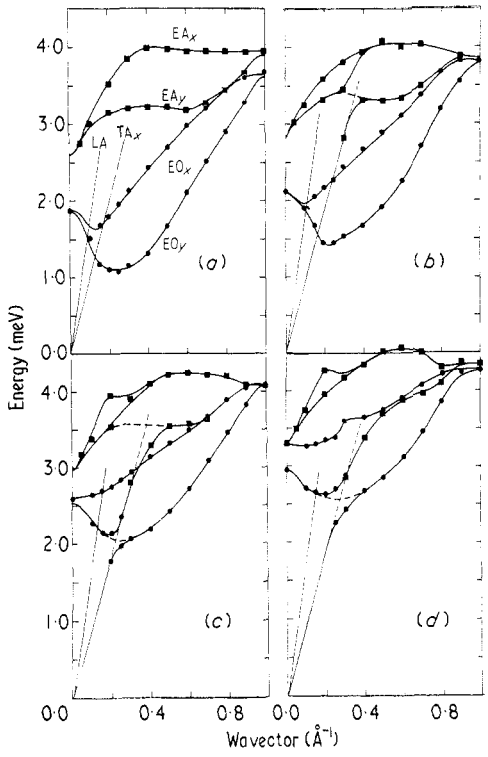

Figure 1. Experimental field dependence of the excitation energies and of the exciton–phonon interactions for excitons propagating in the ⟨100⟩ directions in Pr at 4·2 K. The field is applied along the ⟨110⟩ direction, (after Houmann *et al* 1976). The values of H_E are (*a*) 0 kOe, (*b*) 14·5 kOe, (*c*) 29·0 kOe, (*d*) 43·5 kOe.

and the strains appearing in (19) are

$$\epsilon^{\alpha,1} = \epsilon_{11} + \epsilon_{22} + \epsilon_{33}, \epsilon^{\alpha,2} = \epsilon_{33} - \tfrac{1}{3}\epsilon^{\alpha,1}, \epsilon^{\epsilon} = \epsilon_{13} + i\epsilon_{23}, \epsilon^{\gamma} = \tfrac{1}{2}(\epsilon_{11} - \epsilon_{22}) + i\epsilon_{12}. \tag{20b}$$

This general single-ion Hamiltonian, (19), adequately describes most features of the dynamic phenomena. The inhomogeneous parts of the strains are expanded in phonon operators using the local strain theory of Evenson and Liu (1969). The spin part is treated as above. In this way it is possible to predict all the exciton–phonon couplings appearing in table 1. The energy gap in figure 1 occurring at the crossing point of the dispersion relations of the EA_y and the TA_x modes (wavevector $\boldsymbol{q}$ and energy $E_{2,1}(\boldsymbol{q})$) is determined from (19) by

$$\Delta_{ep} = \{E_{2,1}(\boldsymbol{q})[E_{2,1}(\boldsymbol{q}) + 2V(\boldsymbol{q})]\}^{1/2} - \{E_{2,1}(\boldsymbol{q})[E_{2,1}(\boldsymbol{q}) - 2V(\boldsymbol{q})]\}^{1/2} \tag{21a}$$

$$\cong 2V(\boldsymbol{q})$$

where

$$V(\boldsymbol{q}) = \tfrac{1}{4}\beta|B_{22}|\frac{\hbar}{\sqrt{M}}\frac{f(q)}{[A_{2,1}(\boldsymbol{q}) + B_{2,1}(\boldsymbol{q})]^{1/2}}\sin\theta. \tag{21b}$$

