

## Paramagnetic Resonance Spectra of Rare Earth Ions in the Crystal Field of Calcium Fluoride\*

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We have studied the paramagnetic resonance spectra of rare earth ions in the crystal field of calcium fluoride. These spectra can be classified as belonging to three types: *a.* spectra which indicate that the rare earth ions are exposed to a cubic field; *b.* spectra in which the anisotropic behaviour suggests an axial crystal field along the cubic directions; *c.* spectra in which the axial distortion is along the body diagonals of the cube.

The calcium ion with fluorite structure is surrounded by a cube of eight nearest fluorine ions. The trivalent rare earth ions substitute for the calcium ion. However, a charge compensation has to take place to preserve the neutrality of the crystal. From measurements of the x-ray lattice constants<sup>1)</sup> and of the ionic conductivity<sup>2)</sup> it has been shown that in well annealed crystals the main disorder introduced into the crystal by the addition of the rare earth ion is the formation of F<sup>-</sup> interstitial (see Fig. 1). The empty sites which are available for the inter-

stitial F<sup>-</sup> ion are located at the center of the adjacent cube along one of the cubic axes. Supporting evidence for the F<sup>-</sup> interstitial formation is found in the work of Bleaney *et al.*<sup>3)</sup>.

With proper thermal treatment, part or a large fraction of the interstitial fluorine ions can be removed from the adjacent cube next to the rare earth ion<sup>4)</sup>. In this case, the point symmetry of the rare earth ions approximates O<sub>h</sub>. In some crystals, however, the predominant axial distortion is found from paramagnetic resonance spectra to be along the body diagonals of the cube. The optical spectra shows a number of strong bands and very poor ultraviolet transmission. It is likely that one of the fluorine ions at the corner of the cube is replaced by O<sup>2-</sup> or OH<sup>-</sup> ion. Supporting evidence is found that on heating the crystal in air this spectrum increases in intensity.

$$\begin{aligned}
 a) \quad V_{\text{cubic}} &= B_4^0 [O_4^0 + 5(O_4^4 + O_4^{-4})] \\
 &\quad + B_6^0 [O_6^0 - 21(O_6^4 + O_6^{-4})] \quad (1) \\
 b) \quad V_{\text{axial}} &= B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 \\
 &\quad + B_4^4 (O_4^4 + O_4^{-4}) + B_6^4 (O_6^4 + O_6^{-4}) \\
 c) \quad V_{\text{diagonal}} &= B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 \\
 &\quad + B_4^3 (O_4^3 + O_4^{-3}) + B_6^3 (O_6^3 + O_6^{-3})
 \end{aligned}$$

where  $B_n^m$  are crystal field coefficients proportional to  $r^n/R^{n+1}$  and  $O_n^m$  are operators transforming the corresponding spherical Legendre polynomials. The magnetic properties of these three types of spectra are very different and we shall illustrate this in a few selected examples. A full report of the magnetic properties of the rare earth ions in calcium fluoride will appear elsewhere.

$$\text{Er}^{3+}: {}^4H_{15/2}$$

a) In the cubic field of calcium fluoride, the 16-fold degeneracy splits into 3 quartets ( $\Gamma_8$ ) and two doublets. The lowest levels are given by

$$\begin{aligned}
 &-258.86c - 162d, \Gamma_8 \\
 &-26c - 312d, \Gamma_7
 \end{aligned}$$

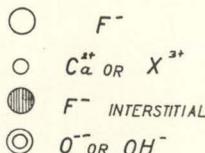
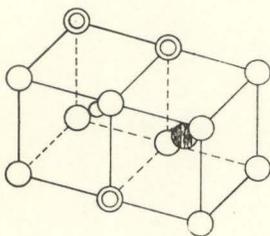


Fig. 1. Crystal Structure of CaF<sub>2</sub>. The figure indicates the possible defect sites near the rare earth ion substituting for the calcium ion.

