## Paramagnetic Resonance of Divalent Holmium in the Cubic Hosts: $CaF_2$ , $SrF_2$ , $BaF_2$ , and $SrCl_2^{\dagger}$

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The paramagnetic-resonance spectra of the ground state of  $Ho^{2+}$  in the four lattices CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub>, and SrCl<sub>2</sub> have been measured at helium temperatures at frequencies of 9 and 27 Gc/sec. The spectrum is isotropic and was fitted to a spin Hamiltonian which was modified to include a pseudonuclear g factor which arises because of matrix elements with the nearest quartet state. The pseudonuclear g factor permitted a determination of the energy separation to the quartet state. The g value identified the ground state as  $\Gamma_6$ for the fluorite lattices and  $\Gamma_7$  for SrCl<sub>2</sub>. It was found that the ratio of the crystal-field constants,  $B_4/B_6$ , decreases as the lattice spacing increases, which is contrary to what is expected from the point-charge model. The experimental g values differ from the theoretical values by about 1.5%, and the discrepancy is attributed to orbit-lattice interaction and/or covalency. The magnetic hyperfine constant for the Ho<sup>2+</sup> ion was found to be reasonably close to that reported for the Ho atom. However, the hyperfine constant for the SrCl<sub>2</sub> lattice differs from that in the fluorite lattices by about 1.5% and is not satisfactorily accounted for.

## I. INTRODUCTION

**`HE energy levels of rare-earth ions in cubic hosts** are being extensively investigated by means of their optical spectra and their electron paramagnetic resonance spectra for two reasons: (1) The cubic symmetry of the lattice lends itself to detailed analytical studies of crystal-field theory, line broadening, and spin lattice relaxation; (2) their potential use in lasers and masers. This paper reports on the paramagnetic resonance spectra of divalent holmium substituted at low concentrations in CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub>, and SrCl<sub>2</sub>. The difference between the experimental and theoretical values of the g values and the magnetic hyperfine constant a of the ground state is discussed. It is shown that the point-charge model does not predict the correct changes in the energy levels for the same ion in different but similar hosts.



<sup>△ 0&</sup>lt;sup>2-</sup>

FIG. 1. A portion of the  $RX_2$  lattice showing the site of the substitutional rare-earth ion and possible locations of charge compensating ions for substitutional trivalent ions.

#### **II. FLUORIDE LATTICE**

 $CaF_2$ ,  $SrF_2$ ,  $BaF_2$ , and  $SrCl_2$  are examples of the  $RX_2$ structure<sup>1</sup> which is shown in Fig. 1. This may be visualized as a cubic lattice of X ions in which every other body-center position is occupied by a divalent R ion. Rare-earth ions enter the lattice substitutionally for an R ion. At such sites, the divalent rare-earth ion experiences a cubic crystalline electric field of symmetry  $O_h$ . The crystal field at the R site can be calculated on a point-charge model and the distances to the first four sets of ions are: eight  $X^-$  at the distance  $(\sqrt{3}/2)a$ , twelve  $R^{2+}$  ions at a distance of  $\sqrt{2}a$ , twenty four X<sup>-</sup> at a distance of  $(\frac{1}{2}\sqrt{11})a$ , and six  $R^{2+}$  ions at a distance of 2a. Table I gives the lattice parameters, density, Debye temperature, and sound velocities of the different host materials.

### III. DIVALENT HOLMIUM IN A CUBIC FIELD

The divalent holmium ion (isoelectronic to trivalent erbium) has eleven electrons in the incomplete 4f shell. The spin-orbit coupling first splits the energy levels with the  ${}^{4}I_{15/2}$  multiplet being lowest and the first excited state is  ${}^{4}I_{13/2}$  from Hund's rule. An ideal cubic field further splits each of these states as shown in Fig. 2, into five levels. The relative positions of these levels are a function of two parameters, the fourth- and sixth-order terms of the cubic potential, which is given by the expression

$$V_{\text{cubic}} = B_4 (4\pi/9)^{1/2} \{ Y_4^0 + (5/14)^{1/2} (Y_4^4 + Y_4^{-4}) \} + B_6 (4\pi/13)^{1/2} \{ Y_6^0 - (7/2)^{1/2} (Y_6^4 + Y_6^{-4}) \}, \quad (1)$$

where the  $Y_L^M$  are normalized spherical harmonics. The levels have been plotted in a convenient way by Lea, Leask, and Wolf.<sup>2</sup> Figure 3, taken from that paper, depicts the energy level scheme for the ground state

Ca 2+

<sup>&</sup>lt;sup>†</sup>This paper is part of a thesis which was submitted in par-tial fulfillment of the requirement for the Ph.D. degree at University of Pennsylvania, 1965.

