

## Magnetic excitations in praseodymium

J. G. Houmann

*Physics Department, Risø National Laboratory, Roskilde, Denmark*

B. D. Rainford

*Department of Physics, Imperial College, London*

J. Jensen and A. R. Mackintosh

*Physics Laboratory I, H. C. Ørsted Institute,  
University of Copenhagen, Denmark*

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The magnetic excitations in a single crystal of dhcp Pr have been studied by inelastic neutron scattering. The excitations on the hexagonal sites, and their dependence on magnetic fields up to 43 kOe applied in the basal plane, have been analyzed in terms of a Hamiltonian in which exchange, crystal-field, and magnetoelastic interactions are included. The exchange is found to be strongly anisotropic, and this anisotropy is manifested directly in a splitting of most branches of the dispersion relations. By considering a variety of magnetic properties, we have been able to determine the crystal-field level scheme for the hexagonal sites fairly unambiguously. The first excited level is 3.5 meV above the ground state. The value of the magnetoelastic coupling deduced from the excitations is in good agreement with values obtained from other measurements. A field-dependent interaction with the phonons has been observed, and a pronounced broadening of the acoustic excitations of long wavelength is ascribed to the influence of the conduction electrons. The first excited state on the cubic ions is about 8.3 meV above the ground state. The corresponding excitations show a pronounced dispersion, but the exchange anisotropy is of less importance than for the hexagonal sites.

### I. INTRODUCTION

The magnetic properties of Pr, which are unique among the elements, have been intensively studied in recent years. The ions of the double hexagonal close-packed (dhcp) allotrope form two nonmagnetic singlet-ground-state systems, which are only weakly coupled to each other. Houmann *et al.*<sup>1</sup> studied the magnetic excitations and their temperature dependence by inelastic neutron scattering. They concluded that, although the two-ion exchange coupling is inadequate to induce magnetic ordering (above 0.1 K), it is approximately 90% of the critical value, and gives rise to a strong dispersion in the magnetic excitations at low temperatures. Pr is thus an excellent example of an almost-critical singlet-ground-state material, and the objective of the experiments described in this paper was to elucidate how the exchange, crystal-field, and magnetoelastic interactions combine to determine its low-temperature magnetic properties, particularly the magnetic excitations.

In dhcp Pr, which has the stacking sequence *ABAC*, the point symmetries at the nonequivalent sites are different, being approximately cubic at the *A* sites and hexagonal at the *B* and *C* sites, which together form an hcp lattice. The ions at the two dif-

ferent kinds of site therefore experience different crystal fields.<sup>2,3</sup> The ground state of the cubic ions is probably close to a  $\Gamma_1$  singlet, with a  $\Gamma_4$  triplet as the dipolar excited state. Rainford and Houmann<sup>4</sup> found an energy separation of about 8 meV between these levels, and a substantially lower dipolar excitation energy on the hexagonal ions. This allows a second-order perturbative decoupling of the excitations on the two kinds of site<sup>5</sup> and in this paper we concentrate primarily on those on the hexagonal sites, although some new results are also presented for the cubic sites. The ground state of the hexagonal ions is  $|J_z=0\rangle$ , and the dipolar excited state comprises the doublet  $|1\rangle_s \equiv 2^{-1/2}(|+1\rangle + |-1\rangle)$  and  $|1\rangle_a \equiv -2^{-1/2}i(|+1\rangle - |-1\rangle)$ , as shown by Rainford.<sup>3</sup> On account of the magnetic coupling between the ions, the normal modes of the magnetic system are nonlocalized collective excitations, often known as magnetic excitons, which exhibit dispersion.

We have studied the dispersion relations on both the hexagonal and cubic sites at 6 K by inelastic neutron scattering, using triple-axis spectrometers with a thermal beam and a beam of cold neutrons from the DR3 reactor at Risø. We studied the same single crystal as did Houmann *et al.*,<sup>1</sup> and their results were supplemented with measurements along other sym-

metry lines in the Brillouin zone. Furthermore, we examined the dependence of the excitations propagating on the hexagonal sites, along an  $a$  or  $b$  axis, on a magnetic field applied in the basal plane and normal to the direction of propagation.

Our analysis of the experimental results is based on the hybrid molecular-field random-phase approximation of Buyers *et al.*,<sup>6</sup> Yang and Wang,<sup>7</sup> and Bak<sup>8</sup> which, in the zero-temperature limit, is equivalent to the pseudoboson theory of Grover.<sup>9</sup> Most of the errors inherent in this approximation may be taken into account by replacing the true two-ion coupling by an effective screened interaction.<sup>8</sup> The effective two-ion coupling may then be somewhat field dependent. As we shall show, it is possible to derive from such an analysis a set of parameters which are both fairly unambiguously determined, and which give a consistent account of our experimental results on the magnetic excitations, and of the variety of other experimental evidence which has recently been reviewed by Jensen.<sup>10</sup> This includes the magnetization, both in moderate<sup>11</sup> and high<sup>12</sup> fields, neutron diffraction in single crystals as a function of field and temperature,<sup>13</sup> the heat capacity,<sup>14</sup> the field dependence of the elastic constants,<sup>15</sup> the magnetostriction,<sup>16</sup> and the dependence of the magnetic properties on uniaxial strain.<sup>17</sup> The parameters are particularly well determined for the hexagonal sites; for the cubic sites further measurement and analysis is still necessary.

We begin in Sec. II by presenting the theory of the magnetic excitations and introducing the parameters which will be used in our analysis of the experimental results. The dispersion relations and the lifetimes of the excitations in zero magnetic field are presented and analyzed in Sec. III. This discussion is extended to include our measurements in a magnetic field in Sec. IV, where we present the field dependence of the energies of the excitations and their coupling with the phonons. In Sec. V it is shown that a consistent picture may be developed for all of those phenomena which involve magnetoelastic effects. The measurements of the dipolar excitations on the cubic sites are presented and discussed in Sec. VI. Finally, we summarize our present understanding of the magnetic excitations in Pr and point out various experiments by which this understanding might be further improved.

## II. THEORY OF THE HEXAGONAL SITES

Houmann *et al.*<sup>1</sup> analyzed the temperature dependence of the excitation energies on the hexagonal sites in terms of a model in which all crystal-field levels except the singlet ground state and the first excited doublet were neglected. For this effective  $S = 1$  system, they deduced a value of 3.2 meV for the crystal-field splitting  $\Delta$  between these levels. Lindgard<sup>18</sup> used a "self-consistent" random-phase ap-

proximation to the effective  $S = 1$  model and found the somewhat higher value of 3.74 meV. The field dependence of the magnetic properties can also be discussed in terms of this model. If the molecular field is adjusted so that the moments on the hexagonal ions agree with the experimental values of Lebech and Rainford,<sup>13</sup> the only remaining adjustable parameter in the effective  $S = 1$  model is  $\Delta$ . The best fit to the field dependence of the excitation energies is then found with the value  $\Delta = 3.2$  meV but, although the qualitative agreement is satisfactory, substantial discrepancies at high fields indicate the necessity of an analysis in which the other crystal-field levels are included.

Accordingly, we have developed such a theory in which the effect of all  $(2J + 1) = 9$  crystal-field levels is included, and in which the magnetoelastic coupling plays an important role. Our aim is to construct a model Hamiltonian for the hexagonal ions which is as simple as is consistent with a realistic description of the magnetic excitations. A number of simplifying assumptions are made, whose importance is estimated whenever possible.

We will consider the single-ion Hamiltonian

$$\mathcal{H}_I = B_{20}O_2^0 + B_{40}O_4^0 + B_{60}O_6^0 + B_{66}O_6^6 - \frac{3}{16} \frac{B_{22}^2}{c_\gamma} \langle O_2^2 \rangle O_2^2 - g\mu_B \bar{\mathbf{H}}_{mf} \cdot \bar{\mathbf{J}} \quad (1)$$

written in terms of the Stevens operators.<sup>19</sup>  $\bar{\mathbf{J}}$  is the total angular momentum and  $\bar{\mathbf{H}}_{mf}$  is the sum of the external field and the molecular field due to the surrounding ions. In addition to the normal single-ion terms, we have included the magnetoelastic term  $B_{22}$ .  $c_\gamma = 4c_{66}/N$  is a reduced elastic constant ( $N$  is the number of ions per unit volume) which takes the value of 14.0 eV at zero temperature.<sup>15</sup> The magnetoelastic coupling also gives rise to interactions between the magnetic excitons and phonons, which have been discussed by Jensen.<sup>5</sup> The coordinate system used in Eq. (1) has the  $x$ ,  $y$ , and  $z$  axes along the  $a$  ( $[11\bar{2}0]$ ),  $b$  ( $[10\bar{1}0]$ ), and  $c$  ( $[0001]$ ) axes, respectively, of the hexagonal lattice.