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where  $c$  and  $d$  are parameters signifying the fourth and sixth order contribution. For a point charge model they are given by

$$c = \frac{2^3}{3^3 \cdot 11.13} \frac{ze^2}{R^5} \quad d = \frac{2^4}{3^3} \frac{.10}{11.13^2} \frac{ze^2}{R^7}$$

The observed  $g$  factor is  $6.785 \pm 0.002^{(5)}$ . This is consistent with a  $\Gamma_7$  ground state which gives  $g_{\text{calculated}} = 6.79$ . A lowest  $\Gamma_7$  level indicates that the rare earth ion spectrum is dominated to a large extent by the sixth order term in the potential.

b) An axial spectrum has been observed by Baker *et al.*<sup>(6)</sup> and by the author with  $g_{\parallel} = 7.76$  and  $g_{\perp} = 6.253$ . This is consistent with the same doublet level except now exposed to an axial field since  $(g_{\parallel} + 2g_{\perp})/3 \sim g_{\text{cubic}}$ .

c) A set of three lines, arising from the three inequivalent sites with axial symmetry along the three body diagonal directions, is observed in some crystals<sup>(7)</sup>. Each ion can be described by  $g$  factors  $g_{\parallel} = 2.23$ ,  $g_{\perp} = 8.9$ , and again  $(g_{\parallel} + 2g_{\perp})/3 \sim g_{\text{cubic}}$ . The  $g$  factors can be explained to arise from a doublet with

$$a| \pm 13/2 \rangle + b| \pm 7/2 \rangle + c| \pm 1/2 \rangle \\ + d| \mp 5/2 \rangle + e| \mp 11/2 \rangle$$

with the coefficients  $b$  and  $d$  larger than  $a$ ,  $c$  or  $e$ .

$$\text{Yb}^{3+}: {}^2F_{7/2}$$

(a) The cubic field suggests that  $\Gamma_7$  is the

| $g$ value | transition                                                                                                                                              | relative intensity |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|
| 2.24      | $0.8722  -5/2 \rangle - 0.4892  +3/2 \rangle \rightarrow 0.8722  +5/2 \rangle - 0.4892  -3/2 \rangle$                                                   | 20                 |
| 1.15      | $0.8722  \pm 5/2 \rangle - 0.4892  \mp 3/2 \rangle \rightarrow 0.05410  \mp 9/2 \rangle - 0.2981  \mp 1/2 \rangle + 0.9530  \pm 7/2 \rangle$            | 4.4                |
| 4.54      | $0.5410  +9/2 \rangle - 0.2981  \pm 1/2 \rangle + 0.9530  -7/2 \rangle \rightarrow 0.05410  -9/2 \rangle - 0.2981  -1/2 \rangle + 0.9530  +7/2 \rangle$ | 0.075              |

The spin Hamiltonian of the  $\Gamma_8$  level in a cubic field as outlined by Bleaney<sup>(9)</sup> applies here. The spectrum has been investigated and corresponds approximately to this Hamiltonian.

$$\mathcal{H} = g\beta(H_x S_x) + \beta\beta(H_y S_y) \quad i = x, y, z.$$

The observed and calculated  $g$  factors are given in Table I<sup>(10)</sup>.

Table I. Measured and calculated  $g$  factor of  $\Gamma_8$  ground state of Nd<sup>3+</sup>.

| Direction | $g$ exp. | $g$ calc. |
|-----------|----------|-----------|
| 100       | 2.26     | 2.24      |
|           | 1.10     | 1.15      |
| 110       | 1.45     | 1.46      |
|           | 1.6      | 1.7       |

ground state level. The  $g$  wave function of the doublet is given by

$$\sqrt{3/4} | \pm 5/2 \rangle - \sqrt{1/4} | \mp 3/2 \rangle$$

and the calculated  $g$  factor = 24/7. The observed  $g$  factor of  $3.441 \pm 0.001$  is in essential agreement<sup>(8)</sup>.

(c) The spectrum along the body diagonals can be represented by the spin Hamiltonian

$$\mathcal{H} = g_{\parallel}\beta H_x S_x + g_{\perp}\beta(H_x S_x + H_y S_y) + A S_z I_z \\ + B(S_x I_x + S_y I_y) + P(I_x^2 - \frac{1}{3}I(I+1)).$$

with  $S = \frac{1}{2}$  and  $I = \frac{1}{2}$  or  $I = 5/2$

The observed  $g$  factor is  $g_{\parallel} = 1.323 \pm 0.001$  and  $g_{\perp} = 4.387 \pm 0.002$  showing that this is the  $\Gamma_7$  anisotropic level. This Kramers doublet can be approximated with

$$0.940| \pm \frac{1}{2} \rangle + 0.264| \pm 7/2 \rangle + 0.209| \mp 5/2 \rangle$$

