

Paramagnetic Resonance Spectra of f^3 Ions in a Cubic Site*

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The paramagnetic resonance spectra of Nd^{3+} and U^{3+} in the cubic field of CaF_2 have been investigated at 3 cm at 20°K. In the case of Nd^{3+} transitions within the lowest quartet $\Gamma_8^{(2)}$ and possibly in the next higher quartet $\Gamma_8^{(1)}$ have been observed. The angular behavior conforms with that predicted by Bleaney's formalism of the spin Hamiltonian of a Γ_8 state. In the case of U^{3+} there are considerable deviations of the experimental g values from the calculated ones. It is suggested that these deviations are caused by the stronger cubic field.

The efficiency of the thermal conversion from axial to cubic site is discussed. Additional lines suggest a new axial center along the [111] direction.

I. INTRODUCTION

IN this paper we present the results of an investigation of the paramagnetic resonance spectra of trivalent neodymium and trivalent uranium ions in the cubic sites of single crystals of calcium fluoride. Spectra of these ions in an axial site have been reported briefly by Bleaney *et al.*¹ The cubic field spectra of the f^3 system are of particular interest in that they can be used as a check on the recently proposed spin Hamiltonian of a Γ_8 state.²

Single crystals of calcium fluoride showing the cubic-site spectra of neodymium were grown by the Stockbarger process as reported by Dvir and Low.³ The crystals containing uranium and neodymium were obtained from R. W. H. Stevenson of the University of Aberdeen. These showed axial-site spectra exclusively.

All measurements reported here were made at 20°K and 3-cm wavelength.

II. SPECTRUM OF NEODYMIUM IN A CUBIC SITE

In a cubic field the ground state of the f^3 configuration ($^4I_{9/2}$) is split into two Γ_8 quartets and one Γ_6 doublet. Neglecting nuclear effects, the Hamiltonian for the problem is given by

$$\mathcal{H} = g\beta(\mathbf{J} \cdot \mathbf{H}) + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4, \quad (1)$$

where O_n^m are operators having the same transformation properties as the corresponding spherical harmonics. B_n^m are crystal field coefficients which can be determined from paramagnetic resonance or optical absorption spectra. In the cubic field case the relation

$$B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4 = B_4^0 (O_4^0 + 5O_4^4) + B_6^0 (O_6^0 - 21O_6^4)$$

holds.

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¹ B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Phys. Soc. (London) **69**, 858 (1956).

² B. Bleaney, Proc. Phys. Soc. (London) **73**, 939 (1959).

³ M. Dvir and W. Low, Proc. Phys. Soc. (London) **75**, 136 (1960).

Evaluation of the matrices using Stevens' operator techniques⁴ yields the following energy levels:

$$\begin{aligned} \Gamma_6: & 28c - 182.5d, \\ \Gamma_8^{(1)}: & 12.18c + 151.0d, \\ \Gamma_8^{(2)}: & -26.18c - 59.5d, \end{aligned} \quad (2)$$

where c and d refer to the fourth- and sixth-order contribution of the crystal field potential, respectively.

For a point-charge model of an eight-coordinated CaF_2 crystal, these can be calculated explicitly to be

$$\begin{aligned} c &= (50/3)(Z_{\text{eff}}e^2/R^5)\beta_{9/2}\langle r^4 \rangle, \\ d &= 50(Z_{\text{eff}}e^2/R^7)\gamma_{9/2}\langle r^6 \rangle, \end{aligned} \quad (3)$$

where $\beta_{9/2}$ and $\gamma_{9/2}$ are multiplicative factors⁵ and Z_{eff} is the effective charge.

For all values of c and d the lowest energy is given by $\Gamma_8^{(2)}$. The predicted transitions and relative intensity within the two quartets along the [100] directions are given in Table I.

The angular dependence as well as the transition probabilities can be calculated using Bleaney's formalism of the spin Hamiltonian of a Γ_8 state² (provided the cubic field splitting is larger than the Zeeman energy):

$$\begin{aligned} \mathcal{H} &= g\beta(H_x S_x + H_y S_y + H_z S_z) \\ &\quad + f\beta(H_x S_x^3 + H_y S_y^3 + H_z S_z^3), \end{aligned} \quad (4)$$

where f and g are constants related to Λ , the Lande g factor.

The angular dependence of the energy levels of the quartet can be expressed in terms of the parameters f and g and the direction cosines l, m, n as²

$$\begin{aligned} (W/\beta H)^2 &= \frac{1}{4}(5\gamma^2 + 3\delta^2) \\ &\quad \pm \gamma\{\gamma^2 + \frac{1}{2}\delta^2[9(l^4 + m^4 + n^4) - 3]\}^{\frac{1}{2}}, \end{aligned} \quad (5)$$

where $\gamma = g + (7/4)f$, and $\delta^2 = f(g + 5f/2)$.