The two-ion Hamiltonian, in which anisotropic coupling must be included, is taken to have the form

$$\mathcal{H}_{II} = - \sum_{i>j} \mathcal{J}(ij) (\bar{\mathbf{J}}_i - \langle \bar{\mathbf{J}}_i \rangle) \cdot (\bar{\mathbf{J}}_j - \langle \bar{\mathbf{J}}_j \rangle) + \frac{1}{2} \sum_{i>j} [K(\bar{\tau}_i - \bar{\tau}_j) J_i^+ J_j^+ + K^*(\bar{\tau}_i - \bar{\tau}_j) J_i^- J_j^-] , \quad (2)$$

where

$$K(\bar{\tau}_i - \bar{\tau}_j) = K(ij) e^{2i\phi_{ij}}$$

$\phi_{ij}$  is the angle between the  $x$  direction and the projection of  $\bar{\tau}_i - \bar{\tau}_j$  on the basal plane.  $\mathcal{J}(ij)$  and  $K(ij)$  are real and independent of  $\phi_{ij}$ . If we define  $\theta_{ij}$  as the angle between  $\bar{\tau}_i - \bar{\tau}_j$  and the  $z$  direction, the rela-

tions between these coupling parameters and those introduced by Bak<sup>8</sup> are

$$\mathcal{J}(ij) = \frac{1}{5}\mathcal{J}_{ij} ,$$

$$K(ij) = -\frac{1}{10}\sin^2\theta_{ij}\mathcal{J}_{ij}^{\text{an}} .$$

The two-ion Hamiltonian (2) is quite general in the case of an  $S = 1$  system because exchange (magnetic multipole) couplings of higher ranks are effectively included, provided that a possible axial two-ion term, which is unimportant in the easy-planar case, is neglected.<sup>5,8</sup> The experimental results require the inclusion of anisotropic two-ion couplings, but do not immediately reveal their origin. Large quadrupole (electric multipole) interactions cannot be excluded *a priori* but would modify the temperature and field dependence of the excitations significantly. Since we are able to interpret the experimental results without invoking quadrupole couplings, we conclude that these terms are probably small.

We define the Fourier transforms of the coupling parameters in Eq. (2) in the following way:

$$\mathcal{J}(\bar{q}) = \sum_j \mathcal{J}(ij) \exp[i\bar{q} \cdot (\bar{r}_i - \bar{r}_j)] , \quad (3)$$

where the sum is taken over terms for which  $i$  and  $j$  are on the same sublattice.  $\mathcal{J}'(\bar{q})$  is defined in the same way, but the sum is taken over terms for which  $i$  and  $j$  are on different sublattices.  $K(\bar{q})$  and  $K'(\bar{q})$  are defined analogously.

The procedure for deriving the excitation spectrum by the hybrid molecular-field random-phase approximation is straightforward. The molecular-field Hamiltonian (1) is diagonalized, yielding the eigenfunctions  $|\nu\rangle$  and the corresponding energies  $E_\nu$  ( $E_0 < E_1 < \dots < E_{2J}$ ). The equations of motion of the basis excitation operators  $a_{\nu\mu}(i) \equiv (|\nu\rangle \langle \mu|)_i$  are then derived and reduced to  $2J(2J+1)$  linear equations by the random-phase decoupling

$$a_{\nu'\mu'}(j) a_{\nu\mu}(i) = \langle a_{\nu'\mu'} \rangle a_{\nu\mu}(i) + \langle a_{\nu\mu} \rangle a_{\nu'\mu'}(j) , \quad i \neq j$$

followed by a Fourier transformation. The thermal averages of single-ion terms in these equations and in Eq. (1) are evaluated using the partition function for the molecular-field Hamiltonian (1). The spectrum in this approximation is the same as that calculated by Bak<sup>8</sup> in zero order of a  $1/Z$  expansion of the Green's functions. He finds that the most important correction to  $1/Z$  is the appearance of an intrinsic linewidth in the excitations, due to scattering against single-site fluctuations, which increases drastically when the temperature is raised. The detailed agreement which he finds between his calculated spectral functions and the experimental neutron scattering results strongly indicates that the higher-order terms are negligible in Pr. Associated with the damping is a shift in the excitation energies which vanishes in the

limit of zero temperature. A small shift is however also expected in this limit since the single-ion partition function deviates slightly from that derived from the molecular-field Hamiltonian, due to zero-point fluctuations.<sup>20,21</sup>

In the zero-temperature limit, which is adequate at 6 K, the excitations determined from Eqs. (1) and (2) only depend on the dipolar coupling between the ground and excited states. We define

$$M_\nu^\alpha \equiv \langle \nu | J_\alpha | 0 \rangle ; \quad \alpha = x, y, z . \quad (4)$$

At zero field, the (molecular-field) ground state  $|0\rangle$  is the singlet  $|J_z = 0\rangle$  and only

$$M_{\nu_1}^x = M_{\nu_2}^y = M = [\frac{1}{2}J(J+1)]^{1/2}$$

are nonzero, where  $|\nu_1\rangle \equiv |1\rangle_s$ ,  $|\nu_2\rangle \equiv |1\rangle_a$ , and  $\Delta = E_{\nu_1} - E_0 = E_{\nu_2} - E_0$ .

When  $\bar{q}$  is along the  $y$  direction ( $\Gamma M$ ), the excitations are pure  $J_x$  or  $J_y$  modes (with acoustic and optical branches),

$$\epsilon_x^z(\bar{q}) = \Delta \{ \Delta - 2M^2[\mathcal{J}(\bar{q}) - K(\bar{q})] \pm |\mathcal{J}'(\bar{q}) - K'(\bar{q})| \} , \quad (5a)$$

$$\epsilon_y^z(\bar{q}) = \Delta \{ \Delta - 2M^2[\mathcal{J}(\bar{q}) + K(\bar{q})] \pm |\mathcal{J}'(\bar{q}) + K'(\bar{q})| \} , \quad (5b)$$

which are degenerate only if  $K(\bar{q})$  and  $K'(\bar{q})$  vanish, which they do by symmetry when  $\bar{q}$  is in the  $c$  direction. When  $\bar{q}$  is in the  $x$  direction ( $\Gamma K$ ), the imaginary part of  $K(\bar{r}_i - \bar{r}_j)$  couples the acoustic and optical branches of the  $J_x$  and  $J_y$  modes.

The most important effect of a field applied in the basal plane is the admixture of  $|1\rangle_{s,a}$  into the ground state. This causes both  $M_{\nu_1}^x$  and  $M_{\nu_2}^y$  to decrease and both  $\Delta_x = E_{\nu_1} - E_0$  and  $\Delta_y = E_{\nu_2} - E_0$  to increase (if the field is applied along the  $x$  direction  $M_{\nu_1}^x < M_{\nu_2}^y < M$  and  $\Delta_x > \Delta_y > \Delta$ ). The energies of the excitations are thereby increased while the dispersion becomes smaller. The other excited levels are also mixed into the lowest-lying levels, the main effect of which is to reduce the field dependence of  $\Delta_x$  and  $\Delta_y$ . The two-ion coupling (2) becomes more complex, as the ground state is now coupled to most of the excited levels. However it may be shown that, of the matrix elements which become finite in a field, only  $M_{\nu_3}^z$ , where  $|\nu_3\rangle_{H=0} \equiv |3\rangle_s$ , has a significant effect. For example,  $M_{\nu_1}^z$  and  $M_{\nu_2}^z$  are about  $0.1M$  at our maximum field and the  $J_z$  coupling contributes to the excitation energy by terms which are only of the order of 0.01 meV. Neglecting all matrix elements except  $M_{\nu_1}^z$ ,  $M_{\nu_2}^y$ , and  $M_{\nu_3}^z$ , we may easily diagonalize the two-ion coupling, the greatest complication being that three modes are coupled when  $\bar{q}$  is along the  $x$  direction.

### III. DISPERSION RELATIONS IN ZERO FIELD

The energies of the doublet excitations on the hexagonal ions in Pr have been measured along the symmetry lines of the Brillouin zone at 6 K. We have supplemented the earlier results of Houmann *et al.*<sup>1</sup> with measurements at the zone boundaries, and the collected dispersion relations are shown in Fig. 1.

At finite wave vectors, with a component perpendicular to the  $c$  axis, the two doublet excitations are nondegenerate. The degeneracy can in principle be removed either by the combined effect of the coupling of the excitations to other levels and the hexagonal anisotropy, or by the magnetic dipolar interac-

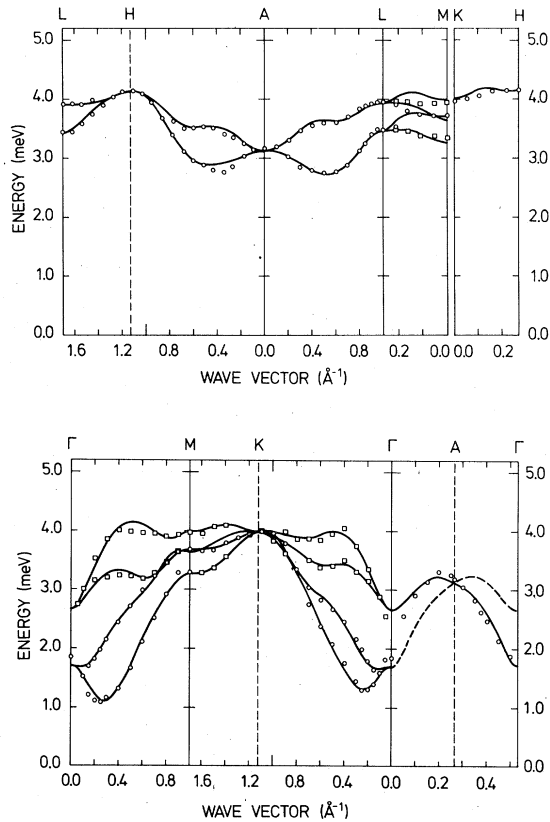


FIG. 1. Dispersion relations for the magnetic excitations propagating on the hexagonal sites of Pr at 6.4 K. In the basal plane ( $\Gamma MK$ ), the squares and circles denote the experimental results for the acoustic and optical modes, respectively. The double degeneracy of these excitations is lifted by anisotropic exchange, and the lower and upper branches correspond respectively to polarizations predominantly parallel and transverse to the wave vector. On the  $AHL$  face of the Brillouin zone, the acoustic and optical excitations are degenerate. The double-zone representation is therefore used for the  $\Gamma A$  direction, along which the two transverse excitations are degenerate by symmetry and therefore form a single branch. The solid lines represent the results of the analysis discussed in the text.

tions, but both of these effects give rise to splittings at least an order of magnitude smaller than those observed. We therefore conclude that our results provide unambiguous evidence for the presence of anisotropic two-ion coupling of the type introduced in Eq. (2).

