

# PHYSICS OF RARE-EARTHS.

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## The magnetism of praseodymium

J. Jensen

Physics Laboratory I. H.C. Ørsted Institute, University of Copenhagen,  
DK-2100 Copenhagen. Denmark

**Résumé.** — Les ions en site cubique et hexagonal du Pr (structure dhcp) constituent deux systèmes d'état fondamental singulet, non magnétiques et faiblement couplés entre eux. Le couplage entre ions en site hexagonal est de peu inférieur au couplage critique pour lequel l'état antiferromagnétique abaisse l'énergie du système. Ce composé est ainsi très sensible à différents paramètres (champ magnétique, compression uniaxiale, impuretés). Les études expérimentales des propriétés de l'état fondamental et du spectre d'excitation dans des conditions variées ont conduit à une compréhension détaillée des propriétés magnétiques des ions en site hexagonal.

**Abstract.** — The hexagonal and cubic ions of dhcp Pr constitute two non-magnetic singlet-ground-state systems, which are coupled only weakly. However, the two-ion coupling between the hexagonal ions is just below the critical value at which an antiferromagnetic ordered phase becomes energetically favoured at low temperatures. This makes the system very sensitive to external influences (magnetic field, uniaxial pressure, impurities), and experimental studies of the ground state properties and of the excitation spectrum under various conditions have led to a very detailed understanding of the magnetic properties of the hexagonal ions.

**1. Introduction.** — The magnetic properties of the light rare-earth metals are generally of greater complexity than those found in the second half of the lanthanide series. Consequently, earlier studies of rare-earth magnetism have tended to emphasize the heavy metals. However, in recent years the emphasis has gradually changed towards the light rare-earths, with Pr as the most studied example.

Pr crystallizes in the double-hexagonal-close-packed (dhcp) structure with stacking sequence ABAC along the *c*-axis. Ions in A layers are in an approximately cubic environment while ions in B and C layers experience a crystal field of hexagonal symmetry. The trivalent Pr-ion, which has two f-electrons ( $S = 1$ ,  $L = 5$ , and  $J = 4$  for the ground state multiplet), is a non-Kramers ion, implying that the crystal field may possibly produce singlet states.

The crystal-field splitting of the  $J = 4$  multiplet of the ions in Pr metals was first discussed in detail by Bleaney [1]. On the basis of the heat capacity and the magnetic susceptibility of polycrystalline Pr, he concluded that the ground states of both of the two kinds of ions are singlets. This implies, as pointed out originally by Trammell [2], that the system remains a Van Vleck paramagnet down to zero temperature, unless the two-ion coupling exceeds a critical value. The magnetism of singlet-ground-state systems has been discussed by many authors, for example by Cooper [3].

In the case of Pr, there has been a controversy about the existence of a magnetically ordered phase at low temperatures. Neutron diffraction measurements on a

polycrystalline sample by Cable *et al.* [4] revealed an antiferromagnetic phase below 25 K, but no traces of magnetic ordering were found in a single crystal at 4.2 K by Johansson *et al.* [5]. A great number of observations on (different) single crystals now consistently indicate that Pr metal is a subcritical system with an exchange coupling very close to the critical value.

The magnetic susceptibility of single crystals, as measured by Johansson *et al.* [5, 6], is highly anisotropic at low temperatures, the component parallel to the hexagonal axis being about ten times smaller than the perpendicular one. By neutron diffraction measurements Lebeck and Rainford [7] separated the contributions of the hexagonal and the cubic ions to the magnetization at 4.2 K, in an applied field of up to 5 T, and they found that the anisotropy was mainly due to the hexagonal ions. The extreme anisotropy of the susceptibility of the hexagonal ions determined unambiguously their ground state to be the  $|J_z = 0\rangle$  singlet (*z* being along the *c*-axis). The dipolar excited state of these ions is then the  $|\pm 1\rangle$  doublet. If the tetragonal distortion of the point symmetry of the cubic ions is neglected their ground state is the  $\Gamma_1$  singlet, with the  $\Gamma_4$  triplet as the excited level. The first experimental study of the excitation spectrum of Pr was carried out by Rainford and Houmann [8] using inelastic neutron scattering. Excitations were observed around 3 meV and 8 meV, which energies were assigned to modes propagating on the hexagonal and the cubic ions respectively.