⁴ K. W. H. Stevens, Proc. Phys. Soc. (London) **65**, 209 (1952); see also W. Low, *Paramagnetic Resonance in Solids* (Academic Press, Inc., New York, 1960), Tables VII(a) and (b) and Tables IX(a) and (b).

⁵ W. Low, Proc. Phys. Soc. (London) **75**, 136 (1960), Table X.

TABLE I. Predicted transition within the Γ_8 quartet along the $[100]$ direction.

	g value	Transition	Relative intensity
$\Gamma_8^{(2)}$	2.24	$0.8722 -\frac{5}{2}\rangle-0.4892 +\frac{3}{2}\rangle \rightarrow 0.8722 +\frac{5}{2}\rangle-0.4892 -\frac{3}{2}\rangle$	2.0
	1.15	$0.8722 \pm\frac{5}{2}\rangle-0.4892 \mp\frac{3}{2}\rangle \rightarrow 0.05410 \mp 9/2\rangle-0.2981 \mp\frac{1}{2}\rangle+0.9530 \pm\frac{7}{2}\rangle$	4.4
	4.54	$0.05410 +9/2\rangle-0.2981 +\frac{1}{2}\rangle+0.9530 -\frac{7}{2}\rangle \rightarrow 0.05410 -9/2\rangle-0.2981 -\frac{1}{2}\rangle+0.9530 +\frac{7}{2}\rangle$	0.075
$\Gamma_8^{(1)}$	1.63	$0.8722 -\frac{5}{2}\rangle-0.4892 +\frac{3}{2}\rangle \rightarrow 0.8722 +\frac{5}{2}\rangle-0.4892 -\frac{3}{2}\rangle$	1.1
	0.789	$0.8722 \pm\frac{5}{2}\rangle-0.4892 \mp\frac{3}{2}\rangle \rightarrow 0.05410 \mp 9/2\rangle-0.2981 \mp\frac{1}{2}\rangle+0.9530 \pm\frac{7}{2}\rangle$	2.02
	4.05	$0.05410 +9/2\rangle-0.2981 +\frac{1}{2}\rangle+0.9530 -\frac{7}{2}\rangle \rightarrow 0.05410 -9/2\rangle-0.2981 -\frac{1}{2}\rangle+0.9530 +\frac{7}{2}\rangle$	0.044

The transition probability is easily calculated from $|\langle\Psi_i|gS_x+fS_x^3|\Psi_j\rangle|^2$, with i and j taking the values 1, 2, 3, 4 of the four eigenvectors Ψ corresponding to the solution of matrix (4).

Investigation of the cubic field spectrum is complicated by the presence of the axial field spectra with the many hyperfine levels of the two odd isotopes of neodymium. We have observed two lines along the $[100]$ direction, one at $g=2.26\pm 0.02$ and a less intense line at $g=1.10\pm 0.05$. Both these lines showed an anisotropic angular dependence.

Along the $[110]$ direction, lines were predicted at $g=1.46$, 1.70, 4.85, and 3.16 with relative intensities in the ratio of 2.02:1.43:0.047:0.0024, respectively. A line was detected along this direction with $g=1.45\pm 0.01$ and approximate full width at half maximum of 75 gauss. An overlapping weak shoulder observed on the low-field end of this line could be identified with the predicted line at $g=1.70$ and has the approximate g value (allowing for overlap) of 1.6.

The angular variation of the transition corresponding to the g value 2.26 along the $[100]$ direction is given in Table II.

The detection of lines associated with the higher energy quartet $\Gamma_8^{(1)}$ and doublet is complicated because of the many hyperfine lines from the axial spectrum. Values of g were calculated for the higher energy quartet along various directions. Along the $[111]$ direction, no axial neodymium lines should interfere with the predicted line at $g=1.63$. A very weak and wide line was observed along this axis at $g=1.55\pm 0.03$, which we tentatively attribute to the $\Gamma_8^{(2)}$ quartet. No line was observed which could be identified with the Γ_6 doublet for which an isotropic line with $g=8/3$ is predicted.

Approximately 20% of the trivalent neodymium in the crystal investigated was in a cubic site.

The optical spectrum of these crystals is now being investigated by one of us (W.L.) at liquid helium temperatures. Preliminary results show differences in the linewidth between the two crystals. The well-annealed crystal of Nd containing only axial sites has much sharper optical absorption lines.

III. SPECTRUM OF URANIUM IN A CUBIC SITE

In a heat-treated crystal of uranium, two extremely weak lines were observed along the $[110]$ direction which can be associated with cubic sites. The g values are 1.57 and 1.62, and the relative intensities are about 1.5:1. The line width taken between points of maximum slope is approximately 50 gauss for both lines.

For a pure $^4I_{9/2}$ ground state of uranium, the calculated g values are the same as for neodymium. The above values should be compared with the predicted g values of $g=1.46$ and $g=1.70$ with calculated relative intensities of 1.4:1. The angular variation of these lines was observed in the (001) plane. Both lines move down in field when the angle is varied from the $[110]$ direction towards the $[100]$ direction. The angular variation of the $g=1.57$ line is in semiquantitative agreement with the predicted variation; however, the $g=1.62$ line is predicted to move up in field. We are, therefore, not certain regarding the origin of the $g=1.62$ line.