The dispersion relations have been analyzed in terms of the parameters defined in Eqs. (1)–(5). The experimental results at zero field only allow a rough estimate of the single-ion parameter  $\Delta$  and we have used the value 3.52 meV, deduced from the field dependence of the excitation energies in Sec. IV. The interionic coupling parameters, deduced by a least-squares fit to the experimental results and presented in Table I, should be considered as effective values, for the following reasons: As mentioned above, the two-ion coupling is renormalized by zero-point fluctuations. The coupling to the cubic ions, which cannot be isolated by these experiments, makes a contribution to the effective  $\mathcal{J}(\vec{q}) \pm |\mathcal{J}'(\vec{q})|$  which at zero wave vector is substantial for the acoustic branch, but does not contribute to the optical branch. Finally  $K'(\vec{q})$  is not determined completely unambiguously since the dispersion relations

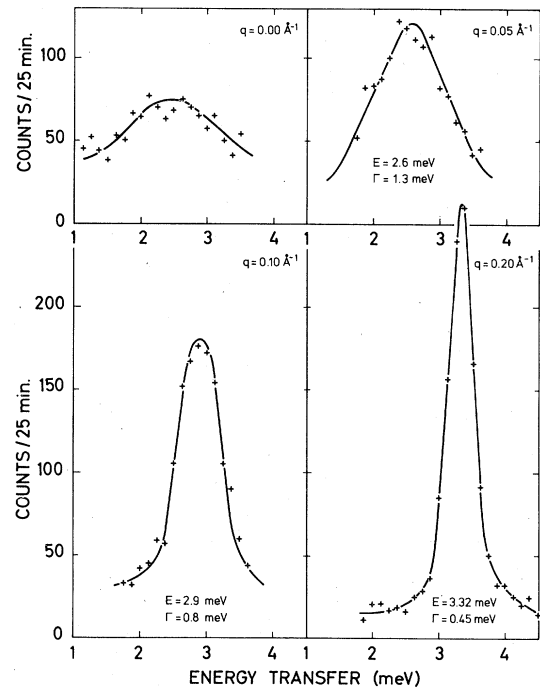


FIG. 2. Neutron scattering spectra from the acoustic excitations propagating along the  $c$  axis. The full width at half maximum increases rapidly as  $q$  decreases. At  $q = 0.20 \text{ \AA}^{-1}$ , it is only slightly greater than the experimental resolution of about 0.35 meV, whereas by  $0.05 \text{ \AA}^{-1}$  the peak has become very broad. At  $q = 0$  it is difficult to identify a well-defined peak, although there is a maximum around 2.5 meV which is so broad that much of the total scattered intensity is masked by the background.

TABLE I. Effective interionic exchange parameters for the hexagonal ions in Pr.  $\mathcal{J}(\vec{R})$  and  $K(\vec{R})$  are defined in the text and given in the table in order of increasing  $R$ . Together with the parameter  $\Delta = 3.524$  meV, they determine the dispersion relations shown by the solid lines in Fig. 1.

Number of ions	$\vec{R}$ (coordinates of typical ion)	$\mathcal{J}(\vec{R})$ ( $10^{-2}$ meV)	$K(\vec{R})$ ( $10^{-2}$ meV)
6	( $a, 0, 0$ )	$1.190 \pm 0.02$	$0.775 \pm 0.04$
6	( $0, -a/(3)^{1/2}, c/2$ )	$-0.945 \pm 0.03$	$-0.091 \pm 0.04$
6	( $0, (3)^{1/2}a, 0$ )	$-0.444 \pm 0.03$	$0.357 \pm 0.03$
6	( $0, 2a/(3)^{1/2}, c/2$ )	$-0.123 \pm 0.04$	$0.359 \pm 0.04$
6	( $2a, 0, 0$ )	$-0.013 \pm 0.02$	$0.391 \pm 0.03$
12	( $a, 2a/(3)^{1/2}, c/2$ )	$0.001 \pm 0.04$	$-0.069 \pm 0.02$
12	( $2a, -a(3)^{1/2}, c/2$ )	$0.215 \pm 0.03$	$0.226 \pm 0.02$
12	( $5a/2, (3)^{1/2}a/2, 0$ )	$0.160 \pm 0.01$	$-0.024 \pm 0.02$
6	( $2a, 2a/(3)^{1/2}, c/2$ )	$0.011 \pm 0.04$	$-0.353 \pm 0.03$
12	( $5a/2, (3)^{1/2}a/6, c/2$ )	$0.066 \pm 0.03$	0
6	( $3a, 0, 0$ )	$0.074 \pm 0.02$	$0.113 \pm 0.03$
2	( $0, 0, c$ )	$0.315 \pm 0.03$	0
12	( $a, 0, c$ )	$0.105 \pm 0.01$	$-0.044 \pm 0.01$
6	( $0, 2(3)^{1/2}a, 0$ )	$-0.019 \pm 0.02$	0
12	( $7a/2, (3)^{1/2}a/2, 0$ )	$-0.021 \pm 0.01$	0
12	( $0, (3)^{1/2}a, c$ )	$0.090 \pm 0.01$	0
12	( $2a, 0, c$ )	$0.034 \pm 0.01$	0
2	( $0, 0, 2c$ )	$0.381 \pm 0.03$	0

as a function of field may also be fitted by a different set of parameters, corresponding to the opposite sign for the anisotropic coupling between the two sublattices. However, the choice which we have made, which also corresponds to that of Bak,<sup>8</sup> is in better agreement with the observed intensities and also gives a slightly better account of the field dependence of the energies. A definitive test would however require a very precise determination of the polarization vectors of the excitations near  $KM$ .

The dispersion relations near zero wave vector vary rapidly, indicating the presence of very long-range interactions. Although our fit includes interactions out to seven nearest neighbors in the basal plane, this is not sufficient to account for the behavior at small wave vectors, and adjusting  $\Delta$  does not resolve this discrepancy. Although the coupling to the cubic sites and magnetic dipole interactions can give rise to rapid variations at small wave vector, these are of minor importance, at least for the optical (lower) branches, the rapid dispersion of which probably reflects the properties of the conduction-electron gas.

In addition to this rapid variation of the energies of the excitations near  $\Gamma$ , the intrinsic linewidths of the acoustic modes also display an unusual behavior. In the low-temperature limit, where the damping due to the single-site fluctuations<sup>8</sup> should vanish, these modes are strongly damped, as illustrated in Fig. 2. The other broadening mechanism which might be of

importance in the metal is the scattering against the electron-hole pair excitations of the conduction electrons, which has been considered in detail by Becker *et al.*<sup>22</sup> We have applied their method to Pr, utilizing the effective  $S = 1$  model for the excitations, and a modified free-electron model for the conduction electrons. The imaginary part of the self-energy is found to consist of two terms, one of which depends on the wave vector of the excitation but varies only slowly with temperature, and another which is independent of wave vector and vanishes at zero temperature. The former, which is the same as that appearing in a singlet-singlet model, is proportional to  $q^{-1}$ , for  $q > 0.001 \text{ \AA}^{-1}$ . The experimental results shown in Fig. 2 behave according to this prediction. The observed linewidths are well described as the combination of two contributions; the experimental resolution of 0.35 meV and the intrinsic linewidth which has a value of about  $0.06 q^{-1}$  meV. The broadening of the optical excitations is estimated to be much less than the experimental resolution at low temperatures, and dominated by the single-site scattering at all temperatures below about 30 K.

The free-electron model is known to be inadequate for the conduction electrons in rare-earth metals, but the small- $q$  behavior is expected to be given correctly, and the parameters which describe the mutual scattering of spin waves and conduction electrons in Tb (Refs. 23 and 24) also give a good account of the

broadening of the excitations at small  $q$  which we observe in Pr.