For a more extensive account of the development

before 1971, which is described briefly above, we refer to the review given by Rainford [9]. Here we shall concentrate on the more recent investigations of the magnetic properties of Pr metal. Houmann *et al.* [10, 11, 12] have made very extensive measurements of the dispersion relations of the hexagonal and cubic excitations. They observed that the degeneracy of the magnetic singlet-doublet excitons is lifted whenever the wavevector has a component perpendicular to the  $c$ -axis, implying that the two-ion coupling is strongly anisotropic. When the temperature is raised, the dispersion is reduced and the linewidths increase drastically. The excitation energies of the hexagonal ions depend strongly on a magnetic field applied in the basal plane, and studies of this effect have made it possible to establish the crystal-field level-scheme for these ions. The field-experiment also revealed the presence of a strong magnetoelastic coupling manifesting itself as energy gaps proportional to the field at the crossing points of the exciton and phonon dispersion relations. A number of associated magnetoelastic phenomena were predicted and later studied experimentally. Most recently McEwen *et al.* [13] have succeeded in inducing the antiferromagnetic phase by applying a uniaxial pressure of 0.8 kbar along an  $a$ -direction at 7.4 K. Most of the experimental observations may be explained in terms of random-phase calculations, and the detailed description of the system which has been achieved makes it suitable for studying more subtle effects due to the conduction electrons, impurities or the nuclei.

**2. The magnetic excitons.** — The study of the elementary magnetic excitations of Pr have given detailed information about the character of the two-ion coupling and the crystalline field acting on the 4f-electrons in the metal. In Pr, as in most of the light rare-earths, the crystal field dominates the relatively weak exchange coupling, and the elementary excitations are magnetic excitons. These collective modes consist of linear combinations of single-ion crystal-field excitations propagating through the crystal because of the magnetic coupling between the ions. The random-phase (RPA) theory for the magnetic excitons has been worked out by several authors [3, 9, 14, 15]. In the case of Pr the two singlet-ground-state systems may be considered independently (at low temperatures), because the large difference between the excitation energies allows a second order perturbative decoupling [16]. At low temperatures the thermal populations of the excited levels are small, and at zero field the hexagonal ions may be considered to constitute an effective  $S = 1$  system described by the singlet-doublet crystalfield splitting  $\Delta_h \approx 3$  meV. Similarly, we may consider the cubic ions as a pure  $\Gamma_1$ - $\Gamma_4$  system with the splitting  $\Delta_c \approx 8$  meV.

The two-ion Hamiltonian which we shall consider is complicated by the inclusion of an anisotropic

exchange coupling besides the normal Heisenberg coupling :

$$\begin{aligned} \mathcal{H}_{II} = & -\frac{1}{2} \sum_{i,j} \mathfrak{J}(\mathbf{r}_i - \mathbf{r}_j) \mathbf{J}_i \cdot \mathbf{J}_j \\ & + \frac{1}{2} \sum_{i,j} \mathcal{K}(\mathbf{r}_i - \mathbf{r}_j) [(J_{x,i} J_{x,j} - J_{y,i} J_{y,j}) \cos 2 \varphi_{ij} \\ & + (J_{x,i} J_{y,j} + J_{y,i} J_{x,j}) \sin 2 \varphi_{ij}] \end{aligned} \quad (1)$$