The discrepancy between the calculated and observed g factors could arise from the partial breakdown of Bleaney's spin Hamiltonian for the case when the spin-orbit coupling is of the same order as the cubic field splitting. The increased cubic field splitting is expected for $5f$ electrons which are not as well shielded and take part in the chemical bonding. Evidence for the greater extension of the wavefunction is found by observation of the fluorine hyperfine structure in the axial spectrum in this crystal. The optical spectrum, moreover, shows linewidths more than 20 times the width of the neodymium spectrum even at liquid helium temperatures, indicative of stronger interactions with the surrounding lattice.

The longer relaxation times of the U^{3+} spectrum as compared with the Nd^{3+} spectrum is further evidence

TABLE II. Angular variation of the $0.8722|-\frac{5}{2}\rangle-0.4892|+\frac{3}{2}\rangle \rightarrow 0.8722|+\frac{5}{2}\rangle-0.4892|-\frac{3}{2}\rangle$ transition in the $\Gamma_8^{(2)}$ quartet.

Angle	g calculated	g experimental ± 0.02
0°	2.24	2.26
10°	2.16	2.15
30°	1.675	1.68
45°	1.46	1.45

of larger crystal field splittings in the U^{3+} case. An additional influence, but probably of smaller magnitude, is the breakdown of Russell-Saunders coupling which is expected to be larger for uranium.

IV. THERMAL TREATMENT OF CRYSTALS

Several attempts were made to convert the neodymium and uranium crystals from axial into cubic sites by the use of the thermal method of Friedman and Low.⁶ In the case of neodymium, no spectral lines arising from cubic sites were detected, thus indicating a maximum limit of the conversion of 10%. Extended heating at 1200°C, as well as reduction of the quenching time to 5 min produced no discernible effects.

Application of the same method to uranium crystals resulted in a loss of the characteristic red color of trivalent uranium and the production of either opaque or transparent colorless crystals. Use of a quartz container instead of the graphite crucible⁶ led to no significant change in results. No trace of the axial resonance lines was observed, nor were any new lines detected. Apparently a valence transformation had been effected. The fact that no new resonances are observed from the resultant valence state finds confirmation in the investigations of Llewellyn⁷ who heat-treated a crystal of $CaF_2:U^{3+}$ in a reducing atmosphere (H_2) and observed a loss of red color and presumably the conversion to divalent uranium. No resonance was observed.

The time of heat treatment was shortened to a few hours and the temperature decreased to 1000°C in order to preserve the trivalent uranium. Both of these modifications should result in a reduced efficiency of conversion. In a crystal heated for 2 hr at 1000°C and quenched in 5 min, about $\frac{1}{2}\%$ of the uranium was converted to a cubic site.⁸

⁶ E. Friedman and W. Low, J. Chem. Phys. **33**, 1275 (1960).

⁷ P. M. Llewellyn, thesis, Oxford University, Cambridge, England, 1956.

⁸ In one particular crystal the conversion efficiency was unaccountably much higher. Unfortunately, on repeating the procedure on the same crystal the valence was changed.

In a nonheated crystal no cubic lines were observed, and the upper limit of uranium in a cubic site was $\frac{1}{4}\%$.

In view of these experiments we tentatively propose that there is a great difference in conversion efficiency between *S*-state and non-*S*-state ions. Further, in the case of non-*S*-state ions, it is probably the rate of lowering through the thermal gradient and not the annealing process which is predominant in determining the point symmetry. It has been previously suggested that *S*-state ions, because of the symmetric charge distribution, tend to preserve the cubic point symmetry.⁹ These experiments seem to give some additional support for this suggestion.

V. ADDITIONAL AXIAL SPECTRA IN THE Nd^{3+} CRYSTAL

In a crystal of Nd containing predominantly axial sites, a number of weak lines were observed with angular variation differing from those associated with the cubic site and the previously investigated axial site. The angular variation indicates that these lines arise from Nd in a new axial site. The site proposed is one in which the excess F^- ion occupies the position at the center of the cube of fluorine ions sharing a corner with the cube containing the Nd ion. Although such a F^- ion is $\sqrt{3}$ times the distance from the rare-earth ion, as in the usual axial site (along the cubic axes), there are $\frac{4}{3}$ as many possible positions. A detailed analysis in the Nd case is made difficult by the presence of the 48 hyperfine lines of the usual axial field spectrum. The trivalent cerium and gadolinium ions are more promising cases of investigation, and in both crystals a number of weak anisotropic lines in the spectrum have been reported previously.^{3,10}

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⁹ W. Low, Phys. Rev. **105**, 801 (1957).

¹⁰ W. Low, Phys. Rev. **109**, 265 (1958).