M is the mass of the ions and $f(q)$ is a factor depending on the wavevector and on the differences in phase of the modes on the four sublattices. An estimate of these phase factors indicates that the expression for $f(q)$ in the long-wavelength limit

$$f(q) = f_a(q) = 2b^{-1} \sin(qb/2) \tag{22a}$$

(b is the lattice parameter) is still applicable at the wavevector of interest ($q \cong 0{\cdot}35$ Å^{-1}). The energy gap of the acoustic-optical interaction (EO_y–TA_x) is determined by (21) if $(\nu, \kappa) = (2, 1)$ is replaced by $(\nu, \kappa) = (2,2)$ and $f(q)$ by

$$f(q) = f_0(q) = b^{-1} \sin^2(qb/4) \tag{22b}$$

$f_a(q)$ is also given roughly by (22a) in the presence of two-ion couplings, because $f_a(q)$ is constrained to be equal to q in the long-wavelength limit if B_{22} is considered as an effective magnetostriction parameter (in which case two-ion couplings only introduce corrections to the order of $(qb)^3$), whereas $f_0(q)$ may deviate substantially from that determined by (22b). The combination of (22a) and (22b) predicts the energy gap, EO_y–TA_x, to be approximately ten times smaller than the acoustic energy gap, EA_y–TA_x, which is a factor of two smaller than the observed value (figure 1), indicating the importance of magnetoelastic two-ion couplings.

The exciton–phonon energy gaps in figure 1 are roughly proportional to the applied field as expected by the factor $\sin\theta$ in (21b) (two-ion γ-strain couplings may introduce deviations proportional to $\sin^3\theta$). In the estimate of an effective value of B_{22} we neglect quadrupole contributions ($K^2_{mm'}(\boldsymbol{q})$) to $E_{\nu,\kappa}(\boldsymbol{q})$ and assume $\sin\theta$ to be determined by equation (11) and the experimental value for the field dependence of the magnetic moments of the hexagonal ions, $\mu = g\mu_B\langle 0'|J_x|0'\rangle$, as measured by Lebech and Rainford (1971). Using $\Delta = \Delta_h = 3{\cdot}2$ meV we find that the energy gap, EA_y–TA_x, and the equivalent one observed in the x-direction (EA_x–TA_y) are reproduced by the single-ion Hamiltonian, (19), when

$$B_{22} = \pm 30 \text{ meV}.$$

We remark that the present choice of parameters does not fulfill the equilibrium condition, (9). Using this equation instead of the experimental value of the magnetic moment, we find that $\sin\theta$ is approximately $\frac{2}{3}$ of that used above (and consequently $|B_{22}| \approx 45$ meV). This inconsistency may partly be due to the presence of quadrupole couplings and of the crystal-field levels which are neglected, but these corrections do not seem to be sufficient (see the Appendix).

If the system is magnetoelastically isotropic ($\mathscr{H}_{me}$, (19), independent of a coordinate transformation) the coupling parameters are related as follows

$$B_{22} = B_{21} = \frac{2\sqrt{6}}{3} B^{(2)}_{20}; \qquad B^{(1)}_{20} = 0. \tag{23}$$

If (23) suggests the right order of magnitudes the γ-strain coupling, B_{22}, is the dominating one also for the interaction between the longitudinal phonons and the excitons, and the energy gap of the EA_x–LA coupling in figure 1 should be of the order of half the energy gap of the EA_x–TA_y interaction. Whether this is the case or not is not clearly resolved in the experimental results.

The absence of the ϵ coupling in the experimental exciton spectrum implies that the ϵ-strain parameter $|B_{21}|$ is at least a factor of three smaller than $|B_{22}|$, in contrast to the condition for magnetoelastic isotropy, (23). The unimportance of the ϵ coupling means that the two-ion anisotropy, which is observed in Pr at zero field (Houmann *et al* 1975a).

is not connected to the phonon field. The phonon-induced interactions appear as quadrupole couplings in the effective spin Hamiltonian. The only quadrupole interaction which may affect the dispersion of the excitons at zero field is $K^2_{1\pm1}(\boldsymbol{q})$, and the ϵ-strain interaction is the only phonon-induced coupling which may contribute to this term.

4. Magnetoelastic effects

In this section we shall discuss the implications of magnetoelastic coupling on the behaviour of the excitons and the phonons in the long wavelength limit in Pr. The single-ion magnetoelastic Hamiltonian, (19), is sufficiently general when considering the main effects, but we shall occasionally include phenomena which are of two-ion origin.

