

Paramagnetic Resonance of Divalent Holmium in Calcium Fluoride*

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The paramagnetic resonance spectrum of the ground state of divalent holmium in calcium fluoride has been observed at a temperature of 4.3°K and at frequencies of 9 and 27 kMc/sec. The spectrum is isotropic and may be fitted to a spin Hamiltonian with $S=1/2$, $I=7/2$, $A=-0.1307$ cm⁻¹, $g=-5.912$ and $G_N=+48$, where G_N is a pseudonuclear g factor. The value of g indicates that the ground state is Γ_6 . The appearance of a pseudonuclear g factor, which arises because the nearest quartet state has matrix elements with the ground state, permits a determination of the energy separation to the quartet state.

INTRODUCTION

SINGLE crystals of calcium fluoride are in the form of a cubic lattice in which the monovalent fluorines are located at the eight corners of the cube and the divalent calcium ions occupy alternate body-centered sites. Bleaney and his co-workers^{1,2} have done extensive paramagnetic resonance work on trivalent rare-earth ions substituted at low concentrations for the divalent calcium. An important product of that work is an indication of the manner in which charge compensation occurs since the compensation mechanism usually destroys the cubic symmetry. Occasionally, cubic sites are found² and these lend themselves to detailed analytical studies of crystal field theory, line broadening, and spin-lattice relaxation.

It is difficult to produce trivalent ions in calcium fluoride in cubic sites. An alternative approach, which avoids reduction of symmetry by charge compensation, is the study of divalent ions in CaF₂ where the divalent state is produced either chemically, or more simply, by γ irradiation. Hayes³ and Twidell have already reported on divalent thulium, a material which was also studied at this laboratory. In thulium, a minor additional observation to those reported is the occurrence of a "forbidden" transition which involves a simultaneous change of electron and nuclear quantum numbers. This paper reports on a study of the paramagnetic resonance spectrum of divalent holmium substituted at low concentration for calcium in a cubic site in calcium fluoride.⁴

Divalent Holmium in a Cubic Field

Divalent holmium (isoelectronic to trivalent erbium) has eleven $4f$ electrons. The ground state of the free ion is $^4I_{15/2}$. In a cubic field, the 16-fold degeneracy of the ground state is split into five levels consisting of three quartets and two doublets. The relative positions of

these levels are a function of two parameters, the fourth- and sixth-order terms of the cubic potential. The levels have been plotted in a particularly convenient way by Lea, Leask, and Wolf.⁵ Figure 1, taken from that paper, indicates that either a Γ_6 or a Γ_7 doublet will be lowest in all cubic fields with four-fold or eight-fold coordination.

Natural holmium consists of a single isotope with a nuclear spin of 7/2. In the presence of a magnetic field, the perturbation to be applied to the ground state is

$$H = \beta(\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H} + a\mathbf{I} \cdot \mathbf{J} - g_N\beta_N\mathbf{H} \cdot \mathbf{I}. \quad (1)$$

If the perturbation calculation is carried out for only the lowest level (necessarily a doublet), a simple spin Hamiltonian of the following form applies:

$$H = g\beta\mathbf{H} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S} - g_N\beta_N\mathbf{H} \cdot \mathbf{I}. \quad (2)$$

It is easy to show that g and A are scalars for an isolated doublet in a cubic field.

Experimental Results

The spectrum was observed at 4.3°K at both 9.331 kMc/sec and 28.09 kMc/sec in a crystal containing ap-

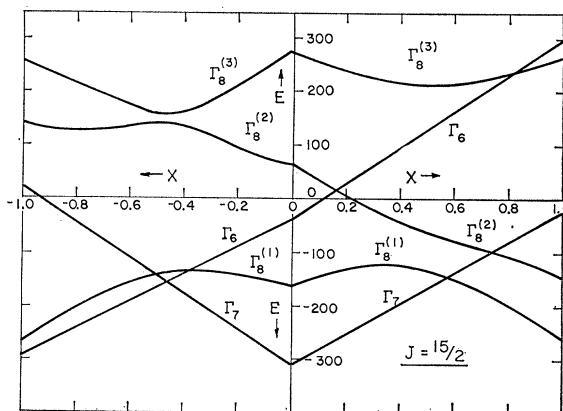


Fig. 1. Energy levels in cubic crystalline field (from Lea, Leask, and Wolf, reference 5).

* K. R. Lea, M. J. M. Leask, and W. P. Wolf, *J. Phys. Chem. Solids* **23**, 1381 (1962).