<sup>&</sup>lt;sup>1</sup> R. W. Wyckoff, Crystal Structures (Interscience Publishers, Inc., New York, 1948), Vol. 1, Chap. 4. <sup>2</sup> K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids 23, 1381 (1962).

Crystal	Lattice constant 2a Å	Density g/cm <sup>3</sup>	Debye temperature at 0°K	Longitudinal sound velocity along cube axis at 4.2°K $v_l = \left(\frac{c_{11}}{\rho}\right)^{1/2}$ (cm/sec)	Transverse sound velocity along cube axis at 4.2°K $v_t = \left(\frac{c_{44}}{\rho}\right)^{1/2}$ (cm/sec)
CaF <sub>2</sub>	5.463ª	3.18 <sup>b</sup> at 300°K 3.21 at 4.2°K	508 <sup>b</sup> specific heat 513 elastic constants	7.36×10 <sup>5 b</sup>	3.34×10⁵ <sup>ь</sup>
$\mathrm{SrF}_2$	5.799ª	4.24° at 300°K	378 <sup>d</sup> elastic constants	5.46×10 <sup>5 d</sup>	2.80×10 <sup>5 d</sup>
$\operatorname{BaF}_2$	6.200ª	4.83° at 300°K	285° elastic constants	4.28×10⁵ °	2.27×10 <sup>5</sup> °
${\rm SrCl}_2$	6.977ª	3.05° at 300°K			

TABLE I. Some characteristics of the cubic hosts: CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub>, SrCl<sub>2</sub>.

<sup>a</sup> See Ref. 1.
<sup>b</sup> D. R. Huffman and M. H. Norwood, Phys. Rev. 117, 709 (1960).
<sup>c</sup> D. Gerlick, Phys. Rev. 135, A1331 (1964).
<sup>d</sup> D. Gerlick, Phys. Rev. 136, A1366 (1964).
<sup>e</sup> Handbook of Chemistry and Physics, edited by Charles D. Hodgman et al. (Chemical Rubber Publishing Company, Cleveland, Ohio, 1965).

and indicates that either a  $\Gamma_6$  or  $\Gamma_7$  doublet will be lowest in all cubic fields with eightfold coordination. [The coefficients  $B_4$  and  $B_6$  given in Fig. 3 and defined in Ref. (2) differ by constant values from the coefficients as defined by Eq. 1. When referring to the coefficients in Ref. (2), the constants will contain the subscript (LLW).7

Natural holmium consists of a single isotope Ho<sup>165</sup> with a nuclear spin of  $\frac{7}{2}$ . In the presence of a magnetic field, the perturbation to be applied to the ground state is

$$H = \beta (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{H} + a\mathbf{I} \cdot \mathbf{J} - g_n \beta_n \mathbf{H} \cdot \mathbf{I}.$$
(2)

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

$$H = g\beta \mathbf{H} \cdot \mathbf{S} + A\mathbf{I} \cdot \mathbf{S} - g_n \beta_n \mathbf{H} \cdot \mathbf{I}, \qquad (3)$$

where g and A are scalars for an isolated doublet in a cubic field.

#### IV. DIVALENT HOLMIUM IN CaF<sub>2</sub>

## **Experimental Results**

The ground-state resonance spectrum was observed at 4.2°K at both 9.331 and 28.90 Gc/sec, in a crystal containing a total holmium concentration of 0.05%.3 The divalent holmium was obtained by  $\gamma$ -irradiation<sup>4</sup> and the resulting divalent concentration was about 0.005%. The spectrum is, as expected, isotropic and the fields at which resonant absorption occurs are given in Table I of I. Because of the large hyperfine splitting, only two resonance lines are observed at the lower frequency. The linewidth at the lower frequency

is 12 G (82 Mc/sec) at 4.2°K and is temperaturedependent above 7°K. The spin lattice relaxation time, measured by pulse techniques, is 0.9 msec at 1.5°K at 9.8 Gc/sec for the  $|\frac{1}{2}, -\frac{7}{2} \rightarrow |-\frac{1}{2}, \frac{7}{2} \rightarrow$  transition. In addition to the isotropic spectrum, other resonance lines were observed with intensities 1/15 of the isotropic spectrum or less. These weaker lines were not studied and are attributed to trivalent holmium in a crystal field of trigonal of tetragonal symmetry.

Using a 0.02% holmium-doped CaF<sub>2</sub> crystal in which the holmium was completely reduced to the divalent state by the calcium baking technique,<sup>5</sup> resonance lines due to the  $\Gamma_7$  excited state were observed at elevated temperatures. Table II gives the magneticfield values for both the ground state  $\Gamma_6$  and the excited state  $\Gamma_7$  for a frequency of 9.69 Gc/sec.



