Magnetic effects on the elastic constants of praseodymium

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Abstract. Ultrasonic studies of the elastic constant, \( c_{66} \), of DHCP Pr are reported. Using CdS thin-film transducers we have measured \( c_{66} \) as a function of temperature and as a function of an applied magnetic field at 4.2 K. \( c_{66} \) is found to be strongly affected by a field applied in the basal plane, whereas the application of a field along the c-axis has almost no effect. This behaviour reflects the anisotropy of the magnetic susceptibility of the hexagonal ions, indicating that they dominate the magnetic effects on \( c_{66} \). Neglecting magnetic contributions from the cubic ions, the observed behaviour of \( c_{66} \) is in agreement with our calculations based on the magnetic Hamiltonian for the hexagonal ions which has been deduced from the field dependence of the magnetic excitations.

1. Introduction

Pr crystallises in the DHCP (double-hexagonal-close-packed) structure with stacking sequence ABAC. Ions on the A sites are in an approximately cubic environment while the B and C sites experience a crystal field of hexagonal symmetry. The ions on each sublattice constitute a singlet ground state system, and the coupling between the ions is only just below the critical value for an induced moment system. For example, the addition of a small amount of Nd produces magnetic order at low temperatures.

At zero field the paramagnetic excitations of the hexagonal ions correspond to transitions between the ground state singlet \( |J_z = 0\rangle \) and the excited doublet \( |\pm 1\rangle \). The experimental behaviour of these excitations is quite well represented by an effective \( S = 1 \) model with a crystal field splitting of \( 3.2 \text{ meV} \) (Houmann et al 1975, Bak 1975). The ground state of the cubic ions is presumably close to be a \( r_1 \) singlet with the \( r_4 \) triplet as the dipolar excited state at an energy of approximately \( 8 \text{ meV} \) (Rainford and Houmann 1971). The magnetic coupling between the two kinds of ions is relatively weak making a second-order perturbative decoupling of the excitations of the two systems a fair approximation (Jensen 1976).

The application of a field in the basal plane admixes the \( |0\rangle \) and \( |\pm 1\rangle \) wavefunctions of the hexagonal ions (corresponding to the development of a magnetic moment parallel to the field). In agreement with the \( S = 1 \) model Houmann et al (1977) (see also Jensen 1976) observed that the hexagonal excitations were strongly dependent on such a field (at 6.4 K). Their 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. Based on the \( S = 1 \) model, Jensen (1976)
predicted that associated with the appearance of these energy gaps the elastic constant $c_{66}$ should be reduced drastically when applying a field in the basal plane, while all the other elastic constants should have a negligible field dependence.

Palmer and Isci (1977) attempted to verify the prediction experimentally by measuring the field dependence of $c_{GG}$ at 4.2 K in Pr. They obtained values for $c_{66}$ by determining the velocity of a shear acoustic mode propagating in the basal plane with particle motion also confined to the basal plane. Their results indicated almost no magnetic field dependence of $c_{66}$ in fields of up to 7 T. The appropriate acoustic mode was generated by a 15 MHz quartz transducer that was bonded to the sample with epoxy resin, a standard technique for samples with high values of thermal expansion and contraction. Using even this very rigid bond the acoustic echo train was badly distorted below 100 K but the value of $c_{66}$ obtained at 4.2 K in zero field was in fair agreement with earlier measurements of Greiner et al (1973) and Lüthi et al (1973). These authors also had bond problems, Greiner et al used vacuum grease with a very slow and controlled cool to 4.2 K while Lüthi et al used an indium bond that allowed only one echo to be observed.

We have now repeated the measurements of $c_{66}$ using a CdS thin-film transducer, vacuum evaporated onto the surface of the sample. These transducers, which adhered directly to the sample surface over a wide range of temperatures, have overcome nearly all the problems associated with measurement of the elastic properties of materials that exhibit large changes in dimensions (Palmer 1976). The results presented here will demonstrate, very forcibly, the care that has to be taken when measuring the elastic properties of the rare earth metals with quartz transducers.

From their studies of the field dependence of the exciton energies Houmann et al (1977) were able to establish the total crystal-field level scheme for the hexagonal ions (see also Jensen 1977) together with a determination of the magnetoelastic coupling parameter (the application of a field in the basal plane induces a distortion of the lattice which in turn affects the excitons). Knowing the total crystal-field Hamiltonian it is possible to perform a more realistic calculation of the magnetic effects on $c_{66}$ than the one based on the $S = 1$ model. In § 3 we derive an expression for the magnetic contributions to $c_{66}$ at a finite field and temperature, valid in the general case. Numerical calculations of $c_{66}$ based on the Hamiltonian determined by Houmann et al (1977), are performed and compared with the experiments.