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¹ B. Bleaney, P. M. Llewellyn, and D. A. Jones, *Proc. Phys. Soc. (London)* **B69**, 858 (1956).

² J. M. Baker, W. Hayes and D. A. Jones, *Proc. Phys. Soc. (London)* **B73**, 942 (1959).

³ W. Hayes and J. W. Twidell, *J. Chem. Phys.* **35**, 1521 (1961).

⁴ A brief account of this work was presented at the August 1962 meeting of the American Physical Society, *Bull. Am. Phys. Soc.* **7**, 449 (1962).

TABLE I. Observed transitions for CaF₂: Ho²⁺ at 4.3°K.

Frequency (kMc/sec)	Observed field (G)	Transition (high-field notation)
9.331	971	$ -1/2, -7/2 \rangle \rightarrow -1/2, -5/2 \rangle$
9.331	2496	$ 1/2, -7/2 \rangle \rightarrow -1/2, -7/2 \rangle$
28.09	4943	$ 1/2, -7/2 \rangle \rightarrow -1/2, -7/2 \rangle$
28.09	4250	$ 1/2, -5/2 \rangle \rightarrow -1/2, -5/2 \rangle$
28.09	3621	$ 1/2, -3/2 \rangle \rightarrow -1/2, -3/2 \rangle$
28.09	3066	$ 1/2, -1/2 \rangle \rightarrow -1/2, -1/2 \rangle$
28.09	2589	$ 1/2, 1/2 \rangle \rightarrow -1/2, 1/2 \rangle$
28.09	2193	$ 1/2, 3/2 \rangle \rightarrow -1/2, 3/2 \rangle$
28.09	1869	$ 1/2, 5/2 \rangle \rightarrow -1/2, 5/2 \rangle$
28.09	1610	$ 1/2, 7/2 \rangle \rightarrow -1/2, 7/2 \rangle$
28.09	4592	$ 1/2, -7/2 \rangle \rightarrow -1/2, -5/2 \rangle$
28.09	3931	$ 1/2, -5/2 \rangle \rightarrow -1/2, -3/2 \rangle$
28.09	3342	$ 1/2, -3/2 \rangle \rightarrow -1/2, -1/2 \rangle$
28.09	2825	$ 1/2, -1/2 \rangle \rightarrow -1/2, 1/2 \rangle$
28.09	2389	$ 1/2, 1/2 \rangle \rightarrow -1/2, 3/2 \rangle$
28.09	2027	$ 1/2, 3/2 \rangle \rightarrow -1/2, 5/2 \rangle$
28.09	1741	$ 1/2, 5/2 \rangle \rightarrow -1/2, 7/2 \rangle$

proximately 0.05% Ho. The spectrum is, as expected, isotropic and the fields at which resonant absorption occurs are given in Table I. Because of the large

hyperfine splitting, only two resonance lines are observed at the lower frequency. The linewidth of all lines is about 15 G. The spin-lattice relaxation time, measured by pulse techniques, is approximately 0.9 msec at 1.5°K.

Theory

The data can be fitted to an accuracy of 0.6% using the simple Hamiltonian of Eq. (2). However, there is a small systematic error which is magnetic field dependent. The approximate theory is presented first and it is followed by a discussion of a possible correction for the systematic error.

1. Approximate Theory

Because of the hyperfine interaction, all but two of the 16 hyperfine levels are mixed spin states. The general form of the eigenfunction is

$$\Psi_{m,M} = N [| m, M \rangle + \epsilon(mM) | -m, M+2m \rangle], \quad (3)$$

where m and M are the electron and nuclear magnetic quantum numbers, N is the normalizing constant, and

$$\epsilon^{Am}(m,M) = \frac{| -g\beta H - (M+m)A + 2m[g^2\beta^2 H^2 + 2(m+M)g\beta HA + 16A^2]^{1/2} |}{| g\beta H + (M+m)A + 2m[g^2\beta^2 H^2 + 2(m+M)g\beta HA + 16A^2]^{1/2} |}.$$

The sign of ϵ is the sign of the numerator of the expression within the absolute value signs. In the region below 5000 G, where these measurements were taken, ϵ is quite large. Therefore, some transitions are observed which involve a change in the nuclear spin quantum number in addition to the normally allowed transitions (Fig. 2).