At equilibrium the derivatives of the free energy with respect to the strains must be zero, implying e.g.

$$\bar{\epsilon}^{\gamma} = B_{22}(0'|\tilde{O}_{2,2}|0')/2c_{\gamma}. \tag{24}$$

We shall be using the reduced, Cartesian elastic constants

$$c_{\gamma} = c_{66}/4N, c_{\epsilon} = c_{44}/4N, c_1 = c_{11}/N, c_3 = c_{33}/N \tag{25}$$

where N is the total number of ions per unit volume (twice the number of the hexagonal ions). In the paramagnetic region only $\tilde{O}_{2,0}$ has a nonzero expectation value at zero field, and consequently only the α strains may differ from zero. The α strains preserve the symmetry of the crystal, and the effect of these strains on the excitons may be described by introducing an effective crystal field splitting, $\Delta(9b)$, which then becomes field (and temperature) dependent. The ϵ strains also vanish identically in the case of a field applied in the basal plane, and we shall be concerned mostly with the γ strains which describe distortions of the hexagonal symmetry of the basal plane.

In the case of an effective spin $S = 1$ system only the γ strains may give rise to magnetic anisotropy in the basal-plane, and this only if the γ strain Hamiltonian includes the pure two-ion term:

$$\mathscr{H}^{\gamma}_{\mathrm{II}} = -\tfrac{1}{2}\sum_{i\neq j} B^{(2)}_{22}(ij)[\epsilon^{\gamma}\tilde{O}_{2,2}(J_i)\tilde{O}_{2,2}(J_j) + (\epsilon^{\gamma})^*\tilde{O}_{2,-2}(J_i)\tilde{O}_{2,-2}(J_j)]. \tag{26}$$

Defining the coupling parameter at zero wavevector

$$B_{44} = B^{(2)}_{22}(0) + \tilde{B}^{(2)}_{22}(0) \tag{27}$$

this parameter corresponds to the magnetostriction parameter $c_{\gamma}A$ considered in the case of Tb (Houmann *et al* 1975*b*). When the field is applied along the x direction the γ strains are determined by (19) and (26) as

$$\bar{\epsilon}^{\gamma}_{x} = \tfrac{1}{2}(\bar{\epsilon}_{11} - \bar{\epsilon}_{22})_x = \frac{1}{2c_{\gamma}}(B_{22} + \beta B_{44}\sin^2\theta)\beta\sin^2\theta \tag{28a}$$

and if the field is applied along the y direction

$$\bar{\epsilon}^{\gamma}_{y} = \tfrac{1}{2}(\bar{\epsilon}_{11} - \bar{\epsilon}_{22})_y = -\frac{1}{2c_{\gamma}}(B_{22} - \beta B_{44}\sin^2\theta)\beta\sin^2\theta. \tag{28b}$$

The B_{44} term introduces an anisotropy in the basal plane, but, besides being of pure two-ion origin, the effect is of higher order in $\sin\theta$.

As in the case of Tb (Houmann *et al* 1975b) the presence of a homogeneous γ strain

modifies the energies of the magnetic excitations. If we neglect two-ion contributions to the γ strain these modifications appear only in Δ_1 and Δ_2, (15), as

$$\delta_{me}(\Delta_1) = -\frac{2c_\gamma(\bar{\epsilon}^\gamma)^2}{\sin^2\theta\cos 2\theta}; \qquad \delta_{me}(\Delta_2) = -(1 - 3\sin^2\theta)\delta_{me}(\Delta_1). \tag{29}$$

In the general case of $\boldsymbol{q}$-dependent γ-strain couplings, the contribution to $A_{\nu,1}(0) + B_{\nu,1}(0)$ is correctly given by (29) to first order in $\sin^2\theta$, but the coupling: $\bar{\epsilon}^\gamma\tilde{O}_{1,-1}(J_i) \times \tilde{O}_{1,-1}(J_j)$ introduces a different γ-strain term in $A_{\nu,1}(0) - B_{\nu,1}(0)$ to first order in $\sin^2\theta$.