$\mathbf{J}_i$  is the total angular moment of the ion at the position  $\mathbf{r}_i$ , and  $\varphi_{ij}$  is the angle between the  $x$ -axis and the projection of  $\mathbf{r}_i - \mathbf{r}_j$  on the basal plane. The  $x$ -,  $y$ -, and  $z$ -axes are defined to be along the  $a$  (1120)-,  $b$  (10 $\bar{1}$ 0)-, and  $c$  (0001)-axes of the hexagonal lattice respectively. When the wavevector,  $\mathbf{q}$ , is along the  $b$ -axis ( $\Gamma M$ ) the excitons propagating on the hexagonal sites are pure  $x$ - and  $y$ -modes, and because the hexagonal lattice has two ions per unit cell (B and C corresponding to an hcp-structure) they are split into acoustic and optical branches. The dispersion relation in this case for the acoustic (optical)  $x$ -mode is given by :

$$(E_{\mathbf{q}}^{xx})^2 = \Delta_h [\Delta_h - 2 M_h^2 R_h (\mathfrak{J}_h(\mathbf{q}) - \mathcal{K}_h(\mathbf{q}) (\pm) | \mathfrak{J}'_h(\mathbf{q}) - \mathcal{K}'_h(\mathbf{q}) |)] \quad (2)$$

where  $M_h^2 = J(J+1)/2 = 10$  and  $R_h$  is the difference in Boltzmann population factors between the singlet and doublet states.  $\mathfrak{J}_h(\mathbf{q})$  and  $\mathfrak{J}'_h(\mathbf{q})$  are the Fourier transforms of the Heisenberg coupling within and between the two hexagonal sublattices, and equivalently for the anisotropic coupling. The same expression applies for the  $y$ -mode, except that the signs in front of  $\mathcal{K}_h(\mathbf{q})$  and  $\mathcal{K}'_h(\mathbf{q})$  are changed, which means that the two kinds of excitons are degenerate only if these anisotropic coupling parameters are zero. This is the case, according to symmetry arguments [16], when  $\mathbf{q}$  is parallel to the  $c$ -axis. In the  $x$ -direction ( $\Gamma K$ ) the last term in (1) gives rise to a coupling between the acoustic (optical)  $x$ -mode and the optical (acoustic)  $y$ -mode.

Houmann *et al.* [10, 11] have measured the energies of the excitons propagating on the hexagonal sites at 6.4 K by inelastic neutron scattering. The dispersion relations of the acoustic and optical doublet excitons were determined in the symmetry directions, shown in figure 1, and at the boundaries of the Brillouin zone. The appearance of four branches instead of two when  $\mathbf{q}$  is along  $\Gamma K$  or  $\Gamma M$ , shows that the doublet-excitons are split into  $x$ - and  $y$ -modes which requires an anisotropic two-ion coupling such as that included in (1). The neutron-scattering cross-section depends on the polarization vector of the modes, which has made it possible to classify the different branches (see figure 1).

The apparent necessity for introducing anisotropic two-ion couplings without knowing the mechanisms responsible for these terms implies that the occurrence of large quadrupole (electric multipole) couplings

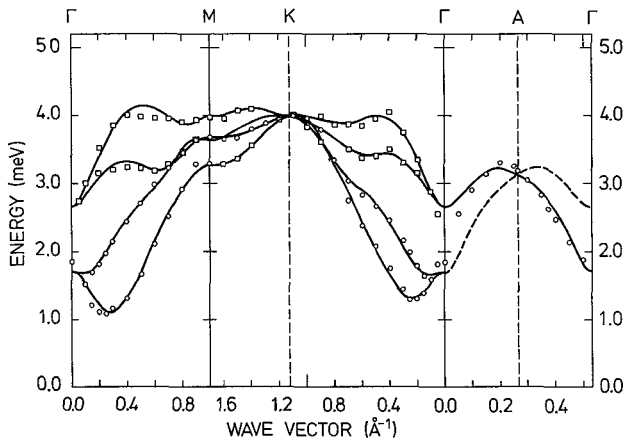


Fig. 1. — The dispersion relations for magnetic excitons propagating on the hexagonal sites in Pr at 6.4 K. The squares and circles denote the experimental results for the acoustic and optical modes respectively. The lower of the optical and acoustic branches are the excitons polarized parallel to the  $\mathbf{q}$ -vector (predominantly) and the upper ones are the transverse excitons. The solid lines represent the result of a Fourier analysis which includes seven nearest neighbours in the basal plane (after Ref. [12]).