The energies are:

$$E_{m,M} = -\frac{1}{4}A + m[g^2\beta^2 H^2 + 2(M+m)Ag\beta H + 16A^2]^{1/2}. \quad (4)$$

The data can be fitted approximately to Eq. (4) using the values $|g| = 5.911$ ($g\beta = 0.2760 \times 10^{-3} \text{ cm}^{-1} \text{ G}^{-1}$) and $|A| = 0.1308 \text{ cm}^{-1}$. As can be seen from Table I, three kinds of transitions have been observed: (a) a change in the spin quantum number only, (b) a change in the nuclear quantum number only, and (c) a simultaneous change of the spin and nuclear quantum numbers. The levels have been labeled in a manner appropriate to the high-field limit.

Using the approximate value of g given above, one can choose between the two possible ground doublets shown in Fig. 1. The wave functions for these states have been tabulated by Polo⁶ and they are also given by Lea, Leask, and Wolf.⁵ The theoretical g value for the

Γ_6 state is -6.0 while it is $+6.8$ for Γ_7 without considering small corrections. Hence, the ground state of Ho²⁺ in CaF₂ is identified as Γ_6 .

2. Corrections

With the parameters $|A| = 0.1308 \text{ cm}^{-1}$ and $|g| = 5.911$, the fit of the strong-field allowed transitions is good to

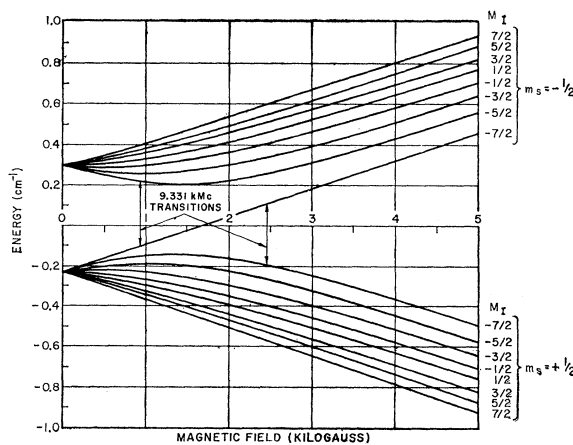


FIG. 2. The ground-state energy levels of divalent holmium in CaF₂.

⁶ S. Polo [Harper & Brothers, New York (to be published)].

0.05%. This is a random error and it is within the precision of the experiment ($\sim 0.1\%$). However, the fit of the seven double spin-flip transitions is poor (0.6%) and shows a systematic variation with magnetic field. Alternatively, the double spin-flip transitions may be fitted exactly and the systematic discrepancy appears in the "allowed" lines. It appears that the problem can be resolved by properly accounting for the mixing of the ground doublet, (see Fig. 1) with the quartet states by the hyperfine interaction.

Baker and Bleaney⁷ have discussed this correction which is of the form:

$$H' = \sum_f \left(\frac{2\langle i | a\mathbf{I} \cdot \mathbf{J} | f \rangle \langle f | \Lambda\beta\mathbf{H} \cdot \mathbf{J} | i \rangle}{E_i - E_f} + \frac{|\langle i | a\mathbf{I} \cdot \mathbf{J} | f \rangle|^2}{E_i - E_f} \right). \quad (5)$$

From Fig. 1 it is clear that just one of the quartets lies near the Γ_6 state and only the mixing with that state needs to be considered. (The perturbations considered here cannot mix Γ_6 with Γ_7 .) Under the conditions of this experiment the field-dependent correction term ranges in magnitude from 2 times to 20 times the field-independent correction. Since the accuracy of the experiment does not warrant retaining both terms, we have used only the field-dependent portion. Although the general form of that term is anisotropic, it is not difficult to show that in a cubic field the correction to a Γ_6 or Γ_7 doublet will be isotropic if the Zeeman energy is small compared to the splitting to the nearest quartet.

To apply the correction, the Hamiltonian given by Eq. (2) can be rewritten as:

$$H = g\beta\mathbf{H} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S} - (G_N + g_N)\beta_N\mathbf{H} \cdot \mathbf{I}, \quad (6)$$

where, from Eq. (5),

$$G_N = \frac{2a\Lambda \sum \langle \Gamma_6 | J_z | \Gamma_8 \rangle^2 \beta}{E(\Gamma_8) - E(\Gamma_6)} \beta_N \quad (7)$$

and g_N is the nuclear g value. Since g_N is found to be negligible compared to G_N , the term including g_N is neglected. Then the eigenenergies are

$$E = -\frac{1}{4}A - (M+m)G_N\beta_N H - m[(g\beta + G_N\beta_N)^2 H^2 + 2(M+m)A(g\beta + G_N\beta_N)H + 16A^2]^{1/2}. \quad (8)$$