2. Experimental details

The Pr boule was grown by Dr D Hukin at the Clarendon Laboratory, Oxford University, using a float zoning technique. The start material was supplied as sublimed grade by Rare Earth Products Ltd with a purity of 99.99% against metal contaminants. The single crystal used for these measurements was spark machined from the boule and was in the form of a cylinder 4.675 mm long and 3 mm diameter. The ends of the cylinder were spark planed flat and parallel to $\pm 1 \mu m$. The $a (11\overline{2}0)$ axis of the sample was parallel to the cylinder axis and the $b (10\overline{1}0)$ and $c (0001)$ axes in the basal plane of the cylinder.

The ultrasound was generated by a 15 MHz CdS thin-film transducer that was vacuum evaporated onto the surface of the sample (Llewelyn et al 1969). The angle between the evaporation direction and the sample surface was 35° so that a shear wave transducer was produced with shear wave displacement parallel to the $a$ direction. This acoustic mode with propagation direction along the $b$ axis and particle motion along the $a$ axis yields directly the elastic constant $c_{66}$ which is associated with the distortion of the
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hexagonal symmetry of the basal plane. The velocity of the acoustic wave \( v_{66} \) is related to \( c_{66} \) by \( c_{66} = \rho v_{66}^2 \), where \( \rho \) is the density of the material.

The velocity of sound was measured by the pulse echo overlap (Papadakis 1964) technique to an absolute accuracy of \( \pm 0.5\% \) and a relative accuracy of 5 parts in 10^5. The sample was maintained at 4.2 K by standard cryogenic techniques either in the pole pieces of an 11” electromagnet or in the bore of a superconducting magnet. The alignment of the appropriate crystallographic direction in the magnetic field was accurate to within \( \pm 15^\circ \) of arc. This accuracy was necessary because of the sharp angular dependence of \( c_{66} \) on magnetic field orientation in particular for a \( c \) axis field.

3. Theory

The coupling between the magnetic system and the transverse sound waves which have their propagation and polarisation vectors lying in the basal plane is described by the Hamiltonian (see for example Jensen 1976)

\[
\mathcal{H}_{me} = - \sum_j B_{22}(j) \epsilon_{12}(j) O(J_j)
\]

where

\[
O(J_j) = \frac{1}{2} i \sqrt{\frac{3}{8}} (J_2^2 - J_+^2)_j
\]

\( J_j \) is the total angular moment of the \( j \)th ion, and \( \epsilon_{ab}(j) \) are defined as usual in terms of the elastic displacement, \( u(x, t) \):

\[
\epsilon_{ab} = \frac{1}{2} \left( \frac{\partial u_a}{\partial x_b} + \frac{\partial u_b}{\partial x_a} \right).
\]

The three cartesian 1, 2 and 3 axes are along the \( x, y \) and \( z \) directions respectively which we define to coincide with the \( a, b \) and \( c \) directions of the hexagonal lattice. In the long-wavelength limit equation (1) might be considered to include the possible two-ion magnetoelastic couplings in an effective fashion. \( B_{22}(j) \) takes on two different values in the case of \( \text{Pr} \) for the moment we neglect this complication considering a crystal with only one ion per unit cell.

The magnetic Hamiltonian is

\[
\mathcal{H}_M = \sum_i \mathcal{H}_c(J_i) - \frac{1}{2} \sum_{i \neq j} \mathcal{J}(ij)J_iJ_j
\]

in which expression \( \mathcal{H}_c \) is the single-ion Hamiltonian including the Zeeman term in the presence of an applied field. The molecular-field (MF) Hamiltonian is diagonalised determining the \( (2J + 1) \) eigenenergies, \( E_n \) and the corresponding eigenfunctions, \( | \Psi_n \rangle \). The two-ion part of \( \mathcal{H}_m \) is expanded in terms of the basis excitation operators, \( a_{\mu}^i \) (Holden and Buyers 1974, Bak 1974) and the \( O(J_j) \) in equation (1) are treated in a similar manner. Here we shall be concerned only with the excitations in the long-wavelength limit in which case \( \epsilon_{12}(j) \) may be expanded in terms of the normal phonon coordinates \( (\beta_{k,s}) \) as

\[
\epsilon_{12}(j) = \langle \epsilon_{12} \rangle + \frac{1}{2} \sum_{k,s} i(k_1 F_{k,s}(2) + k_2 F_{k,s}(1)) \times \exp(ik \cdot R_j)(\beta_{k,s} + \beta_{-k,s})
\]

where \( \langle \epsilon_{12} \rangle \) is the homogeneous strain (the effect of which is to be included in the MF
Hamiltonian) and

\[ F_{k,s}(x) = \left[ 2NM\omega_s(k) \right]^{-1/2} f_{k,s}^x \]