The polarization dependence of the neutron scattering cross section makes it possible to distinguish between the (acoustic or optical)  $J_x$  and  $J_y$  excitations. When  $\vec{q}$  is along the  $y$  direction ( $\Gamma M$ ), the two types of mode are orthogonal and the intensities in the two geometrically different scans shown in Fig. 3 show unambiguously that the lower branches of both the acoustic and optical modes are the  $J_y$  excitations. Similarly the lower branches of the acoustic and optical excitations propagating along  $\Gamma K$  may be classified as (predominantly)  $J_x$  modes.

In the fit to the dispersion relations, the chosen value of  $\Delta$  is only crucial for the determination of  $\mathcal{J}(0, 0, c)$  and  $\mathcal{J}(0, 0, 2c)$ , since the rest of the coupling parameters are merely scaled with a constant factor if  $\Delta$  is changed. As may be seen from Table I,  $\mathcal{J}(0, 0, 2c)$  appears to be anomalously large, but this may be an artifact of the analysis, since this parameter may be reduced substantially by making a small decrease in  $\Delta$ .

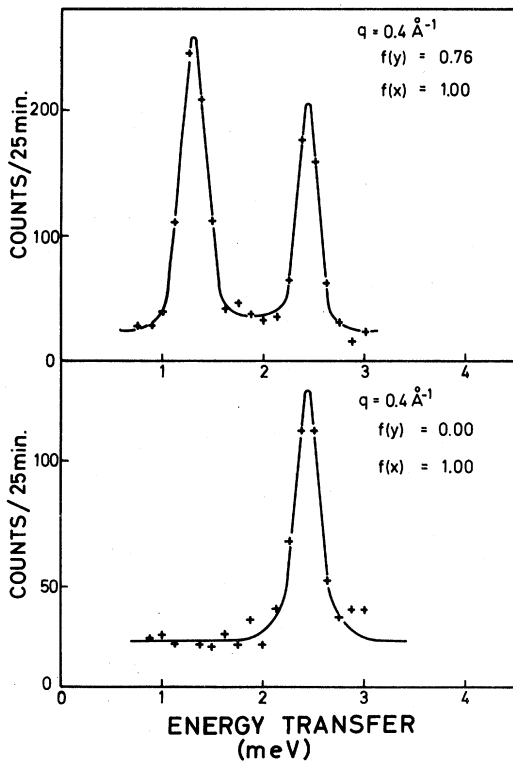


FIG. 3. Example of the determination of the polarization vector of the excitations. The neutron scattering cross section is proportional to the factor  $f(\alpha) = 1 - (\kappa_\alpha/\kappa)^2$ , where  $\vec{\kappa} = \vec{\tau} + \vec{q}$  is the scattering vector and  $\vec{\tau}$  is reciprocal-lattice vector. For a fixed  $\vec{q}$  of  $0.4 \text{ \AA}^{-1}$  along  $\Gamma M$  ( $y$  axis), a change of  $\vec{\tau}$  produces a drastic modification in the spectrum of scattered neutrons, showing unambiguously that the lower peak corresponds to the longitudinal (optical) mode.

#### IV. FIELD DEPENDENCE OF THE EXCITATIONS

We have measured the energies of the excitations propagating in the  $x$  and  $y$  directions as a function of a magnetic field applied in the basal plane and perpendicular to the wave vector. These experiments supplement those of Rainford and Houmann,<sup>4</sup> who studied the field dependence of the magnetic excitons propagating in the  $z$  direction. In zero field, the lowest-energy excitations are characterized by the three wave functions  $|0\rangle$ ,  $|1\rangle_s$ , and  $|1\rangle_a$ , corresponding to a system with  $S = 1$ . This remains true to leading order in the applied field, which only couples the other excited levels to the ground state indirectly, via  $|1\rangle_{s,a}$ . The effective  $S = 1$  model thus accounts qualitatively for the field dependence of the excitations when the value  $\Delta = 3.2 \text{ meV}$  is used, but satisfactory quantitative agreement is only obtained at small fields.

The most important effect of the cubic ions is their contribution at finite fields to the molecular field acting on the hexagonal ions. The total molecular field may be determined by the requirement that the calculated magnetic moments at the hexagonal sites be equal to the values measured by Lebeck and Rainford.<sup>13</sup> The  $\vec{q}$ -dependent contributions from the cubic ions behave similarly to those of the hexagonal ions as a function of field, giving rise to discrepancies with the measured energies at the highest fields of only about  $0.1 \text{ meV}$  in the most unfavorable case, the acoustic modes near  $\Gamma$ . If the cubic ions had excited levels lying below the dipolar excited states at  $8 \text{ meV}$  and close to the  $|\pm 1\rangle$  levels on the hexagonal ions, larger effects would be expected. Both the interpretation of the magnetic heat capacity<sup>3</sup> (also discussed in Sec. VI), and the absence of signs of hybridization between magnetic excitations on the hexagonal and cubic sites, provide evidence against this possibility.

The importance of the screening of the effective two-ion coupling may be estimated from the theory of Lindgard.<sup>18</sup> He finds a relative renormalization of the two-ion contributions  $R$  which is independent of wave vector. In the limit of zero temperature,  $1 - R$  is approximately proportional to

$$N^{-1} \sum_{\vec{q}} (\lambda_{\vec{q}}^{x,y})^2,$$

where

$$\lambda_{\vec{q}}^x = (M_{y_1}^x)^2 \mathcal{J}(\vec{q}) / \Delta_x$$

and similarly for  $\lambda_{\vec{q}}^y$ . At zero field and temperature he calculates  $R$  to be  $0.92$ .  $R$  should increase with field to a value of about  $0.96$  at our highest fields, implying that the two-ion coupling is field dependent, and giving an increase of about  $0.1 \text{ meV}$  in the dispersion. This estimate may not be particularly ac-

curate, since the self-consistent single-ion partition function is not determined uniquely by a random-phase decoupling, but we use the indication that the effect is small as a justification for ignoring it.

The application of a field may induce interactions between magnetic excitons and phonons which are absent in zero field.<sup>5</sup> Clear indications of such phonon interactions may be seen in the excitation spectra shown in Fig. 4. We note that the energy gaps induced by such interactions have a characteristic behavior which is quite different from that which would be observed in the event of hybridization between two relatively flat branches of magnetic excitons. The interaction between the magnetic excitations and the transverse phonons is directly related to the magnetoelastic term in Eq. (1). From the energy

gaps resulting from this interaction, Jensen<sup>5</sup> estimated  $B_{22}$  to be 30 meV in an analysis based on the effective  $S = 1$  model. Within this model, the magnetoelastic term makes a contribution to the energies of the magnetic excitons at our highest field of about  $-5\%$  and  $2.5\%$  for the longitudinal and transverse modes, respectively, defined in relation to the field direction. The inclusion of these contributions diminishes the splitting between the  $J_x$  and  $J_y$  modes in both cases, which clearly improves the agreement between the observed field dependence of the excitation energies and the predictions of the effective  $S = 1$  model.

This model predicts the field dependence of the excitations much better when the field is along the  $y$  direction than when it is along the  $x$  direction. This