All of the 17 observed resonances may now be fitted to Eq. (7) to an accuracy of 0.05% using the values $g = -5.912$ ($g\beta = -0.2760 \times 10^{-3} \text{ cm}^{-1} \text{ G}^{-1}$) $A = -0.1307 \text{ cm}^{-1}$, $G_N = +48$ ($G_N\beta_N = +1.2 \times 10^{-6} \text{ cm}^{-1} \text{ G}^{-1}$). The signs of these parameters were determined in the following way. The sign of g is calculated to be negative for the Γ_6 doublet. The sign of A cannot be determined uniquely from the data and Eq. (8), but the sign of G_N is uniquely determined. Then, from Eq. (7), the sign of a is positive. The relation between a and A is defined by

Eqs. (1) and (2) and it is easily shown that $a = -\frac{1}{3}A$. Hence, the sign of A is negative.

The exact value of the matrix element involved in Eq. (7) depends on the ratio of the crystal field parameters. However, in the entire range where Γ_6 is lowest, the matrix element is nearly 3.7. Thus, one can calculate the energy above ground of the Γ_8 state to a precision limited by G_N . Using the values Λ (the Landé g factor) = 6/5, and $a = -\frac{1}{3}A = 0.026 \text{ cm}^{-1}$, this energy is $32 \pm 4 \text{ cm}^{-1}$. This agrees reasonably well with a value of 30.1 cm^{-1} obtained from recent optical experiments.⁸

Discussion

For the case of Er^{3+} in a cubic site in CaF_2 , Baker, Hayes, and Jones² have found that the ground state is a Γ_7 doublet in contrast to Γ_6 for holmium. A crude argument may be made to explain the observed change in the ground state in going from Er^{3+} to Ho^{2+} . The ground state is determined by the ratio of the fourth to the sixth-order cubic potentials, i.e., by $R^2/(\langle r^6 \rangle / \langle r^4 \rangle)$, where r is the radius of the f electrons and R is the distance to the fluorine ions. In changing from Er^{3+} to Ho^{2+} one can expect both R and r to increase. Roughly speaking, the fluorines see a change in charge of 3 to 2 while the $4f$ electrons see only a unit change in a somewhat larger charge. Thus, the effect on the fluorines should be somewhat larger than the effect on the f electrons, and the ratio of fourth- to sixth-order potentials should increase. This will increase the value of $|x|$ in Fig. 1 in agreement with the observed change in the ground state. One might also expect that a change in the ratio of the crystal field parameters should not be very large between the isoelectronic ions. This implies that for both trivalent erbium and divalent holmium the value of x (in the Lea, Leask, and Wolf notation) is probably not far from -0.45 , the crossing point of Γ_6 and Γ_7 states.

The 1.5% departure of the g value from -6.0 , the theoretical value obtained assuming Russell-Saunders coupling, is difficult to explain. A departure from Russell-Saunders coupling will mix in the ${}^2K_{15,2}$ state which is approximately $20\,000 \text{ cm}^{-1}$ above the ground state. Assuming a spin-orbit constant of 2000 cm^{-1} , and using the matrix element calculated by Judd and Loudon,⁹ this correction is only 0.2%. One might expect that the remainder of the discrepancy could be due to: (a) a mixing of the ${}^4I_{13/2}$ state into the ground state by the crystal field; (b) a small axial distortion; or (c) a third-order Zeeman effect due to the mixing of the Γ_8 state with the Γ_6 state. However, the contribution of (a) is exactly zero for the Γ_6 state. Nor can the effect be due to an axial field since any significant contribution of the axial field must cause a detectable anisotropy. This may be seen from a formula stated by Low,¹⁰ $g_{11} + 2g_{\perp} = 3g$,

⁸ H. Weakliem and Z. J. Kiss (to be published).

⁹ B. R. Judd and R. Loudon, Proc. Roy. Soc. (London) **A251**, 127 (1959).

¹⁰ W. Low, J. Phys. Soc. Japan, **17**, Suppl. B-1 (1962).

⁷ J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156 (1958).

where g is the isotropic value in a cubic field. A proof of this relation for any Γ_6 or Γ_7 state is given in the Appendix. Finally, the third-order Zeeman effect is negligible in this case. Thus, the major portion of the discrepancy is not accounted for.

ACKNOWLEDGMENTS

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APPENDIX: THE PERTURBATION OF THE ENERGY LEVELS OF A Γ_6 OR Γ_7 DOUBLET BY AN AXIAL DISTORTION AND A MAGNETIC FIELD

Assumption: The total perturbation energy is small compared to the separation of the doublet from the nearest quartet.