(5b)

where \( N \) is the number and \( M \) the mass of the ions. \( \omega_s(k) \) is the eigenfrequency of the \( s \)th phonon mode, and \( f_{k,s}^x \) is the \( x \) component of its polarisation vector.

The coupled equations of motion for \( a_{\nu}^k \) and \( \beta_{k,s} \) are deduced, and they are reduced to a linear set by a random-phase decoupling (\( a_{\nu}^k a_{\mu}^l = \langle a_{\nu}^l a_{\mu}^k + a_{\mu}^l a_{\nu}^k, i \neq j \) followed by a Fourier transformation. The thermal average values of single-ion quantities in these equations are evaluated using the partition function of the MF Hamiltonian. The energies of the normal modes are then the roots of the determinant of the linear set of equations (or equivalently the poles of the corresponding Green functions).

The amplitude of the coupling between the magnetic excitons and the phonons goes to zero \((\propto \sqrt{q})\) as \( q \) goes to zero, and the energies of the uniform modes are not changed. However, the slopes of the phonon dispersion relations (i.e., the acoustic velocities) are modified which may be expressed as changes of the corresponding elastic constants. In the case considered we find

\[ \Delta c_{66}/c_{66}^0 = -1/c_\gamma B_{22}^2 \Xi \]

where \( c_\gamma = 4c_{66}^0/N \) \( (c_{66}^0 \) is the non-magnetic value of the elastic constant). \( \Xi \) is a quadrupole susceptibility. The (zero-frequency) susceptibility of the operator set \((A, B)\) is defined in terms of the MF Hamiltonian as

\[ \chi_{A, B} = \sum_{E_\nu \neq E_\mu} \langle v | A | \mu \rangle \langle \mu | B | v \rangle \frac{n_\mu - n_v}{E_\nu - E_\mu} + \frac{1}{k_B T} \left( \sum_{E_\nu \neq E_\mu} \langle v | A | \mu \rangle \langle \mu | B | v \rangle n_\mu - \langle A \rangle \langle B \rangle \right) \]

(7)

where \( n_\mu \) is the population of the \( \mu \)th level. In terms of \( \chi_{A, B} \), \( \Xi \) is given by

\[ \Xi = \chi_{0, 0} + \mathcal{J}(0) \sum_q \chi_{0, q}^2 [1 - \mathcal{J}(0)\chi_{q, q}]^{-1}. \]

(8)

The equations (6)–(8) are consistent with the results obtained by Thalmeier and Fulde (1975). At zero field \( \chi_{0, 0} \) vanishes identically (because of time reversal symmetry) and (6)–(8) reduce to the result of Dohm and Fulde (1975). We neglect here the terms introduced by the rotational invariance condition as these terms are an order of magnitude smaller than the one we are going to consider. In the case of the effective \( S = 1 \) model the expressions above are equivalent to that obtained by Jensen (1976) at 0 K.

The generalisation to the case of two different magnetic ions (denoted by \( h \) and \( c \)) is straightforward to achieve. Here we write down the result when only one of the two coupling parameters, \( B_{22}(h) = B_{22}(c) \), is nonzero, namely

\[ \Xi = \frac{1}{2} \chi_{0, 0}(h) + \sum_q \chi_{0, q}^2 (h)[\mathcal{J}_{hh} - \chi_{q, q}(c)(\mathcal{J}_{hc}^2 - \mathcal{J}_{cc}^2)] \times [1 - \chi_{q, q}(h)(\mathcal{J}_{hh} - \chi_{q, q}(c)(\mathcal{J}_{hc}^2 - \mathcal{J}_{cc}^2) - \mathcal{J}_{cc}^2)]^{-1} \]