The hyperfine part is expressed as

$$A^{171} = 354.6 \quad B^{171} = 1168 \quad P = 85 \pm 3. \\ A^{173} = 96 \quad B^{173} = 320 \quad (g_{\parallel} B / g_{\perp} A) \sim 1$$

all in  $10^{-4} \text{ cm}^{-1}$ . These results indicate a large quadrupole moment of about 3.1 barns.

$$\text{Nd}^{3+}: {}^4I_{9/2}$$

(a) Calculations show that the ground state for all reasonable ratios of the fourth to sixth order parameters is given by a quartet  $\Gamma_8$ . The wave functions and  $g$  factors are given by

| $g$ value | transition                                                                                                                                              | relative intensity |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------|
| 2.24      | $0.8722  -5/2 \rangle - 0.4892  +3/2 \rangle \rightarrow 0.8722  +5/2 \rangle - 0.4892  -3/2 \rangle$                                                   | 20                 |
| 1.15      | $0.8722  \pm 5/2 \rangle - 0.4892  \mp 3/2 \rangle \rightarrow 0.05410  \mp 9/2 \rangle - 0.2981  \mp 1/2 \rangle + 0.9530  \pm 7/2 \rangle$            | 4.4                |
| 4.54      | $0.5410  +9/2 \rangle - 0.2981  \pm 1/2 \rangle + 0.9530  -7/2 \rangle \rightarrow 0.05410  -9/2 \rangle - 0.2981  -1/2 \rangle + 0.9530  +7/2 \rangle$ | 0.075              |

(b) The axial field spectrum has been investigated by Bleaney *et al.*<sup>(3)</sup> and remeasured by us<sup>(10)</sup>. The  $g$  factors are given  $g_{\parallel} = 4.412$  and  $g_{\perp} = 1.301$ . The ground state can be described possibly by

$$\varphi = a| \pm 3/2 \rangle + b| \pm 1/2 \rangle + c| \mp 7/2 \rangle$$

(c) A weak spectrum is also observed with the axial field along the body diagonals. We have, in addition, observed the cubic field spectrum of Ce<sup>3+</sup>, Dy<sup>3+</sup>, Tm<sup>3+</sup> and Gd<sup>3+</sup>, the axial field spectra of these ions. The axial spectra of ions with even number of electrons such as Tb<sup>3+</sup>, and Tm<sup>3+</sup> has been observed as well<sup>(7)</sup>.

A large part of this work has been performed in collaboration with Mr. M. Dvir, U. Rosenberger and Dr. G. Vincow.

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## DISCUSSION

W. P. WOLF: I should like to ask Professor Low what assumption he made with regard to the ratio of fourth to sixth degree crystal fields in deriving the calculated  $g$  value for Nd in the cubic site. From the preprint it would appear that you have neglected the admixtures between the two types of terms. When a particular irreducible representation occurs more than once the  $g$  values depend explicitly on the ratio  $B_4/B_6$  and the linear interpolation formula given for the energy is then not correct.

W. Low: In the case of  $\text{Nd}^{3+}$  in  $\text{CaF}_2$  it is found that the  $g$  factor can be fitted well using effectively only the fourth order potential. In  $\text{Dy}^{3+}$  and  $\text{Er}^{3+}$  the  $g$  values of  $\Gamma_8$  states are very sensitive to the ratio of the fourth to sixth order potential terms. This is generally true for all ions having more than one  $\Gamma_8$  level. The  $\text{Nd}^{3+}$   $g$  factor is not very sensitive to this ratio.

W.P. WOLF: I cannot agree with your statement about the insensitivity of the  $g$ 's to the ratio  $B_4/B_6$  even in the case of Nd. For certain values of the ratio some of the  $g$ 's even change sign and I would suggest that the close agreement with experiment is quite fortuitous.

J. H. Van Vleck: Can you establish at least a qualitative correlation between any of the crystalline fields at the rare earth sites in garnets?

W. Low: We have not yet made the investigation of the correlation between our data on  $\text{CaF}_2$  and the rare earth garnets. We feel that we have to understand the spectra and the crystal field in calcium fluoride, which has a simple structure, first before attempting to understand the spectra in the more complicated structure of garnets.