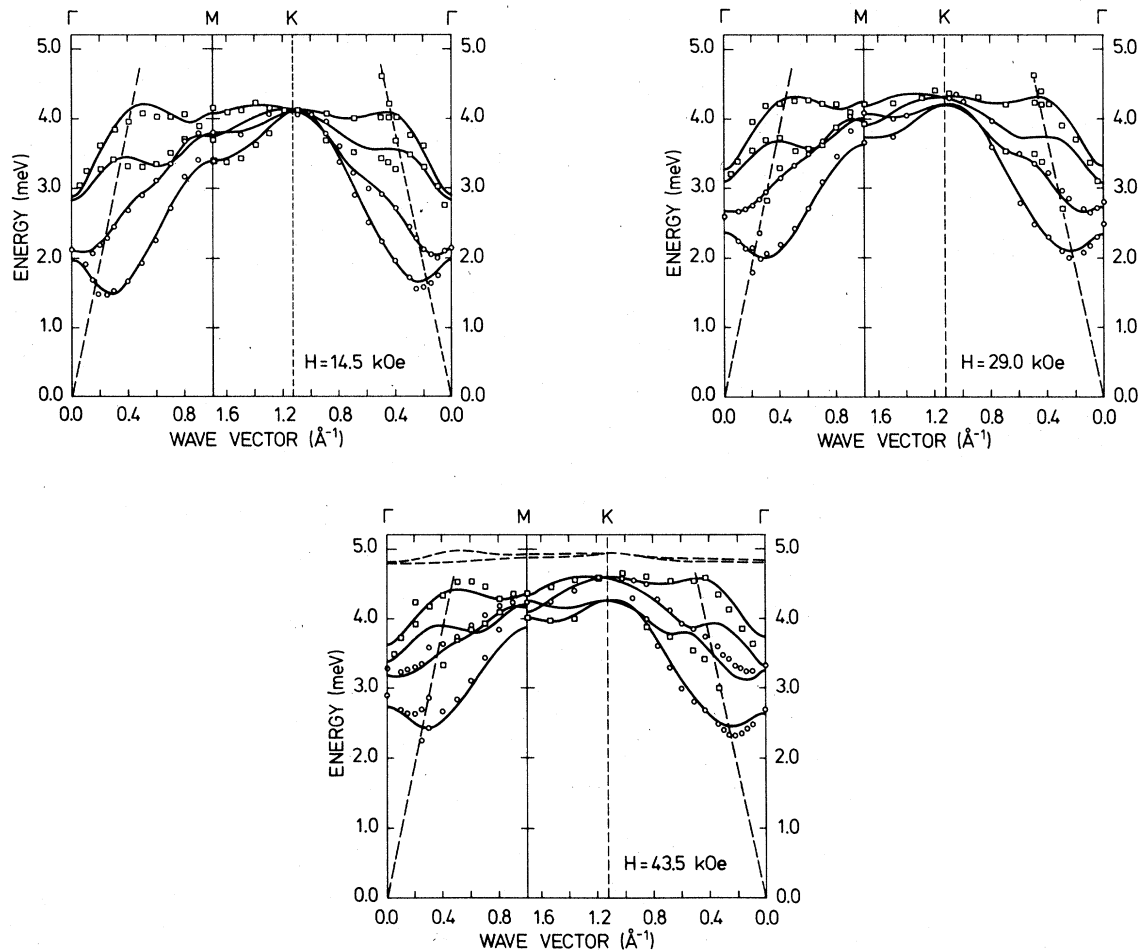


FIG. 4. Energies of the excitations propagating on the hexagonal sites of Pr at 6.4 K in an applied field. The field is in the basal plane and perpendicular to the wave vector, so that there is a discontinuity in the results at  $M$ , corresponding to a rotation of the field through  $90^\circ$ . The solid lines are the results of the least-squares analysis discussed in the text, in which the coupling between the magnetic excitons and phonons was not included. The most pronounced hybridization is between the transverse-acoustic phonons (indicated by dashed lines) and the longitudinal-acoustic excitons, giving rise to energy gaps proportional to the field (see Ref. 5). We have indicated the calculated dispersion relations for the excitations originating from the  $|3\rangle_z$  state, at the highest field.

anisotropic behavior shows that the hexagonal anisotropy term  $B_{66}$  is of importance at finite fields and indicates the limited validity of the effective  $S = 1$  model. These small deviations may be used to fix one crystal-field parameter and, if we use our knowledge of  $\Delta$  and  $B_{22}$ , this leaves two parameters undetermined. We may reduce this further by making use of the relation  $B_{66} = -\frac{77}{8} B_{60}$ , which is predicted by a rather general superposition model<sup>25</sup> and has been observed to be satisfied in a large number of dilute alloys of magnetic rare earths in Sc, Y, and Lu by Touborg<sup>26</sup> and his co-workers. The remaining parameter may be fixed from the observation of McEwen *et al.*<sup>12</sup> of a magnetic transition at low temperatures in a field of 320 kOe applied in the  $c$  direction.

In these experiments the total moment is found to increase smoothly until the critical field, at which a discontinuous jump from 0.85 to  $1.95 \mu_B/\text{ion}$  is observed. The neutron-diffraction measurements of Lebeck and Rainford<sup>13</sup> show that no moment is present on the hexagonal ions at low fields, and the transition is therefore interpreted, to a first approximation, as the appearance of a moment of  $2.2 \mu_B/(\text{hexagonal ion})$ , neglecting possible small changes on the cubic ions. Taking into account the above relation between  $B_{66}$  and  $B_{60}$ , this jump in the moment can only be accounted for by the  $|+3\rangle$  state with a slight admixture of  $|-3\rangle$ . A simple model can account for the transition if  $|B_{66}|$  is about  $1.1 \times 10^{-3}$  meV, giving rise to a  $|3\rangle_s$  or  $|3\rangle_a$  level approximately 3.7 meV above the ground state at zero field.

The actual phase transition is however presumably of a rather complicated nature. As well as the influence of the cubic ions, it is necessary to take into account that the hexagonal ions are probably ordered antiferromagnetically below  $H_c$ . A straightforward calculation of the excitation energies reveals that the energy of the lowest mode in the  $\Gamma M$  direction goes to zero at an applied field, in the  $c$  direction, of about 205 kOe. As a result, there is a second-order transition to a phase with no  $c$  axis moment, but a periodic ordered structure in the basal plane in which the polarization vector lies on an ellipse. When the field is further increased, a small  $c$  axis component might develop and, at the transition, the ordering in the plane will be substantially affected by the large  $c$  axis moment. The simplified model, in which the ordering in the plane is neglected, can therefore only be used to provide estimates of certain parameters, but the conclusion that a singlet  $|3\rangle_s$  or  $|3\rangle_a$  level lies close to the lowest doublet is reliable.

The largest deviations from the effective  $S = 1$  model occur for the field dependence of the excitations propagating in the  $y$  direction with the field in the  $x$  direction. This indicates that it is  $|3\rangle_s$ , which lies close to these excitations, corresponding to a neg-

ative  $B_{66}$ , because this state is coupled indirectly to the ground state when the field is applied along the  $x$  direction, whereas it is  $|3\rangle_a$  which is coupled to the ground state when the field is along the  $y$  direction.  $B_{66} = -1.1 \times 10^{-3}$  meV was therefore used as a starting value in the analysis.

A least-squares fit to the field dependence of the excitations was performed using the variables  $\Delta$ ,  $B_{22}$ , and  $\Delta_3 = (E_{\nu_3} - E_0)_{H=0}$  where  $|\nu_3\rangle_{H=0} \equiv |3\rangle_s$ . The two-ion coupling parameters, which depend on  $\Delta$ , were determined self-consistently from the dispersion relations at zero field, as described in Sec. III. The remaining degree of freedom in the molecular-field Hamiltonian is the position  $\Delta_4$  of the predominantly  $|4\rangle_{s,a}$  doublet. A variation of this parameter in the range 8–35 meV was found to affect the results very little. The final fit is shown in Fig. 4 and the parameters determined from the least-squares analysis are

$$\Delta = 3.52 \pm 0.08 \text{ meV} ,$$

$$\Delta_3 = 4.43 \pm 0.25 \text{ meV} ,$$

$$B_{22}^2/c_\gamma = 0.035 \pm 0.004 \text{ meV} .$$

The remaining discrepancies between theory and experiment are of the order of 0.1 meV at maximum field, which is small compared with the absolute shifts and on the borderline of the experimental accuracy. In Fig. 4 the energies of the  $|\nu_3\rangle$  excitations are shown at the highest fields. Their intensities are approximately an order of magnitude less than those of the doublet excitations and we have not yet been able to detect them. Experiments in even higher fields would be useful for this purpose.

The value of  $B_{22}$  determined from the least-squares fit is somewhat smaller than that estimated on the basis of the effective  $S = 1$  model. It is, however, consistent with the observed splittings due to the interaction with the phonons. The matrix element which determines the strength of the magnetic exciton-phonon coupling is almost a factor of 2 larger than that occurring in the effective  $S = 1$  model, because of the strong influence of the  $|3\rangle_s$  wave function. Following the procedure of Jensen,<sup>5</sup> we find that  $B_{22} = 18 \pm 3$  meV accounts for the observed splittings when the complete crystal-field level scheme is used.

The value of  $\Delta_4$ , which is not determined by the field dependence of the excitations, may be estimated from the high-field transition. A lower limit may be obtained by noting that, if  $|B_{66}|$  were less than about  $8.7 \times 10^{-4}$  meV,  $\Delta_4$  would be so small that  $|4\rangle$  would become the ground state before  $|3\rangle$ , giving rise to a jump in magnetic moment of about  $3.3 \mu_B$ , which is much greater than observed. We therefore choose a value

$$B_{66} = (-9.6 \pm 1) \times 10^{-4} \text{ meV} ,$$



TABLE II. Crystal-field parameters for the hexagonal sites in dhcp Pr, in meV, compared with those of Pr dissolved in Y and Lu, taken from Ref. 26.

	$10^2 B_{20}$	$10^4 B_{40}$	$10^4 B_{60}$	$10^4 B_{66}$
Metal	$19 \pm 4$	$-5.7 \pm 5$	$1.00 \pm 0.1$	$-9.6$
Solute		$-2.7 \pm 1$	$0.89 \pm 0.06$	$-9.3 \pm 1.8$

which gives a critical field of  $380 \pm 40$  kOe and a jump in the hexagonal moment of  $(2.24 \pm 0.04) \mu_B$ . In view of the simplifications in the model of the transition, these values are in satisfactory agreement with the experimental results. From the values of  $\Delta$  and  $\Delta_3$  and the relation between  $B_{60}$  and  $B_{66}$  we may