(9)

where the argument of the exchange coupling parameters within and between the two sublattices is \( q = 0 \).
The MF Hamiltonian for the hexagonal ions is
\[ \mathcal{H}_{\text{MF}} = B_{20}O_x^0 + B_{40}O_x^0 + B_{60}O_x^0 + B_{6\text{h}}O_x^0 - \frac{3}{16}(1/C_\gamma)\mathcal{B}^2_{22}(O_x^2)O_x^2 - g\mu_BJ_\text{MF} \]
written in terms of Stevens operators. The molecular field, \( \mathbf{H}_{\text{MF}} \) (parallel to one of the Cartesian axes), is determined by the condition, that the MF value of the magnetisation, \( \langle g\mu_BJ_\text{MF} \rangle \), of the hexagonal ions agrees with the experimental value of Lebech and Rainford (1971). The parameters in equation (10) have been determined by Houmann et al (1977) from the field dependence of the magnetic excitations of the hexagonal ions, and they are given in table 1.

<table>
<thead>
<tr>
<th>( B_{20} )</th>
<th>( B_{40} )</th>
<th>( B_{60} )</th>
<th>( B_{6\text{h}} )</th>
<th>( \mathcal{B}^2_{22}/C_\gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>(-5.7 \times 10^{-4})</td>
<td>(1.0 \times 10^{-4})</td>
<td>(-9.6 \times 10^{-4})</td>
<td>0.0345</td>
</tr>
</tbody>
</table>

In their experiment Lebech and Rainford (1971) observed that the magnetisation of the cubic ions is very nearly half the magnetisation of the hexagonal ions at all values of the basal plane field (at 4.2 K), which combined with the value of \( \mathcal{H}_{\text{MF}} \) in equation (10) determine \( \mathcal{J}_{hh} + 0.5\mathcal{J}_{hh} \) to be approximately 0.116 meV. Their result further implies that \( \chi_{J_x,J_y}(c) \approx 0.5\chi_{J_x,J_y}(h) \), \( x = x, y \), when the field is in the basal plane. The last relation relies somewhat on the assumption that \( \mathcal{J}_{hh} \simeq \mathcal{J}_{hc} \simeq \mathcal{J}_{cc} \) which seems reasonable when compared with the corresponding two-ion couplings in the heavy rare earths. Introducing all the three estimates into equation (9) we finally get
\[ \Xi = \frac{1}{2}(\rho_{0,0}(h) + \rho_{0,1}(h)\mathcal{J}_{hh}[1 - 0.5\chi_{J_x,J_y}(h)\mathcal{J}_{hh}]^{-1}) \quad H \parallel \beta\text{-axis} \]
where \( \mathcal{J}_{hh} = 0.077 \) meV and \((x, y) = (x, y) \) or \((y, x) \) using the fact that \( \chi_{J_x,J_y}(h) \), \( \gamma \neq x \), vanishes identically.

The MF Hamiltonian, equation (10), of the hexagonal ions may be considered to include the effect of the cubic ions if it is assumed that their contribution to the homogeneous strain \( \langle \epsilon_{11} - \epsilon_{22} \rangle \) amounts to a constant fraction, \( \kappa \), of that of the hexagonal ions (a reasonable assumption when considered in conjunction with the constant ratio between the magnetisation of the two sublattices). In this case \( \mathcal{B}_{22} \) in equation (10), and table 1, is an effective coupling parameter equal to \( \sqrt{(1 + \kappa)\mathcal{B}_{22}(h)} \). From preliminary measurements of the field dependence of the strains in Pr (K McEwen, private communication) an estimate shows \( \kappa \) to be of the order of 0.2 which corresponds to \( B_{22}(c) \approx B_{22}(h) \) when using a \( \Gamma_1 - \Gamma_4 \) model for the cubic ions. This model further suggests that although \( B_{22}(c) \) might be of the order of \( B_{22}(h) \) the contribution due to \( B_{22}(c) \) to the field dependence of \( c_{66} \) is relatively small, namely of the order of 2% of the shift produced by the hexagonal ions when the field is in the basal plane. Alternatively, taking into account the isotropic behaviour of the magnetisation of the cubic ions (Lebech and Rainford 1971) the influence of the cubic ions on \( c_{66} \) should be about the same whether the field is applied in the basal plane or in the \( c \)-direction. In the latter case the effect of the hexagonal ions is negligible (calculated to be 0.1% at 5 T). Experimentally we find that the shift of \( c_{66} \) produced by a field in the \( c \) direction only amounts to about 1% of that produced by the field applied in the basal plane (at 4.2 K), showing that the effect of the cubic ions on the
field dependence of \( c_{66} \) is indeed very small. Without knowing precisely the crystal-field parameters of the cubic ions it is not possible to produce a reliable estimate of the absolute value of \( \gamma_{0,c}(c) \) at zero field, we may state only that \( \gamma_{0,0}(c) \) is presumably small in comparison with \( \gamma_{0,6}(h) \) (maybe a factor of four) but not negligible. This means that although the magnetic contributions of the cubic ions to \( c_{66} \) are not strongly field dependent they may be of some importance for determining the absolute value of \( c_{66} \)(i.e. the temperature dependence).