cannot be excluded *a priori*. However, in this case both the temperature- and the field-dependence of the excitons would be significantly altered [16], and the consistent and successful interpretation of the experiments which has been achieved without introducing quadrupole couplings guarantees reasonably well that these terms are small. Higher order magnetic multipole couplings are included effectively in (1) (see Ref. [16]) as is the normal magnetic-dipole coupling, but this coupling is negligible compared to the anisotropy observed.

Of particular interest is the exciton of lowest energy, which is the optical  $y$ -mode with a wavevector of  $0.25 \text{ \AA}^{-1}$  along the  $y$ -axis ( $\Gamma M$ ), see figure 1. This excitation is the incipient magnetic soft mode, i.e., it is that mode which corresponds in wavevector and polarization with the magnetic structure formed when the system is forced to order. Indeed this mode shows a very rapid temperature dependence [10], e.g. the energy of this mode is reduced by a factor of two when the temperature is changed from 20 to 7 K. However, between 7 and 0.1 K neither it or any other exciton changes appreciably. The simple RPA-expression, (2), describes accurately the temperature dependence of the excitons, and also of the incipient soft mode, using  $\Delta_h = 3.2 \text{ meV}$  [10, 15]. With this value of  $\Delta_h$  the exchange is deduced to be approximately 90 % of that which is required to drive the energy of the soft mode to zero.

The dispersion relation, (2), is the same as derived by Bak [15] in zero order of a high-density ( $1/Z$ ) expansion of the Green's functions. To next order in this expansion Bak found that the most important correction is the appearance of an intrinsic linewidth of the excitons, which increases drastically when the temperature is raised above 7 K. This damping is due

to scattering of the excitons on single-site fluctuations, whereas the effect of exciton-exciton interaction is of second order in  $1/Z$ . To first order in  $1/Z$  the theoretical lineshapes are determined self-consistently by  $\Delta_h$  and the (experimental) density of states of the excitons. The spectral functions convoluted with the experimental resolution function gave an almost complete agreement between the theory and the neutron scattering experiments for the optical excitons. The intrinsic linewidth of the acoustic modes close to zero wavevector shows a special behaviour [12] by being large in the low temperature limit, which is in contrast to the theory of Bak. The other damping mechanism which might be of importance in the metal is the scattering of the magnetic excitations against the electron-hole pair excitations of the conduction electrons treated in detail by Fulde and coworkers [17]. The application of their approach [12, 18], utilizing a free-electron-like model for the conduction electrons, indicates that this damping mechanism is of minor importance compared either with the one considered by Bak (at temperatures below 30 K) or, in the limit of zero temperature (below 7 K), with the experimental resolution, except for the acoustic excitons at small wavevectors ( $|\mathbf{q}| < 0.2 \text{ \AA}^{-1}$ ). At these wavevectors and below 7 K the electron-hole pair scattering gives rise to a linewidth of the excitons proportional to the inverse of  $|\mathbf{q}|$  ( $\geq 0.001 \text{ \AA}^{-1}$ ). This prediction is consistent with the experimental findings at 6.4 K, and the observation of a linewidth (full width at half-maximum) which at  $|\mathbf{q}| = 0.05 \text{ \AA}^{-1}$  is about 1 meV, agreeing reasonably with the model calculation.