The contributions to the exciton energies of the dynamic exciton–phonon coupling vanish in the long-wavelength limit, corresponding to the 'frozen lattice' model of Tb (Houmann *et al* 1975b). The two-exciton–one-phonon interactions may cause a zero point correction to this result equivalent to a perturbative modification of the dispersion relations, (13)–(17), due to higher-order exciton–exciton interactions. The two-exciton–one-phonon interactions are of greater importance at elevated temperatures and may perturb appreciably the temperature dependence of the elastic constants (Jensen 1971). The direct one-exciton–one-phonon interaction is of most interest at zero temperature, and it gives rise to a change of the velocity of the sound waves which we shall express as modifications of the corresponding elastic constants. We consider the case of a field applied along the x direction and magnetoelastic two-ion contributions are neglected except in the case of c_{66}. The notation is simplified using $A_\nu \pm B_\nu$ instead of $A_{\nu,1}(0) \pm B_{\nu,1}(0)$.

The velocities of the longitudinal sound waves in the three symmetry (1, 2, and 3) directions are changed according to

$$\begin{aligned}
\Delta c_{11}/c_{11} &= (c'_{11} - c_{11})/c_{11} = -(16c_1)^{-1}(3B_{20}^{(1)} - B_{20}^{(2)} + \beta B_{22})^2\sin^2 2\theta/(A_1 + B_1)\\
\Delta c_{22}/c_{11} &= -(16c_1)^{-1}(3B_{20}^{(1)} - B_{20}^{(2)} - \beta B_{22})^2\sin^2 2\theta/(A_1 + B_1)\\
\Delta c_{33}/c_{33} &= -(16c_3)^{-1}(3B_{20}^{(1)} + 2B_{20}^{(2)})^2\sin^2 2\theta/(A_1 + B_1).
\end{aligned} \tag{30}$$

The transverse sound waves propagating or polarized along the c direction are described by

$$\begin{aligned}
\Delta c_{44}/c_{44} &= -\frac{3\alpha^2}{16c_\epsilon}B_{21}^2\cos^2\theta/(A_2 - B_2)\\
\Delta c_{55}/c_{44} &= -\frac{3\alpha^2}{16c_\epsilon}B_{21}^2/(A_1 - B_1)
\end{aligned} \tag{31}$$

according to whether the propagation or polarization vector in the basal plane is along the x or the y direction. The transverse sound waves propagating along the x or the y direction which have their polarization vector in the basal plane are represented by

$$\Delta c_{66}/c_{66} = -\frac{\beta^2}{c_\gamma}B_{22}^2\sin^2\theta/(A_2 + B_2). \tag{32a}$$

If we generalize the equation (28) for the γ strain so as to include all possible couplings, by allowing B_{22} to depend on $\sin^2\theta$, then we deduce the following general relation

$$\Delta c_{66}/c_{66} = -\frac{\beta^2}{c_\gamma}(B_{22} - 2\beta B_{44}\sin^2\theta)^2\sin^2\theta/(A_2 + B_2), \tag{32b}$$

when the field is applied along the x axis, and in the case of a field applied in the y direction

$$\Delta c_{66}/c_{66} = -\frac{\beta^2}{c_\gamma}(B_{22} + 2\beta B_{44}\sin^2\theta)^2 \sin^2\theta/(A_1 + B_1). \tag{32c}$$

The numerators of the two expressions are simply related to $\bar{\epsilon}^\gamma$ in (28). Notice that $A_2 + B_2$ in (32*b*) and $A_1 + B_1$ in (32*c*) are equal except for the anisotropy term proportional to $B_{22}B_{44}\sin^4\theta$. The equations (30) and (31) are easily generalized to the case of a field applied along the y-direction ($A_1 \pm B_1$ and $A_2 \pm B_2$ are interchanged, βB_{22} is replaced by $-\beta B_{22}$, and Δc_{44} and Δc_{55} are interchanged).