4. Results

The temperature variation of \( c_{66} \) in zero applied field is shown in figure 1, where the elastic constant has been measured with both quartz transducers bonded with epoxy resin and with the CdS transducer described in § 2. The measurements with quartz transducers are unreliable below \( \sim 90 \) K due to bond damage caused by the different thermal expansion and contractions of the sample and transducer. However, the echo train

![Figure 1](image1)

**Figure 1.** The zero magnetic field temperature dependence of \( c_{66} \) in Pr. The open and full circles are the results obtained using quartz and CdS thin-film transducers respectively. These results are compared with those of Greiner et al (1973) denoted by open squares. The solid lines show the results of the calculation described in the text (\( c_{66}^0 \) is the estimated result for the non-magnetic value of the elastic constant).

![Figure 2](image2)

**Figure 2.** The experimental results for \( c_{66} \) in Pr as a function of field applied in all the three symmetry directions at 4.2 K (\( H \parallel c \), \( H \parallel a \) and \( H \parallel b \)). The broken lines are only connecting the experimental points.
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produced by the CdS transducers is of very high quality all the way down to 4.2 K and the results obtained are in good agreement with the earlier work of Greiner et al (1973).

Figure 2 shows the field dependence of \( c_{66} \) at 4.2 K for magnetic fields of up to 2 T applied along the \( a, b \) and \( c \) directions.

In the analysis of the experimental results for \( c_{66} \) we neglect the cubic contributions in equation (6) by the use of equation (11) for \( \Xi \), only we take into account that \( B_{22} \) in (6) may differ slightly from \( B_{22} \) in table 1, as discussed in § 3.

The best fit to the data is obtained using \( B_{22}^2/c_{ij} = 0.029 \) meV which is almost within the standard deviation regime of \( B_{22}^2/c_{ij} \) corresponding to \( \kappa = 0.19 \pm 0.13 \). The solid lines in figure 1 show the final fit to the temperature dependence of \( c_{66} \). The analysis suffers because the temperature dependence of the non-magnetic value of the elastic constant, \( c_{66}^0 \), is not known. However, as the only possible procedure, we have calculated the value of \( c_{66}^0 \) from the experimental \( c_{66} \) for temperatures above 200 K and extrapolated this result to the lower temperatures as shown in the figure. The fit obtained in this way is quite good. The calculation accounts for the position of the minimum around 20 K only the calculated shift is somewhat larger than observed. The value of \( c_{66}^0 \) at 0 K obtained by the extrapolation is \( 1.62 \times 10^{19} \) N m\(^{-2}\) corresponding to \( c_{ij} = 14.0 \) eV and hence \( B_{22}^2(h) = 20.2 \) meV.

In figure 3 we show the field dependence (0-7 T) of \( c_{66} \) relative to the value at zero field, \( c_{66}(H)/c_{66}(H = 0) \), as obtained at 4.2 K. The two most important features of these results are the large shift in \( c_{66} \) (11-16% at 4 T) when applying the field in the basal plane, and the great difference (5% at 4 T) between the cases where the field is parallel to an \( a \) axis (the easy axis) or to a \( b \) axis.

The effective \( S = 1 \) model accounts for the large shift (but not for the basal-plane anisotropy) only by the use of an effective coupling parameter which is about 50% larger than the one used in the present calculation. However, the smaller value of \( B_{22} \) is still consistent with the exciton-phonon energy gaps observed at finite wavevectors, because the matrix element determining the strength of the couplings is almost twice that predicted by the effective \( S = 1 \) model. Following the procedure of Jensen (1976) it is found that \( B_{22} = 18 \pm 3 \) meV accounts for the observed behaviour of the exciton-phonon energy gaps when the complete crystal-field level scheme is used.