Houmann *et al.* [12] have also measured the dispersion relation of the  $x$ - $y$  excitons propagating on the cubic sites, shown in figure 2. The dispersion is less pronounced than in the case of the hexagonal excitons, which is consistent with  $\Delta_c$  lying between 8.3-8.4 meV and  $M_c^2 = 20/3$  corresponding to the  $\Gamma_1$ - $\Gamma_4$  model (the dispersion relation is given by (2) with the index  $h$  replaced by  $c$ ). The most significant difference is that

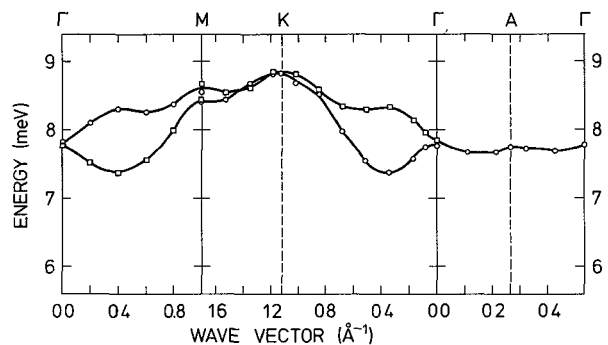


Fig. 2. — The dispersion relations for the excitons which propagate on the cubic sites in Pr at 6.4 K. The two branches are the acoustic and optical modes, the optical one lying below the acoustic branch. The polarization vector of the excitons is perpendicular to the  $c$ -axis. A possible splitting of the branches into two different modes was not resolved by the experiment. The full lines are guides for the eyes (after Ref. [12]).

the anisotropic coupling,  $\mathcal{K}(\mathbf{r}_i - \mathbf{r}_j)$ , seems to be unimportant for these excitons. In the neutron scattering experiment the  $x$ - and  $y$ -excitons had (almost) equal weight, and the experimental resolution was not sufficient to detect a small separation in energy of the two modes. In order to resolve the possible splitting of the  $x$ - and  $y$ -modes further experiments are planned. It seems, however, that the splitting must be smaller than 0.5 meV.

**3. Field dependence of the magnetic excitons.** — The application of a magnetic field in the basal plane admixes the singlet and one of the doublet states of the hexagonal ions, corresponding to the development of a magnetic moment parallel to the field. In agreement with the effective  $S = 1$  model, Houmann *et al.* [12] observed that the hexagonal excitons are strongly dependent on such a field. At 6.4 K they measured the energies of the hexagonal excitons propagating along an  $a$ - or  $b$ -direction perpendicular to the field applied in the basal plane at three values of the field (approx. 1.5, 3, 4.5 T). In figure 3 is shown the result at the intermediate field. The most striking detail is the very large shift of the lowest energy mode (from 1 to 2 meV).

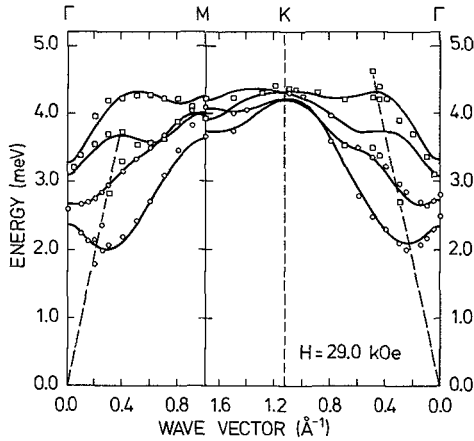


Fig. 3. — The energies of the excitons propagating on the hexagonal sites of Pr at 6.4 K, when an external field of 2.9 T is applied. The field is along the basal-plane direction perpendicular to the  $\mathbf{q}$ -vector. The solid lines are the result of the least-squares analysis explained in the text, neglecting the hybridization effects of the exciton-phonon interactions, which are most pronounced for the acoustic excitons polarized along the  $\mathbf{q}$ -direction (after Ref. [12]).

The change of symmetry produced by the magnetic field may allow interactions between the excitons and the phonons which are absent in zero field [16]. Clear indications of such couplings to the phonons are seen in the excitation spectrum shown in figure 3. The selection rules for the exciton-phonon interaction in the presence of a magnetic field were determined in Ref. [16], and the coupling manifested in the excitation spectrum was shown to be produced by a distortion

of the hexagonal symmetry of the basal plane (a  $\gamma$ -strain deformation). In the quantitative analysis of the field experiment the magnetoelastic change of the crystal-field energy was found to affect the excitons significantly.