We start with basis functions appropriate to a cubic crystalline field. Since the two kinds of doublets are not mixed by either a magnetic field or an axial distortion, only one doublet and the nearest quartet need be considered. To simplify notation, we refer to the doublet as Γ_6 . The proof is identical for Γ_7 . A six by six matrix of the operator

$$H = (\Delta\beta H \cos\theta J_z + V) + \Lambda\beta H \sin\theta J_x$$

must be diagonalized, where θ is the angle between the magnetic field and the Z axis and the magnetic field is taken in the Zx plane for simplicity. The axial potential, V , is of the form $c_1 J_z^2 + c_2 J_z^4 + c_3 J_z^6$.

The calculation can be made in a very simple and general way by using coupling coefficients given by Polo.⁶ These show that the matrix elements of J connecting a doublet with a quartet are:

$$\langle \Gamma_8 | J_z | \Gamma_6 \rangle = C \begin{pmatrix} 1/2 & -1/2 \\ (\frac{2}{3})^{1/2} & \\ & (\frac{2}{3})^{1/2} \\ & & & -3/2 \end{pmatrix} \begin{matrix} 3/2 \\ 1/2 \\ -1/2 \\ -3/2 \end{matrix}$$

$$\langle \Gamma_8 | J_x | \Gamma_6 \rangle = C \begin{pmatrix} 1/2 & -1/2 \\ -(\frac{1}{2})^{1/2} & \\ & -(\frac{1}{6})^{1/2} \\ (\frac{1}{6})^{1/2} & \\ & & & (\frac{1}{2})^{1/2} \end{pmatrix} \begin{matrix} 3/2 \\ 1/2 \\ -1/2 \\ -3/2 \end{matrix}$$

where C is a constant to be calculated for a specific crystal field. It is also easy to show that

$$\langle \Gamma_{8,1/2} | V | \Gamma_{6,1/2} \rangle = -\langle \Gamma_{8,-1/2} | V | \Gamma_{6,-1/2} \rangle = V, \\ \langle \Gamma_{8,1/2} | V | \Gamma_{6,-1/2} \rangle = 0 = \langle \Gamma_{8,-1/2} | V | \Gamma_{6,1/2} \rangle.$$

To apply perturbation theory, it is necessary to use linear combinations of $\Gamma_{6,1/2}$ and $\Gamma_{6,-1/2}$ that diagonalize the doublet in the presence of the magnetic field. When this is done, a second-order calculation shows that

$$E(\Gamma_{6,+}) = \Lambda\beta H J_z + \langle + | V | + \rangle - \frac{1}{E(\Gamma_8) - E(\Gamma_6)} \\ \times \{ \frac{2}{3} \Lambda^2 \beta^2 H^2 + V^2 + (8/3)^{1/2} \Lambda \beta H C V \cos^2 \theta \\ - (2/3)^{1/2} \Lambda \beta H C V \sin^2 \theta \}, \quad (A1)$$

$$E(\Gamma_{6,-}) = -\Lambda\beta H J_z + \langle + | V | + \rangle - \frac{1}{E(\Gamma_8) - E(\Gamma_6)} \\ \times \{ \frac{2}{3} \Lambda^2 \beta^2 H^2 + V^2 - (8/3)^{1/2} \Lambda \beta H C V \cos^2 \theta \\ + (2/3)^{1/2} \Lambda \beta H C V \sin^2 \theta \}. \quad (A2)$$

The splitting of the doublet is

$$E(\Gamma_{6,+}) - E(\Gamma_{6,-}) = 2\Lambda\beta H J_z - \frac{(8/3)^{1/2} \Lambda \beta H C V}{E(\Gamma_8) - E(\Gamma_6)} \\ \times (2 \cos^2 \theta - \sin^2 \theta). \quad (A3)$$

From Eqs. (A1), (A2), and (A3) we can conclude that: (i) There is an isotropic second-order Zeeman shift which moves both doublet levels equally in the same direction. (ii) The second-order term in the axial field also moves both levels an equal amount, as it must be because of Kramers' theorem. (iii) The cross-term between the axial distortion and the magnetic field produces an anisotropic g value of the form $g = g_0 + g'(2 \cos^2 \theta - \sin^2 \theta)$. Equation (A3) can be used to deduce the matrix element of the axial field from an observed axial spectrum. Note that $g_{11} + 2g_1$ is three times the g value of the cubic field.