The case of a ferromagnetic ordering in the basal plane is of greatest interest and we shall discuss it briefly. As mentioned in § 2 the quadrupole interactions do not alter the condition that $\lambda(0)$, (10), has to exceed 1 to produce a ferromagnetic ordering of the magnetic moments, which also holds true when the γ-strain couplings are introduced (but the quadrupole interactions themselves may be strong enough to induce an ordering of the quadrupole moments corresponding to $\sin\theta = 1$). The α strains are only of interest as far as they contribute to the effective Δ. At the critical value of $\lambda(0)$ $(= 1)$ $A_{\nu,1}(0) + B_{\nu,1}(0)$ are both zero ($\nu = 1$ or 2) and hence the energies of the two uniform exciton modes vanish. The velocity of the transverse sound waves which have their polarization and propagation vectors both lying in the basal plane will also be zero ($\Delta c_{66}/c_{66} = -1$), whereas the velocities of the longitudinal sound waves will stay finite. If $\lambda(0)$ is greater than 1 the exciton energies and the velocity of the transverse sound waves are all finite. The energy of the uniform transverse exciton mode is only non-zero because of the magnetoelastic γ-strain contribution, (29). If only one of the two γ-strain parameters B_{22} (effective) and B_{44} are different from zero it is not possible to define a magnetically easy or hard planar axis, and the velocity of the transverse sound waves will again be zero. If this is not the case then the application of a field along the hard planar axis, of a magnitude corresponding to the anisotropy field, will produce the Goldstone mode in the phonon spectrum. These features of the γ-strain coupling are entirely equivalent to those of the basal-plane ferromagnet Tb (Houmann *et al* 1975b).

The elastic constants of Pr have been measured as functions of temperature by Greiner *et al* (1973). Using their value for c_{66} and B_{22} estimated in § 3 we find

$$\tfrac{1}{2}(\bar{\epsilon}_{11} - \bar{\epsilon}_{22}) = \pm 8{\cdot}13 \times 10^{-3}\sin^2\theta.$$

If $B_{20}^{(1)}$ and $B_{20}^{(2)}$ are of the same order of magnitude as B_{22} (as suggested by the condition of magnetoelastic isotropy, (23)) then the γ-strain contribution to $\bar{\epsilon}_{11}$ is a factor of 10 larger than the α-strain contributions. $\bar{\epsilon}_{11}(H) - \bar{\epsilon}_{11}(0)$ has been measured by Ott (1976) at a field of 10 kOe applied along the x axis and found to be equal to $1{\cdot}6 \times 10^{-4}$. Using $\frac{1}{2}(\bar{\epsilon}_{11} - \bar{\epsilon}_{22}) \gg \frac{1}{2}|\bar{\epsilon}_{11} + \bar{\epsilon}_{22}|$ and $B_{22} = +30$ meV we get $\bar{\epsilon}_{11} = 1{\cdot}44 \times 10^{-4}$ in fair agreement with the experimental result.

The relative changes of the elastic constants as functions of field (at zero temperature) are estimated to be negligible ($\Delta c_{11}/c_{11} = -0{\cdot}01$ at a field of 40 kOe) with the exception of $\Delta c_{66}/c_{66}$. c_{66} is found to be reduced by approximately 15% of its zero field value when a field of 40 kOe is applied in the basal plane. This reduction should reach a maximum of about 19% at a field of the order of 60–80 kOe. In this estimate we have used the same assumptions as in the calculation of B_{22} ($= 30$ meV) in § 3.

The γ-strain contributions to the longitudinal and transverse exciton energies, (29), are found to be equal -5% and $2{\cdot}5\%$ respectively at a field of 40 kOe. The application of an external stress may induce a magnetic ordering of the spin system (at zero field). The largest effect is attained by a uniaxial pressure along a planar axis, and assuming B_{22}(eff) to be roughly independent of $\boldsymbol{q}$ we find that a uniaxial pressure of 0·9 kbar

applied along an a direction should be sufficient to induce an antiferromagnetic ordering of the b-axis components of the magnetic moments in Pr.

The presence of the cubic ions and the crystal field levels which are neglected may influence considerably the field dependence of the strains and the elastic constants. The field induced mixing of the crystal-field levels Γ_1 and Γ_4 of the cubic ions may enhance the γ strain, $\bar{\epsilon}^{\gamma}$, by about 25% (assuming B_{22}(cubic) $\approx B_{22}$(hexagonal)), which is the only correction to lowest order in the field. An order of magnitude estimate of the effects of the crystal field levels which are neglected, shows that the field dependence of c_{66} may deviate by 10–20% from the result deduced above.