The experimental results of the field-dependence of the excitons were analysed in terms of the following molecular-field Hamiltonian for the hexagonal ions :

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

written in terms of Stevens operators.  $\mathbf{H}_{\text{MF}}$  is the sum of the external field and the molecular field of the surrounding ions (including the cubic ones). Besides the usual single-ion term we include the magnetoelastic  $\gamma$ -strain term,  $B_{22}$ , where  $c_\gamma = 4 c_{66}/N$  ( $N$  is the total number of ions per unit volume) see Ref. [16]. The number of parameters is reduced by utilizing the relation  $B_{66} = -\frac{77}{8} B_{60}$ , valid in a point charge model with an ideal  $c/a$ -ratio. This assumption seems plausible as the relation is nearly fulfilled in the case of rare-earth ions diluted in Y, Lu, and Sc, which have been studied by Touborg and coworkers [19, 20].

The parameters in (3) were determined by a least-squares fit to the field-dependence of the hexagonal excitons [12]. The molecular field was determined by the requirement that the magnetic moment of the hexagonal ions should be equal the experimental one determined by Lebeck and Rainford [7]. In the fit we used the Fourier analysis of the zero-field dispersion relation, which result is given by the solid line in figure 1, and the quality of the fit obtained is exemplified by figure 3. In table I are given the crystal-field parameters determined by this analysis, and they are compared with the ones derived by Touborg *et al.* [20] from their study of Pr diluted in Y and Lu. The comparison is very satisfactory and indicates that the magnetic couplings between the Pr ions only have a minor influence on the crystal-field parameters, which is not the case in other rare-earth metals, for instance Tb. This is discussed further in a review [21] of the importance of two-ion magnetic anisotropy in the rare-earth metals. In table II are given the wavefunctions and the relative energies of the crystal-field levels of the hexagonal ions in zero field, using

Table I. — *The crystal-field parameter for the hexagonal ions of Pr metal (after Ref. [12]) compared with the parameters determined in dilute Pr (after Ref. [20]) in units of meV. The field-dependence of the exciton energies determined also the magnetoelastic coupling parameter  $(B_{22})^2/c_\gamma = (0.035 \pm 0.004)$  meV.*

	$B_{20} \times 10^2$	$B_{40} \times 10^4$	$B_{60} \times 10^4$	$B_{66} \times 10^4$
Metal	$19 \pm 4$	$-5.7 \pm 5$	$1.00 \pm 0.1$	$-9.6$
Dilute	$13 \pm 5$	$-2.7 \pm 1$	$0.89 \pm 0.06$	$-9.3 \pm 1.8$

Table II. — *The wavefunctions and the relative energies of the crystal-field levels as determined by the parameters in table I for the hexagonal ions of Pr metal. In general, the uncertainties (given for the lower levels) increase with increasing energy.*

Wavefunction	Energy (meV)
$ 0\rangle$	0
$ \pm 1\rangle$	$3.52 \pm 0.08$
$ 3^s\rangle$	$4.42 \pm 0.25$
$0.925 \pm 2\rangle + 0.379 \mp 4\rangle$	7.82
$ 3^a\rangle$	9.26
$0.925 \pm 4\rangle - 0.379 \mp 2\rangle$	13.03

the parameters derived from the field-experiment. We may notice that the singlet-doublet splitting,  $\Delta_h = 3.52$  meV, is slightly larger than the value determined from the temperature dependence of the excitons.

