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PARAMAGNETIC RESONANCE SPECTRA OF RARE EARTH IONS IN THE CRYSTAL FIELD OF CALCIUM FLUORIDE *

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ABSTRACT

Paramagnetic resonance data of various rare earth ions in the crystal field of Calcium Fluoride are presented. It is found that there are at least three types of symmetries, cubic, axial and trigonal. Some of the spectra of Ce^{3+}*, Yb^{3+}, Er^{3+}*, Nd^{3+}* are presented.

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* CERIUM (3+), YTTERBIUM (3+), ERBIUM (3+), AND NEODYMIUM (3+)

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[1] and of the ionic conductivity[2] 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^- interstitial (see Fig. 1). The empty sites which are available for the interstitial F^- ion are located at the center of the adjacent cube along one of the cubic axes. Supporting evidence for the F^- interstitial formation is found in the work of Bleaney et al.[3]

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.[4] In this case, the point symmetry of the rare earth ions approximates O_h. 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^{2-} or OH^- ion. Supporting evidence is found that on heating the crystal in air this spectrum increases in intensity.

The respective crystal fields are given by

a) $V_{\text{cubic}} = B_4^0 \left[O_4^0 + 5(O_4^4 + O_4^{-4}) \right] + B_6^0 \left[O_6^0 - 21(O_6^4 + O_6^{-4}) \right]$

b) $V_{\text{axial}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 (O_4^4 + O_4^{-4}) + B_6^4 (O_6^4 + O_6^{-4})$

c) $V_{\text{diagonal}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^3 (O_4^3 + O_4^{-3}) + B_6^3 (O_6^3 + O_6^{-3})$

where B_n^m are crystal field coefficients proportional to $\frac{r^n}{R^{n+1}}$ and O_n^m are operators transforming the corresponding spherical Legendre polonomials. 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.

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

a) In the cubic field of calcium fluoride, the 16-fold degeneracy splits into 3 quarters (Γ_8) and two doublets. The lowest levels are given by

$$-258.86\ c - 162\ d,\ \Gamma_8$$

$$-26\ c - 312\ d,\ \Gamma_7$$

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

$$c = \frac{2^3}{3^3 \cdot 11 \cdot 13} \frac{\langle r^4 \rangle}{R^5} \qquad d = \frac{2^4}{3^3} \frac{10}{11 \cdot 13^2} \frac{\langle r^6 \rangle}{R^7}$$

The observed g factor is $6.785 - 0.002$.[5] This is consistent with a Γ_7 ground state which gives g calculated = 6.79. A lowest Γ_7 level indicates that the rare earth 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[6] 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 $\frac{g_\parallel + 2g_\perp}{3} \sim g$ 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.[7] Each ion can be described by g factors

$g_{\parallel} = 2.23, \qquad g_{\perp} = 8.9$ and again $\frac{g_{\parallel} + 2g_{\perp}}{3} \sim g$ 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.

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

(a) The cubic field suggests that Γ_7 is the ground state level. The wave function of the doublet is given by

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

and the calculated g factor = 24/7. The observed g factor of 3.426 ± 0.001 is in essential agreement.[8]

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

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta\left[H_x S_x + H_y S_y) + AS_z I_z + B(S_x I_x + S_y I_y) + P(I_z^2 - 1/3I(+1)\right]$$

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 Γ_7 anisotropic level. This Kramers doublet can be approximated with

$$0.940\,|\pm 1/2\rangle + 0.264\,|\pm 7/2\rangle + 0.209\,|\mp 5/2\rangle$$

The hyperfine part is expressed as

$A^{171} = 354.6$ $\qquad B^{171} = 1168$

$A^{173} = 96$ $\qquad B^{173} = 320$

$$P = 85 \pm 3. \qquad \frac{g_n}{g_\perp}\frac{B}{A} \sim 1$$

all in 10^{-4} cm. These results indicate a large quadrupole moment of about 2.4 barns.

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

(a) Calculations show that the ground state for all ratios of the fourth to sixth order parameters is given by a quartet Γ_8. The wave functions and g factors are given by

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

The spin Hamiltonian of the Γ_8 level in a cubic field as outlined by Bleaney[9] applies here. The spectrum has been investigated and corresponds approximately to this Hamiltonian.

$H = gB(H_i S_i) + fB(H_i S_i^3) \qquad i = x, y, z.$

The observed and calculated g factors are given in Table I.[10]

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

$$= a\,|\pm 9/2\rangle + b\,|\pm 1/2\rangle + c\,|\mp 7/2\rangle$$

(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^{3+}, Dy^{3+} and Gd^{3+}, the axial field spectra of these ions. The axial spectra of ions with even number of electrons such as Tb^{3+}, and Tm^{3} has been observed as well.[7]

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TABLE I

Measured and calculated g factor of Γ_8 ground state of Nd^{3+}.

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

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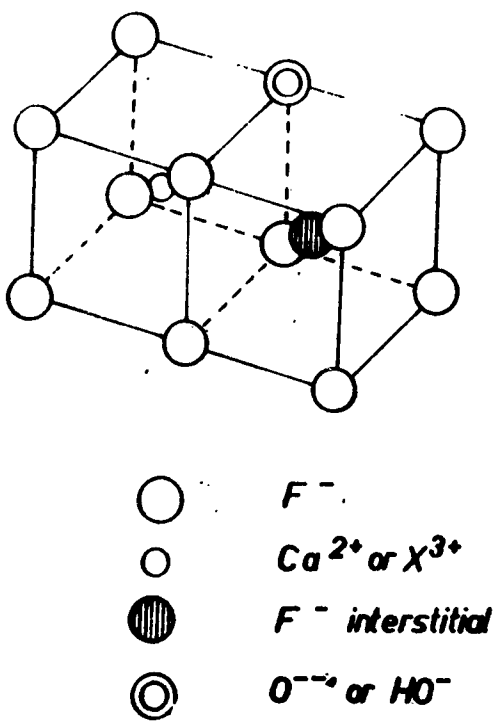
Fig. 1.

Crystal Structure of CaF_2

The figure indicates the possible defect sites near the rare earth ion substituting for the calcium ion.



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