5. Summary

The dispersion of the magnetic excitations of the hexagonal ions in Pr was deduced from a general spin Hamiltonian. In the calculations were used the simple pseudo-boson technique and the hexagonal ions were assumed to constitute an effective spin $S = 1$ system. Within this framework the selection rules for the linear coupling between the magnetic excitations and the phonons were determined. The excitation spectrum was considered in both the cases of an applied field along an a and a b direction.

The field induced exciton-phonon interactions in Pr observed by Houmann *et al* (1976) behave in accordance with the present account. The acoustic–optical magnon–phonon interaction in the c-direction of Tb (Jensen and Houmann 1975), which violates the selection rules for a simple basal-plane ferromagnet, does not seem to have its counterpart in Pr. The abnormal magnon–phonon interaction in Tb is explained by a small deviation of the spin polarization of the conduction electrons from the direction of the localized moments (due to the spin–orbit coupling). This complication of the ground state (in the presence of an external field) does not appear to be of any importance in Pr.

The amplitude of the exciton–phonon coupling observed by Houmann *et al* was extrapolated to zero wavevector, and the value of the γ-strain parameter, B_{22}, obtained in this way was utilized in a prediction of the effects of magnetoelastic couplings in Pr. The most pronounced effect was found to be a strong field dependence of c_{66} which may be reduced by as much as 19% of its zero field value when a field of the order of 60 kOe is applied in the basal plane (at zero temperature).

The large γ-strain coupling, B_{22}, present in Pr, further, raises the possibility of forcing the nearly critical system to order by the application of a uniaxial pressure of 1 kbar along an a direction.

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Appendix

We wish to discuss here the possible effects of a magnetic coupling between the two

types of ions in DHCP Pr. Because of the complications introduced by such a coupling we shall consider only the simplified two-ion Hamiltonian:

$$\mathscr{H}_{\text{II}} = -\tfrac{1}{2}\sum_{i\neq j}\sum_{\nu}\mathscr{J}^{\nu}(i,j)J_i^{\nu}J_j^{\nu} \tag{A.1}$$

J_i^{ν} is the νth component ($\nu = x$, y or z) of the angular moment on site i. The summation includes both the hexagonal and the cubic ions. The excitations of the 'cubic' ions are assumed to arise from the Γ_1–Γ_4 transition, and we define the effective two-ion coupling parameters:

$$\lambda_{\text{hh}}^{\nu}(\boldsymbol{q}) = \frac{\alpha^2}{\Delta_{\text{h}}}\mathscr{J}_{\text{hh}}^{\nu}(\boldsymbol{q}); \qquad \lambda_{\text{hc}}^{\nu}(\boldsymbol{q}) = \frac{\alpha\gamma}{\sqrt{\Delta_{\text{h}}\Delta_{\text{c}}}}\mathscr{J}_{\text{hc}}^{\nu}(\boldsymbol{q}); \qquad \lambda_{\text{cc}}^{\nu}(\boldsymbol{q}) - \frac{\gamma^2}{\Delta_{\text{c}}}\mathscr{J}_{\text{cc}}^{\nu}(\boldsymbol{q}) \tag{A.2}$$

$\alpha = \sqrt{20}$ and $\gamma = \sqrt{40/3}$. $\mathscr{J}_{\text{hh}}^{\nu}(\boldsymbol{q})$ is the Fourier transformed coupling between the hexagonal ions (the two-sublattice structure of the HCP lattice is neglected), $\mathscr{J}_{\text{hc}}^{\nu}(\boldsymbol{q})$ is the coupling between the two types of ions and $\mathscr{J}_{\text{cc}}^{\nu}(\boldsymbol{q})$ the coupling within the cubic lattice.