The total crystal-field Hamiltonian also allows for the presence of a basal-plane anisotropy (\( B_{66} \)). Although the effect of \( B_{66} \) on the magnetisation is negligible, \( c_{66} \) is strongly affected in accordance with the experiments. The reason is that the \( |3\rangle \rangle \) singlet (\( s \) denotes the symmetric sum of \(| \pm 3 \rangle \rangle \)) using the crystal-field parameters in table 1, is placed just above the \( | \pm 1 \rangle \rangle \) doublet, whereas the \( |3\rangle \rangle \) level lies at much higher energy (as determined by \( B_{66} \)). Because the ground state is mixed, it is coupled to the (modified) \( |3\rangle \rangle \) and \( |3\rangle \rangle \) levels by the \( O \) operator, equation (2), when a field is being applied along the \( x(a) \) or \( y(b) \) directions respectively. However, owing to the energy denominators in the susceptibilities much the largest effect on \( c_{66} \) is produced in the second case.

The calculation of the relative field dependence of \( c_{66} \), the solid lines in figure 3, agrees in all details with the experimental result obtained when applying the field in the \( a \) direction, and accounts reasonably well for the anisotropy. In the calculations \( \chi_{0, c}(h) \) and the second term in equation (11) contribute almost equally. The estimate of the effective exchange coupling parameter, \( J_{xy} \), appearing in equation (11) may be given an uncertainty of the order of 10%, which is also the magnitude of the normal magnetic dipole coupling, hence producing an uncertainty on the calculated shift, \( \Delta c_{66} \), of 5-10% (an introduction of the magnetic dipole coupling will tend to diminish the calculated basal plane anisotropy of \( c_{66} \)). In comparison with these uncertainties neglecting the
magnetic effect of the cubic ions on the field dependence of $c_{66}$ should be of no significance. The same contributions to the absolute value of $c_{66}$ should be of greater importance, however, the fit to the temperature dependence of $c_{66}$ does not leave much room for the presence of further contributions, suggesting that $|B_{22}(c)|$ is actually somewhat smaller than $B_{22}(h)$. The difference between the values of $B_{22}$ and $B_{22}$ we have obtained may reflect only the uncertainties involved rather than $\kappa$ being non-zero. The continuing studies of the field dependence of the strains (K McEwen, private communication) may allow a more conclusive answer to this question.

![Figure 3](image_url)

**Figure 3.** $c_{66}$ in Pr as a function of field applied in the basal plane at 4.2 K relative to the value at zero field (○ $H \parallel a$ and ● $H \parallel b$). The solid lines are the theoretical values.

### 5. Conclusions

The use of CdS thin-film transducers has enabled a detailed study of $c_{66}$ in Pr as a function of temperature and as a function of field at 4.2 K.

An expression for the magnetic effects on the elastic constants is deduced, valid, in general, to leading order in the magnetic two-ion coupling (RPA).

The presence of a relatively strong magnetoelastic coupling, $B_{22}$, in Pr leads to a number of phenomena, magnetostriction, exciton–phonon coupling, magnetic effects on the elastic constants, and strain dependence of the exciton energies. All of these effects have now been observed experimentally (the last one only indirectly). The quantitative analysis of the different phenomena (the magnetostriction data are only preliminary, K McEwen, private communication) are consistent with each other.

The possible contributions of the cubic ions to the magnetoelastic effects are estimated to be small (if $B_{22}(c) \lesssim B_{22}(h)$), and, at present, a model which neglects $B_{22}(c)$ accounts reasonably well for all the experiments.

The magnetoelastic Hamiltonian, equation (1), which we have assumed to be solely of single-ion origin may include effectively some two-ion coupling without effecting the
results. However, the lowest-order (and hence the most probable) two-ion magnetoelastic coupling, which is a dipolar coupling, cannot be of great importance, because it would contribute negligibly to the observed basal-plane anisotropy of the field dependence of $c_{66}$.

The crystal-field parameters of the hexagonal ions, in Table 1, are those determined by Houmann et al. (1977) by a least-squares analysis of the field dependence of the exciton energies. In order to deduce the total level scheme they had to rely on a number of assumptions. The successful analysis of $c_{66}$ as a function of field and temperature, which we present, strongly supports this level scheme, only the fit to the temperature dependence of $c_{66}$ might suggest minor corrections. However, on account of the uncertainties involved, both experimentally and theoretically, these suggestions might not be entirely reliable.

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