McEwen *et al.* [22] have measured the bulk magnetization of Pr in high fields, and they detected a first order transition at low temperatures when a field of about 32 T was applied along the  $c$ -direction. At the transition the average moment changes discontinuously by  $1.04 \mu_B/\text{ion}$ . In view of the magnitude of this jump in magnetization the most likely explanation for the transition is that the crystal-field level  $|+3\rangle$  slightly mixed with  $| - 3 \rangle$  and the former ground state level,  $\sim |0\rangle$ , of the hexagonal ions are crossing each other [22]. This interpretation is consistent with the level scheme in table II, as these parameters, using a simplified model for the transition, predict that it occurs at a field around 38 T with a change of the hexagonal moments by  $2.24 \mu_B$  (corresponding to a change of the average moment of  $1.12 \mu_B$ ).

**4. Magnetoelastic effects.** — The presence of the quite strong magnetoelastic coupling,  $B_{22}$ , leads to a number of effects which are discussed in [16] using the simplified level scheme of the effective  $S = 1$  model for the hexagonal ions. The couplings at finite field between the acoustic excitons and the transverse phonons propagating in the basal plane are directly related to the magnetoelastic term in (3). From the magnitudes of the exciton-phonon energy gaps,  $B_{22}$  was estimated to be about 30 meV using the  $S = 1$  model [16]. However, the  $|3^s\rangle$  singlet which is deduced to lie close the  $|\pm 1\rangle$  doublet (see table II) has a pronounced effect on the strength of the interaction, and it is found that a value of  $|B_{22}| = (18 \pm 3)$  meV accounts for the dynamic couplings when the total level scheme is used [12].

The dynamic coupling between the magnetic and elastic excitation has also been studied in the long wavelength limit. Palmer and Jensen [23] have measured the velocity of the ultrasonic waves corresponding to the elastic constant  $c_{66}$  as a function of field

and of temperature. At 4.2 K,  $c_{66}$  was found to be very sensitive to a field applied in the basal plane, whereas it was almost independent of a field along the  $c$ -axis, which anisotropy reflects the behaviour of the magnetic susceptibility of the hexagonal ions. The experiment also disclosed a large difference between the cases where the field is parallel to an easy  $a$ -axis or to a  $b$ -axis ( $c_{66}$  was found to be reduced by 11 % and 16 % respectively at a field of 4 T). This anisotropy is explained by the splitting of the  $|3^s\rangle$  and  $|3^a\rangle$  levels (due to  $B_{66}$ ). Using the total crystal-field level scheme given in table II, Palmer and Jensen [23] obtained a very satisfactory fit to both the field and temperature dependence of  $c_{66}$ . Neglecting a possible magnetoelastic coupling to the cubic ions, they determined  $(B_{22})^2/c_\gamma$  to be  $(0.029 \pm 0.003)$  meV and for the non-magnetic value of  $c_{66}$  at zero temperature they obtained  $1.62 \times 10^{10} \text{ Nm}^{-2}$ . These values correspond to  $c_\gamma = 14.0$  eV and  $B_{22} = 20.2$  meV, and they agree within the uncertainties with the results deduced from the exciton data (see table I).

K. A. McEwen (private communication) has measured the field dependence of the  $\gamma$ -strain at low temperatures, and also in this case a satisfactory account is obtained using the same model calculations as above. The quantitative analysis of all the different magnetoelastic phenomena (the magnetostriction data are only preliminary) are consistent with each other, when using a model which neglects the possible magnetoelastic effects of the cubic ions, and which applies the crystal-field level scheme of table II for the hexagonal ions.

Based on the  $S = 1$  model, it was predicted [16] that it should be possible to induce a longitudinal polarized antiferromagnetic phase, corresponding to the incipient soft mode in figure 1, by the application of a uniaxial pressure along an  $a$ -axis of about 0.9 kbar in the low temperature limit. Recently, McEwen *et al.* [13] have observed this transition at a pressure of 0.8 kbar at 7.4 K. A calculation which includes all the crystal-field levels in table II and uses the parameters deduced from the field-dependence of  $c_{66}$  predicts the critical pressure to be 0.76 kbar at 7.4 K in close agreement with the experiment. At higher temperatures the calculation indicates a drastic increase of the critical pressure corresponding to the temperature dependence of the incipient soft mode, such that at 25 K it should be about 10 kbar. The agreement between the experiment and the calculation provides decisive support for the model Hamiltonian for the hexagonal ions, and, specifically, it means that the exchange coupling of the incipient soft mode has to be close to 92 % of the critical value (corresponding to  $\Delta_h = 3.52$  meV).