Using the same approximations as in §2 the normal excitations are pure x, y and z modes. If $\lambda_{\text{hc}}(\boldsymbol{q})$ is zero the dispersion relations are

$$\begin{aligned}\varepsilon_{\text{hh}}^{\nu}(\boldsymbol{q}) &= \Delta_{\text{h}}[1 - \lambda_{\text{hh}}^{\nu}(\boldsymbol{q})]^{1/2}, \quad \nu = x, y\\ \varepsilon_{\text{cc}}^{\nu}(\boldsymbol{q}) &= \Delta_{\text{c}}[1 - \lambda_{\text{cc}}^{\nu}(\boldsymbol{q})]^{1/2}, \quad \nu = x, y, z\end{aligned} \tag{A.3}$$

If $\lambda_{\text{hc}}^{\nu}(\boldsymbol{q})$ is different from zero the excitations of the hexagonal and cubic ions are coupled, and the energies of the normal modes are the positive roots, E, of the following equation

$$[E^2 - (\varepsilon_{\text{hh}}^{\nu}(\boldsymbol{q}))^2][E^2 - (\varepsilon_{\text{cc}}^{\nu}(\boldsymbol{q}))^2] - (\Delta_{\text{c}}\Delta_{\text{h}}\lambda_{\text{hc}}^{\nu}(\boldsymbol{q}))^2 = 0, \quad \nu = x, y. \tag{A.4}$$

Because $\Delta_{\text{c}} \gg \Delta_{\text{h}}$ the excitations of the hexagonal ions (and the cubic ions) may still be considered as normal modes only $\lambda_{\text{hh}}^{\nu}(\boldsymbol{q})$ in (A.3) is to be replaced by an effective coupling parameter

$$\begin{aligned}\lambda_{\text{hh. eff}}^{\nu}(\boldsymbol{q}) &= \lambda_{\text{hh}}^{\nu}(\boldsymbol{q}) + (\Delta_{\text{c}}\lambda_{\text{hc}}^{\nu}(\boldsymbol{q}))^2/[(\varepsilon_{\text{cc}}^{\nu}(\boldsymbol{q}))^2 - (\varepsilon_{\text{hh}}^{\nu}(\boldsymbol{q}))^2]\\ &\cong \lambda_{\text{hh}}^{\nu}(\boldsymbol{q}) + (\lambda_{\text{hc}}^{\nu}(\boldsymbol{q}))^2/[1 - \lambda_{\text{cc}}^{\nu}(\boldsymbol{q})].\end{aligned} \tag{A.5}$$

If we assume $\mathscr{J}_{\text{hh}}^{\nu}(\boldsymbol{q}) \approx \mathscr{J}_{\text{hc}}^{\nu}(\boldsymbol{q})$ then $\lambda_{\text{hh. eff}}^{\nu}(\boldsymbol{q})$ is of the order of 10% larger than $\lambda_{\text{hh}}^{\nu}(\boldsymbol{q})$ ($\approx 0{\cdot}5$) showing that the perturbative decoupling of the two spin systems should work reasonably well when considering the excitation spectrum.

When an external field is applied along the ν axis in the basal plane the expectation values of the moments on the hexagonal ions (equation (11) with $\theta = \theta_{\text{h}}$) and on the cubic ions

$$\langle J^{\nu}\rangle_{\text{c}} = \frac{\gamma}{\sqrt{2}}\sin 2\theta_{\text{c}} \tag{A.6}$$

are determined by the coupled equations (molecular-field approximation)

$$\begin{aligned}\tan 2\theta_{\text{h}} &= \frac{\sqrt{2}\alpha}{\Delta_{\text{h}}}\text{h} + \lambda_{\text{hh}}(0)\sin 2\theta_{\text{h}} + \sqrt{(\Delta_{\text{c}}/\Delta_{\text{h}})}\lambda_{\text{hc}}(0)\sin 2\theta_{\text{c}}\\ \tan 2\theta_{\text{c}} &= \frac{\sqrt{2}\gamma}{\Delta_{\text{c}}}\text{h} + \lambda_{\text{cc}}(0)\sin 2\theta_{\text{c}} + \sqrt{(\Delta_{\text{h}}/\Delta_{\text{c}})}\lambda_{\text{hc}}(0)\sin 2\theta_{\text{h}}.\end{aligned} \tag{A.7}$$

The condition for an induced magnetic ordering described by a wavevector $\boldsymbol{Q}$ is

$$(1 - \lambda_{\text{hh}}^{\nu}(\boldsymbol{Q}))(1 - \lambda_{\text{cc}}^{\nu}(\boldsymbol{Q})) - (\lambda_{\text{hc}}^{\nu}(\boldsymbol{Q}))^2 = 0 \tag{A.8}$$

in which case the energy of one of the normal ν modes at $\boldsymbol{q} = \boldsymbol{Q}$, (A.4), will be zero (consistent with the approximations involved).