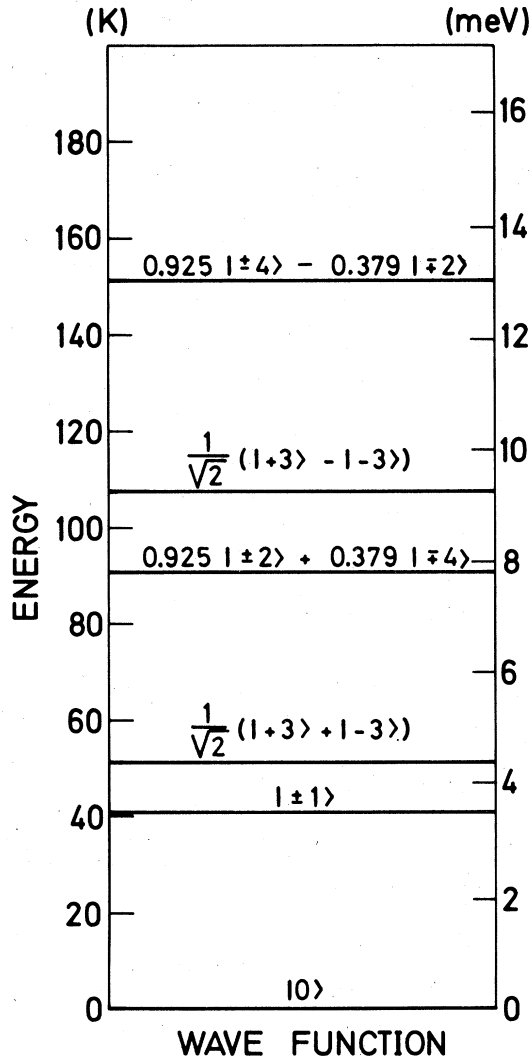


FIG. 5. Wave functions and relative energies of the crystal-field levels for the hexagonal sites in Pr, determined from the parameters in Table II.

then deduce the remaining crystal-field parameters which are given in Table II. These parameters are close to those deduced by Touborg<sup>26</sup> from his studies of dilute rare-earth alloys, which are also given in Table II. The crystal-field level scheme for the hexagonal ions in Pr, deduced from our parameters, is shown in Fig. 5.

## V. MAGNETOELASTIC EFFECTS

The presence of the strong magnetoelastic coupling term  $B_{22}$  gives rise to a number of effects which have been discussed by Jensen<sup>5</sup> on the basis of the simplified effective  $S = 1$  model for the hexagonal ions. We now extend this model to finite temperature and include the effects of the higher-lying crystal-field levels shown in Fig. 5. We thus rewrite the magnetoelastic contribution to the molecular-field Hamiltonian of the hexagonal ions, Eq. (1), in the form<sup>5,15</sup>

$$\mathcal{H}_{me}(h) = -B_{22}(h) \bar{\epsilon}_\gamma \left(\frac{3}{8}\right)^{1/2} O_2^2, \quad (6)$$

where the equilibrium strain is determined by

$$\begin{aligned} \bar{\epsilon}_\gamma &= \frac{1}{2} (\bar{\epsilon}_{11} - \bar{\epsilon}_{22}) \\ &= (2c_\gamma)^{-1} \left(\frac{3}{8}\right)^{1/2} [B_{22}(h) \langle O_2^2 \rangle_h + B_{22}(c) \langle O_2^2 \rangle_c] \\ &\quad + (T_{11} - T_{22})/4c_{66}. \end{aligned} \quad (7)$$

$B_{22}(h)$  and  $B_{22}(c)$  are the coupling parameters for the hexagonal and cubic ions, respectively, and  $T_{\alpha\beta}$  is the applied stress. 1, 2, and 3 represent the  $a$ ,  $b$ , and  $c$  axes, respectively.

The field dependence of  $\bar{\epsilon}_{11}$  has been measured by McEwen<sup>16</sup> at 4.2 K. His results indicate that  $\frac{1}{2}(\bar{\epsilon}_{11} + \bar{\epsilon}_{22})$  is small and hence that  $\bar{\epsilon}_{11} \approx \bar{\epsilon}_\gamma$ . Furthermore  $\bar{\epsilon}_{11}$  is accurately described by Eq. (7), up to an applied field of 60 kOe, if  $B_{22}(c)$  is neglected and  $B_{22}(h)/c_\gamma$  takes the value  $1.44 \times 10^{-3}$ .  $B_{22}(c)$  might in fact be comparable with  $B_{22}(h)$ , but this approximation is validated by the weak field dependence of  $\langle O_2^2 \rangle_c$ , which is only about 10% of that of  $\langle O_2^2 \rangle_h$ .

The dynamic coupling between the magnetic and elastic excitations has been studied in the long-wavelength limit by Palmer and Jensen.<sup>15</sup> They studied the field and temperature dependence of  $c_{66}$  by measuring the velocity of the corresponding ultrasonic waves. At 4.2 K,  $c_{66}$  was found to be very sensitive to a field applied in the basal plane, but insensitive to a field along the  $c$  axis, indicating that  $B_{22}(c)$  is unimportant. There is furthermore a considerable

anisotropy in the basal plane, due to the effect of  $B_{66}$  in splitting the  $|3\rangle_s$  and  $|3\rangle_a$  levels, as illustrated in Fig. 5. Using this crystal-field level scheme, they were able to obtain a very satisfactory fit to both the field and temperature dependence of  $c_{66}$ . Neglecting the small effects of  $B_{22}(c)$ , they determined the parameters given in Table III. The exchange parameters they used are not the same as those which we estimate in Sec. VI, but their effective susceptibility function is very close to the one which we deduce.

The quantitative analyses of the different magnetoelastic phenomena are mutually consistent, as shown in Table III. This consistent description is obtained with the simplest magnetoelastic model, neglecting the cubic ions, and using the crystal-field parameters of Sec. IV for the hexagonal ions. The magnetoelastic Hamiltonian (6), which is implicitly assumed to be solely of single-ion origin, may effectively include two-ion contributions without essentially changing the results. However, an estimate based on the stress dependence of the magnetic transition temperatures of the heavy rare-earth metals indicates that such contributions are negligible.<sup>15</sup> A coupling between the quadrupole moments  $O_2^2$  on different ions, mediated by the conduction electrons, would contribute to the effective value of  $(B_{22})^2/c_\gamma$  in Eq. (1), and give rise to a field dependence of the effective exchange, but would not directly affect the elastic properties. The comparison in Table II shows, however, that the magnetoelastic coupling alone accounts for the quadrupole term in Eq. (1). The discrepancy is barely significant and may, in any case, be accounted for by the contribution of the cubic ions.

Using the effective  $S = 1$  model, Jensen<sup>5</sup> predicted that it should be possible to induce an antiferromagnetic phase in Pr with the symmetry of the incipient soft mode, the excitation of lowest energy in the  $b$  direction ( $\Gamma M$ , see Fig. 1), by applying a uniaxial pressure,  $P = -(T_{11} - T_{22})$ , of about 1 kbar along an

TABLE III. Values of the magnetoelastic coupling parameters,  $c_\gamma = 4c_{66}/N$  and  $B_{22}$ , determined in various combinations by different experiments.

Experiment	Parameter	Value	Unit
MF Contribution <sup>a</sup>	$B_{22}^2/c_\gamma$	$35 \pm 4$	$10^{-3}$ meV
Field dep. of $c_{66}$ <sup>b</sup>	$B_{22}^2/c_\gamma$	$29 \pm 3$	$10^{-3}$ meV
Field dep. of $\bar{\epsilon}_{11}$ <sup>c</sup>	$B_{22}/c_\gamma$	$1.44 \pm 0.2$	$10^{-3}$
Exciton phonon <sup>a</sup>	$ B_{22} $	$18 \pm 3$	meV
Ultrasonic <sup>b</sup>	$c_\gamma$	$14 \pm 1$	eV

<sup>a</sup>See Sec. IV.

<sup>b</sup>Reference 15.

<sup>c</sup>Reference 16

$a$  axis at low temperatures. Recently, McEwen *et al.*<sup>17</sup> have observed such a transition at 4.8 and 7.4 K when applying pressures of 0.6 and 0.8 kbar, respectively. Using the parameters deduced from the field dependence of  $c_{66}$ , and Eqs. (1) and (6), we have calculated the critical pressure, as a function of temperature, at which a second-order phase transition occurs. The results are shown in Fig. 6 and agree well with the experimental results. The calculated steep increase of the critical pressure at higher temperatures reflects the corresponding rapid increase in energy of the incipient soft mode. This agreement provides decisive support to the model Hamiltonian which we have deduced for the hexagonal ions. In particular, it shows that the exchange must be close to 92% of the critical value at zero pressure, and hence that the crystal-field splitting  $\Delta$  is close to 3.52 meV.

## VI. CUBIC SITES

On account of the large splitting between the ground state and the excited levels of the cubic ions, their influence on the magnetic properties of Pr is less pronounced than is that of the hexagonal ions. Consequently it is more difficult to construct a model based on experimentally derivable parameters for the cubic ions.

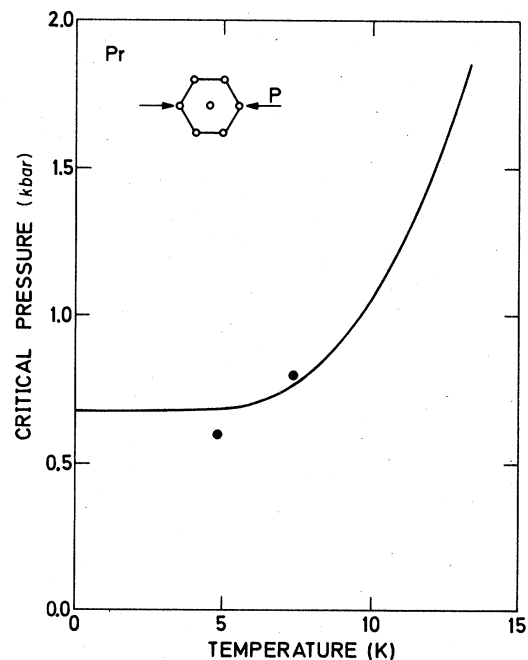


FIG. 6. Calculated critical uniaxial pressure, applied along an  $a$  direction, which induces the longitudinally polarized antiferromagnetic phase in Pr. The closed circles indicate the experimental results of McEwen *et al.* (Ref. 17).