**5. Induced magnetic ordering in dhcp Pr.** — The barely undercritical value of the exchange coupling in dhcp Pr makes it a unique singlet-ground-state system which is very sensitive to external pertur-

bations. As we have seen in the preceding sections, the incipient soft mode in particular depends strongly on temperature, magnetic field, and uniaxial stress.

Besides the application of the uniaxial pressure there exist other possibilities for inducing the magnetically ordered phase in Pr. The magnetic hyperfine interaction between the ionic and nuclear spins is one of them. Murao [24] has calculated the effect of the nuclear contributions to the total magnetic susceptibility, which is found to be of importance below 100 mK. An estimate based on the previously presented parameters gives a Néel temperature of about 40 mK and a maximum value of the ionic moments of  $0.6 \mu_B$  at zero temperature. The first of these estimates is consistent with the observation of an anomaly in the nuclear heat capacity by Lindelof *et al.* [25] indicating  $T_N$  to lie between 25 and 30 mK. The ordered phase below  $T_N$  should be equivalent to the one observed in Nd, which Bak and Lebech [26] propose to be a *triple-q* modulated structure. This structure consists of a superposition of the three *single-q* domains of the antiferromagnetic phase. In the case of the pressure induced magnetic phase, the symmetry is lower and energetically two of the *single-q* domains are suppressed, leaving only the one for which  $\mathbf{q}$  is perpendicular to the pressure axis.

Finally, the introduction of magnetic impurities may enhance the low temperature susceptibility and thereby increase  $T_N$ . Lebech *et al.* [27] have studied the behaviour of the Pr-Nd alloy system, and in a single crystal containing 3 % Nd they found  $T_N$  to be 6.3 K.

Below 10 K, Houmann *et al.* [11] have observed a weak quasielastic peak in Pr at the critical  $\mathbf{q}$ -vector, the intensity of which increases steadily with decreasing temperature (down to 1 K). In contrast to a singlet-triplet system (at finite temperature), for instance Pr<sub>3</sub>Tl [28], there are no elastic contributions to the

ionic susceptibility within the RPA. There exists a number of other possibilities for the occurrence of a small central peak in Pr, most of which contributions, however, should reflect the saturation of the ionic susceptibility around 7 K, and hence stay constant (or decrease) below this temperature. This should apply to the contributions due to either the coupling to the cubic singlet-triplet system, or the single-site fluctuations [15], or the scattering against electron-hole pair excitations [18], and in the temperature range considered the nuclei are unimportant. The two possibilities which are candidates for explaining the temperature dependence of the central peak are the influence of small concentrations of magnetic impurities (here Nd is a very likely possibility), or that the Pr-ions close to the surface may possibly be magnetic at low temperatures. The latter is due to the fact that, for the ions near the surface, the change of symmetry will lift the degeneracy of the doublet state and thus create a situation equivalent to the application of the uniaxial pressure.

The existence of magnetic ordering in polycrystalline Pr below 25 K [4] might be produced by (large) internal stresses, as suggested by McEwen *et al.* [13]. However, we expect that the two mechanisms which may be responsible for the central peak in the single crystal may also be the necessary elements for explaining the behaviour of polycrystalline Pr.

**Acknowledgments.** — The paper presents the result of a combined effort of many people, and I am much indebted to all of them. I should especially like to acknowledge the comprehensive experimental work of J. G. Houmann, and also the many helpful and useful comments and contributions of K. A. McEwen, B. D. Rainford, S. B. Palmer, P. Fulde, D. Yang, P. Bak, P. Touborg, and A. R. Mackintosh.

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