In the limit of small fields the equation determining θ_h may be written

$$\tan 2\theta_h = \sqrt{2}\alpha h/\Delta_h + \lambda_{hh,\,MF}(0) \sin 2\theta_h \tag{A.9}$$

where

$$\lambda_{hh,\,MF}(0) = \lambda_{hh}(0) + \frac{(\lambda_{hc}(0))^2 + \tau\lambda_{hc}(0)(1 - \lambda_{hh}(0))}{1 - \lambda_{cc}(0) + \tau\lambda_{hc}(0)} \tag{A.10}$$

τ is a constant equal to $\gamma\sqrt{\Delta_h/\Delta_c}/\alpha \cong 0{\cdot}5$. A comparison of (A.5) and (A.10) shows that the effective $\lambda_{hh}(0)$ determined from the excitation energy at zero wavevector ($\lambda_{hh,\,eff}(0) = 0{\cdot}4$ using $\Delta_h = 3{\cdot}2$ meV) deviates from the effective two-ion contributions to the MF-equilibrium equation to first order in $\lambda_{hc}(0)$. The field dependence of the moments on the hexagonal sites, as measured by Lebech and Rainford (1971), suggests $\lambda_{hh,\,MF}(0) = 0{\cdot}6$ (in the limit of zero field). (A.10) also shows that the value of the magnetic moments of the hexagonal ions (as used in § 3) is a more reliable measure for the mixing of the wavefunctions $|0)$ and $|1)$ than the equilibrium equation. The crystal-field levels of the hexagonal and the cubic ions, which are neglected above, are unimportant in the limit of small fields because these states are coupled only indirectly to the ground state. The presence of these states and the coupling between the cubic and hexagonal ions will both introduce corrections of the order of $\sin^2\theta$ to the field dependence of the hexagonal excitation energies, equations (13)–(17) (where the coupling parameters are the effective ones defined as in (A.5)).

In the neutron diffraction studies of the Pr–Nd system by Lebech *et al* (1975) the appearance of an ordered moment on the hexagonal ions was not accompanied by any detectable moments on the cubic ions (in pure Nd the cubic moments order at a lower temperature than the hexagonal moments). This behaviour does not necessarily imply that the coupling between the two types of ions, $\mathcal{J}^{\nu}_{hc}(\boldsymbol{q})$, is small. Only $\mathcal{J}^{\nu}_{hc}(\boldsymbol{Q})$, where $\boldsymbol{Q}$ is the wavevector of the ordered moments on the hexagonal ions, has to be small. It is very plausible that this is the case, because the ordering is antiferromagnetic along the c direction ($Q \cong \pi/2b$ and parallel to the b axis, corresponding to the minimum in the energy spectrum of Pr attained by the optical mode at this wavevector (figure 1)). An estimate of $\mathcal{J}^{\nu}_{hc}(\boldsymbol{Q})$ gives $\mathcal{J}^{\nu}_{hc}(\boldsymbol{Q}) \approx \mathcal{J}_{hc}(0)/10$ (including the effect of an estimated phase factor for the coupling between the two hexagonal sublattices) and, assuming $\mathcal{J}_{hc}(0) \approx \mathcal{J}_{hh}(0)$, this implies that the ordering of the moments on the hexagonal sites only induces a magnetic moment on the cubic ions which is a factor of about 30 times smaller. A magnetic coupling between the two types of ions in Pr of this order of magnitude may account for at least half the difference between $\lambda_{hh,\,eff}(0)$ and $\lambda_{hh,\,MF}(0)$ and will introduce important contributions to the susceptibility of the cubic ions which has been observed to be relatively large (Lebech and Rainford 1971).

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