The dispersion relations for the magnetic excitations propagating on the cubic sites have been measured along the symmetry lines in the Brillouin zone at 6 K, and the results are shown in Fig. 7. The dispersion is less than that of the hexagonal excitations, partly because  $M_c^2 = \frac{20}{3}$  in the  $\Gamma_1 - \Gamma_4$  model, compared with the value  $M_h^2 = 10$  for the hexagonal ions. The splitting  $\Delta_c$  probably lies between 8.3 and 8.4 meV. The dispersion relations are determined by equations equivalent to Eq. (5), and the most significant difference from the hexagonal excitations is that the cubic anisotropic coupling  $K_c(\bar{q})$  is too small to be observed. In the experimental neutron scans, the  $x$  and  $y$  excitations had almost equal weight and the experimental resolution was not sufficient to detect any splitting between these modes. We conclude therefore that it must be less than about 0.5 meV. Furthermore the excitations propagating along the  $c$  direction have negligible dispersion, in contrast to those on the hexagonal sites, indicating that the total coupling between different layers of cubic ions is very small. Possible  $z$  excitations are not observed in

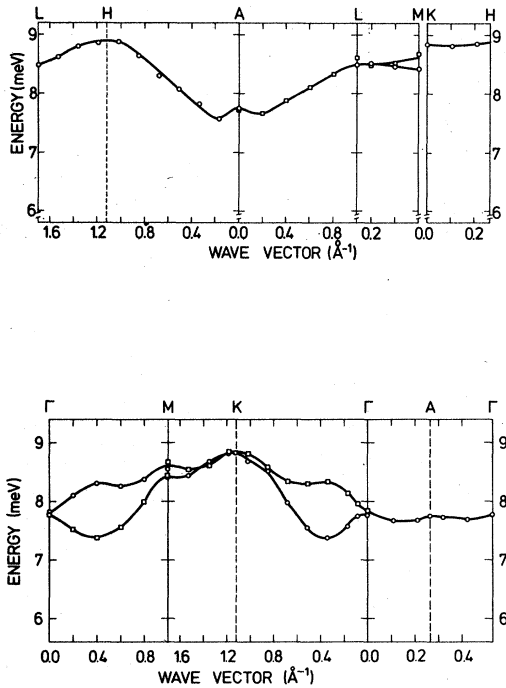


FIG. 7. Dispersion relations for the excitations propagating on the cubic sites in Pr at 6.4 K. The upper and lower branches in the basal plane ( $\Gamma MK$ ) are, respectively, the acoustic and optical modes. The polarization vector of the excitations is perpendicular to the  $c$  axis. No splitting of these branches by anisotropic exchange was observed with an experimental resolution of about 0.5 meV. The full lines are drawn arbitrarily through the points. The results are plotted in the Brillouin zone for the dhcp structure, as in Fig. 1.

TABLE IV. Provisional values for the crystal-field parameters for the cubic ions in dhcp Pr, as defined in Ref. 3, and the exchange parameters at zero wave vector, in meV.

$B_{40}(c)$	$B_{60}(c)$	$\mathcal{J}_{hh}$	$\mathcal{J}_{hc}$	$\mathcal{J}_{cc}$
$29 \times 10^{-4}$	$0.8 \times 10^{-4}$	0.02	0.19	0.14

these experiments, on account of the particular neutron scans employed.

We shall use the available experimental information to construct a molecular-field model for Pr, including the cubic ions, similar to that of Rainford.<sup>3</sup> In addition to the parameters previously determined, we require the crystal-field parameters for the cubic ions, and the three long-wavelength exchange parameters  $\mathcal{J}_{hh}$ ,  $\mathcal{J}_{hc}$ , and  $\mathcal{J}_{cc}$ .  $\mathcal{J}_{hh}$  is equal to  $\mathcal{J}(0) + \mathcal{J}'(0)$  defined in Eq. (3), but excluding the contribution from the cubic ions, which is incorporated in the exchange parameters deduced in Sec. III.  $\mathcal{J}_{hc}$  and  $\mathcal{J}_{cc}$  are defined analogously.

The molecular field acting on the hexagonal ions, appearing in Eq. (1), is

$$\bar{H}_{mr}(h) = \bar{H} + (g\mu_B)^{-1}(\mathcal{J}_{hh}\langle\bar{J}\rangle_h + \mathcal{J}_{hc}\langle\bar{J}\rangle_c), \quad (8)$$

where  $\bar{H}$  is the applied field and  $g\mu_B\langle\bar{J}\rangle_h$  is the moment on the hexagonal ions. The molecular field for the cubic ions is obtained by interchanging the indices  $h$  and  $c$  ( $\mathcal{J}_{hc} = \mathcal{J}_{ch}$ ). Neglecting effects due to the trigonal distortion of the point symmetry of the cubic ions, we may use the available experimental information to deduce the parameters given in Table IV. The values given in Tables II and IV give a good account of the magnetization at 4.2 K,<sup>13</sup> as may be seen by the comparison shown in Table V. They also describe the high-field magnetization<sup>12</sup> fairly satisfactorily. The exchange contributions to the free-energy reduce the calculated critical field along the  $c$  axis to 360 kOe, again ignoring possible ordering of the moments in the plane. The magnetic contribution to the heat capacity agrees well with the experimental measurements.<sup>14</sup> Finally, the comparison between the calculated and experimental excitation energies and the cubic-crystal-field splitting  $\Delta_c$ , also given in Table V, are satisfactory, except for  $\epsilon_h(0)$  which, as discussed earlier, behaves anomalously.

The parameters of Table IV should however, be considered as provisional, since no account is taken of the trigonal distortion of the cubic sites. If we compare with the hcp heavy rare-earth metals, and ignore the effect of the structural difference, we should expect  $\mathcal{J}_{hh} \sim \mathcal{J}_{cc} \sim \mathcal{J}_{hc} \sim 0.1$  meV. It is therefore somewhat surprising that  $\mathcal{J}_{hh}$  is so much smaller than the others.  $B_{60}$  is almost the same for the two

TABLE V. Properties of dhcp Pr calculated from the parameters of Table II and IV and compared with experiment. The  $\chi$  values are the initial susceptibilities at 4.2 K for the different types of site, in units of  $10^{-2}\mu_B/\text{kOe}$ , and the superscripts  $\parallel$  and  $\perp$  indicate that the field is applied respectively parallel and perpendicular to the  $c$  axis. The experimental values are taken from Ref. 13.  $\epsilon_h(0)$  and  $\epsilon_c(0)$  are the energies in meV of the two uniform modes, and  $\Delta_c$  is the crystal-field splitting between the ground state and the first-excited state of the cubic ions.

	$\chi^\perp(h)$	$\chi^\perp(c)$	$\chi^\parallel(h)$	$\chi^\parallel(c)$	$\epsilon_h(0)$	$\epsilon_c(0)$	$\Delta_c$
Experiment	$6.3 \pm 0.1$	$3.2 \pm 0.1$	$0.2 \pm 0.2$	$0.78 \pm 0.04$	$2.50 \pm 0.05$	$7.83 \pm 0.05$	$8.35 \pm 0.1$
Calculated	6.21	3.16	0	0.75	2.30	7.80	8.42

kinds of sites, but there is a pronounced difference in  $B_{40}$ , and also probably in  $B_{20}$ .

The calculated temperature dependence of the susceptibilities, which is very similar to that of Rainford,<sup>3</sup> is not entirely in agreement with the experimental results of Johansson *et al.*<sup>11</sup> The introduction of a finite  $B_{20}$  for the cubic sites leads to only minor improvements. It would be valuable to extend the neutron-diffraction measurements<sup>13</sup> to higher temperatures, in order to obtain separately the contributions from the two kinds of sites. This might allow a test of the relation  $B_{66} = -(\frac{77}{8})B_{60}$ , which is used for both types of site. It may be that part of the difficulty in accounting for the temperature dependence is due to a variation of the crystal-field parameters, since McEwen *et al.*<sup>17</sup> have reported a strongly anisotropic thermal expansion in Pr.

## VII. CONCLUSION

By considering the variety of information available on Pr, we have been able to deduce a set of exchange, crystal field, and magnetoelastic parameters for the hexagonal sites which are consistent with all of the magnetic properties. The dispersion relations for the magnetic excitations, and particularly their field dependence, allow the determination by a least-squares procedure of the isotropic and anisotropic components of the exchange interactions between the ions on the hexagonal sites, and of the magnetoelastic parameter  $B_{22}$  and the crystal-field splittings  $\Delta$  and  $\Delta_3$ . The critical field in the  $c$  direction at which the magnetic transition on the hexagonal sites occurs, together with the increase in moment which is observed, give further information on  $\Delta_3$  and place limits on the splitting  $\Delta_4$  which, in combination with the assumed relation between  $B_{60}$  and  $B_{66}$ , allows the determination of these parameters, plus  $B_{20}$  and  $B_{40}$ . The resulting crystal-field level scheme of Fig. 5 gives a good account of the magnetic contribution to the heat capacity. The temperature dependence of both the energies and widths<sup>8</sup> of the magnetic excitations are also well described, and their interaction

with the phonons is accounted for by the value of  $B_{22}$ , as are all the other magnetoelastic phenomena which have been studied.

We have noted above that the effective two-ion coupling which we have deduced includes the effect of the cubic sites and neglects possible field-dependent renormalization due to zero-point fluctuations, and that there remains a slight residual ambiguity about the sign of the anisotropic coupling between the two sublattices. There exists the further possibility that the form of the two-ion coupling may differ from that given by Eq. (2). Exchange interactions of higher ranks would behave similarly to some of the interactions which we have considered. Quadrupole couplings, or other multipole couplings of even rank, would however give rise to a number of effects discussed by Jensen<sup>5</sup> which have not been observed, and they are therefore probably unimportant. The good agreement between the value of  $B_{22}$  deduced from the molecular field and that found from magnetoelastic measurements also provides evidence that the quadrupole couplings are small.

The lower-lying crystal-field splittings  $\Delta$  and  $\Delta_3$  are rather well determined by our experiments. In particular, the field dependence of the excitations, and their dependence on uniaxial strain, show that  $\Delta$  must be close to 3.5 meV. The calculation by the random-phase approximation of the temperature dependence of the energies in the effective  $S = 1$  model<sup>1</sup> gives the somewhat lower value 3.2 meV, but when the full crystal-field level scheme is used, and possible effects of self-consistency and temperature-dependent crystal-field parameters are considered, a value of 3.5 meV accounts for the results within the combined uncertainties of the experiments and theory.  $\Delta_4$  and the other levels are not measured directly by neutron scattering and the values which we assign to the crystal-field parameters therefore depend on our interpretation of the high-field magnetic transition, and particularly on our assumption of the relationship between  $B_{60}$  and  $B_{66}$ . The temperature dependence of both the susceptibility and of  $c_{66}$  indicate that the splitting  $\Delta_2$  to the predominantly  $|\pm 2\rangle$  third-excited level might be underestimated in

Fig. 5, and hence that this assumption may not be valid.

We may therefore summarize the situation by saying that the effective exchange, crystal-field, and magnetoelastic parameters which we have deduced, when used in a Hamiltonian comprising  $\mathcal{H}_I$  and  $\mathcal{H}_{II}$  in Eqs. (1) and (2), give a good account of the magnetic properties of the hexagonal sites in Pr. On the other hand, we cannot exclude the possibility that different interactions are present, although presumably they are small, nor that further experiments will require some modifications in our parameters.

Our description of the cubic ions is much less complete. The crystal-field splitting  $\Delta_c$  to the first-excited state is known with good accuracy and the exchange parameters could in principle be deduced from the dispersion relations. It appears that the exchange anisotropy is of less importance for the cubic than for the hexagonal excitons. However, our values for crystal-field parameters must be considered as provisional, especially because of the discrepancy between the calculated and experimental temperature dependence of the susceptibility. The molecular field deduced from the magnetization on the hexagonal and cubic sites, measured by neutron diffraction, gives uniform mode energies on both types of site in generally good agreement with those observed.

Although our understanding of Pr has now reached a rather sophisticated level, additional experiments would further elucidate its magnetic properties. As mentioned earlier, a neutron-diffraction study of the temperature dependence of the susceptibility on the two types of site would be particularly helpful. The measurements of the excitation energies in higher magnetic fields would provide further information on the position of the  $|3\rangle$  level, and a more detailed study of the excitations on the cubic sites, especially in a magnetic field, would clarify the nature of the dipolar excited level, and hence of the influence of the trigonal distortion.

The observation by McEwen *et al.*<sup>17</sup> of a transition to an antiferromagnetic phase on the application of uniaxial stress opens up the prospect of studying this ideal metallic magnetic soft-mode system in both its ordered and disordered phases. Similarly, the nuclear ordering which has been detected by Lindelof *et al.*<sup>27</sup> at about 25 mK in heat-capacity experiments should give rise to interesting effects on the electronic magnetism. It has been predicted by Jensen<sup>10</sup> that this nuclear ordering should be accompanied by an electronic ordering of about  $0.5\mu_B$  per hexagonal ion, which should be readily observable. It would also be of interest to study the mechanism which induces magnetic ordering in crystals of Pr in which a small amount of, for example, Nd has been dissolved. Finally, it is important to determine the origin of the weak, quasielastic central peak observed by Houmann *et al.*<sup>28</sup> At present, it appears most likely that this is due to impurities, or possibly magnetic ordering of the ions near the surface of the crystal. The former explanation could be tested by studying crystals of varying purity, and the latter by investigations of the surface properties. Although the properties of Pr have been studied in unusual detail, many areas of its magnetic behavior still await further elucidation.

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<sup>1</sup>J. G. Houmann, M. Chapellier, A. R. Mackintosh, P. Bak, O. D. McMasters, and K. A. Gschneidner, Jr., *Phys. Rev. Lett.* **34**, 587 (1975).

<sup>2</sup>B. Bleaney, *Proc. R. Soc. London Sect. A* **276**, 39 (1963).

<sup>3</sup>B. D. Rainford, in *Proceedings of 17th Conference on Magnetism and Magnetic Materials, Chicago, 1971*, edited by C. D. Graham, Jr. and J. J. Rhyne, AIP Conf. Proc. No. 5 (AIP, New York, 1972), p. 591.

<sup>4</sup>B. D. Rainford and J. G. Houmann, *Phys. Rev. Lett.* **26**, 1254 (1971).

<sup>5</sup>J. Jensen, *J. Phys. C* **9**, 111 (1976).

<sup>6</sup>W. J. L. Buyers, T. M. Holden, and A. Perreault, *Phys. Rev. B* **11**, 226 (1975).

<sup>7</sup>D. H. Yang and Y. Wang, *Phys. Rev. B* **10**, 4714 (1974).

<sup>8</sup>P. Bak, *Phys. Rev. Lett.* **34**, 1230 (1975); *Phys. Rev. B* **12**,

5203 (1975).

<sup>9</sup>B. Grover, *Phys. Rev.* **140**, A1944 (1965).

<sup>10</sup>J. Jensen, *J. Phys. (Paris)* **40**, C5-1 (1979).

<sup>11</sup>T. Johansson, K. A. McEwen, and P. Touborg, *J. Phys. (Paris)* **32**, C1-372 (1971).

<sup>12</sup>K. A. McEwen, G. J. Cock, L. W. Roeland, and A. R. Mackintosh, *Phys. Rev. Lett.* **30**, 287 (1973).

<sup>13</sup>B. Lebech and B. D. Rainford, *J. Phys. (Paris)* **32**, C1-370 (1971).

<sup>14</sup>D. A. Parkinson, F. E. Simon, and F. H. Spedding, *Proc. R. Soc. London Sect. A* **207**, 137 (1951).

<sup>15</sup>S. B. Palmer and J. Jensen, *J. Phys. C* **11**, 2465 (1978).

<sup>16</sup>K. A. McEwen (private communication).

<sup>17</sup>K. A. McEwen, W. G. Stirling, and C. Vettier, *Phys. Rev. Lett.* **41**, 343 (1978); and *J. Phys. (Paris)* **40**, C5-26 (1979).

- <sup>18</sup>P. A. Lindgård, *J. Phys. C* **8**, L 178 (1975).  
<sup>19</sup>P. A. Lindgård and O. Danielsen, *J. Phys. C* **7**, 1523 (1974).  
<sup>20</sup>R. B. Stinchcombe, *J. Phys. C* **6**, 2484 (1973).  
<sup>21</sup>E. F. Shender, *Zh. Eksp. Teor. Fiz.* **66**, 2198 (1974) [*Sov. Phys. JETP* **39**, 1083 (1974)].  
<sup>22</sup>K. W. Becker, P. Fulde, and J. Keller, *Z. Phys. B* **28**, 9 (1977).  
<sup>23</sup>N. Hessen Andersen and H. Smith, *Phys. Rev. B* **19**, 384 (1979).  
<sup>24</sup>H. Bjerrum Møller and A. R. Mackintosh, *J. Phys. (Paris)* **40**, C5-28 (1979).  
<sup>25</sup>D. J. Newman, *Adv. Phys.* **20**, 197 (1971).  
<sup>26</sup>P. Touborg, *Phys. Rev. B* **16**, 1201 (1977); P. Touborg, R. Nevald, and T. Johansson, *Phys. Rev. B* **17**, 4454 (1978).  
<sup>27</sup>P. E. Lindelof, I. M. Miller, and G. R. Pickett, *Phys. Rev. Lett.* **35**, 1297 (1975).  
<sup>28</sup>J. G. Houmann, B. Lebech, A. R. Mackintosh, W. J. L. Buyers, O. D. McMasters, and K. A. Gschneidner, Jr., *Physica (Utrecht) B* **86-88**, 1156 (1977).