FIG. 2. Energy levels of Ho<sup>2+</sup> in cubic field of RX<sub>2</sub> lattice. Splittings given in expanded view are the measured values of Weakliem.

<sup>5</sup> Z. J. Kiss and P. N. Yocum, J. Chem. Phys. 41, 1511 (1964).

<sup>&</sup>lt;sup>8</sup> The ground-state data and part of the analysis have been given by H. R. Lewis and E. S. Sabisky, Phys. Rev. 130, 1370 (1963) and W. Hayes, G. D. Jones, and J. W. Twidell, Proc. Phys. Soc. (London) 81, 371 (1963), but will be partially reproduced for continuity and completeness. The paper by Lewis and Sabisky will be referred to a L will be referred to as I. <sup>4</sup>E. S. Sabisky, J. Appl. Phys. 36, 1788 (1965).

CaFe

(3)

Sr Cl<sub>2</sub>

Γ,<sup>(2)</sup>





300

200

100

FIG. 3. Energy levels in cubic crystalline field (from Lea, Leask, and Wolf, Ref. 2).

## Theory

The data can be interpreted as discussed in the paper by Lewis and Sabisky (see I). It was shown that the data can be fitted approximately using the values |g| = 5.911 and |A| = 0.1308 cm<sup>-1</sup>. From the g value,

TABLE II. Observed transitions for CaF<sub>2</sub>:Ho<sup>2+</sup> at 25°K at 9.69 Gc/sec.

Observed field (kG)	Linewidth Mc	Transition	Intensity	Energy level
0.91		$\left -\frac{1}{2},-\frac{7}{2}\right\rangle \rightarrow \left -\frac{1}{2},-\frac{5}{2}\right\rangle$	20	$\Gamma_6$
1.09		$\left -\frac{1}{2},-\frac{5}{2}\right\rangle \rightarrow \left -\frac{1}{2},-\frac{7}{2}\right\rangle$	5	$\Gamma_7$
2.55	620	$\left -\frac{1}{2},-\frac{7}{2}\right\rangle \rightarrow \left \frac{1}{2},-\frac{7}{2}\right\rangle$	20	$\Gamma_6$
2.36	630	$\left \frac{1}{2}, -\frac{7}{2}\right\rangle \rightarrow \left -\frac{1}{2}, -\frac{7}{2}\right\rangle$	5	$\Gamma_7$

the ground state is identified at  $\Gamma_6$  which has a theoretical g value of -6.0. Using the above approximate values, the fit of the strong field allowed transitions is within the precision of the experiment. However, the fit of the seven double spin-flip transitions is poor 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 (see Fig. 4). It was shown (see I) that the discrepancy could be resolved by properly accounting for the mixing of the  $\Gamma_6$  ground doublet (see Figs. 2 and 3) with the quartet states by the hyperfine interaction.<sup>6</sup> A first-order perturbation between the ground state  $\Gamma_6$  and the quartet states is given by the expression

$$H' = \sum_{f} \frac{\langle i | \beta (\mathbf{L}+2\mathbf{S}) \cdot \mathbf{H} | f \rangle \langle f | \beta (\mathbf{L}+2\mathbf{S}) \cdot \mathbf{H} | i \rangle}{E_{i} - E_{f}} + \sum_{f} \left[ \frac{2 \langle i | \beta (\mathbf{L}+2\mathbf{S}) \cdot \mathbf{H} | f \rangle \langle f | a\mathbf{I} \cdot \mathbf{J} | i \rangle}{E_{i} - E_{f}} + \frac{|\langle i | a\mathbf{I} \cdot \mathbf{J} | f \rangle|^{2}}{E_{i} - E_{f}} \right], \quad (4)$$

where  $E_i$  is the energy of the ground state and  $E_f$  that of the excited states. From Fig. 3, it is clear that just one of the quartet states lies near the  $\Gamma_6$  state and only the mixing with that state needs to be considered. The perturbations being considered here cannot mix the  $\Gamma_6$  and  $\Gamma_7$  states. The first term in the above expression shifts all the energy levels of the  $\Gamma_6$  by an equal amount in the same direction. This correction would not be reflected in the data since only energy differences are measured.

The second part of Eq. (4) arises from a combination of the Zeeman effect and the hyperfine structure. This part can be written for  $\mathbf{H} \| z$  and a particular  $M_J$  value as

10 77 7

where  

$$g_{n}' = \frac{2a\Lambda}{E(\Gamma_{8}) - E(\Gamma_{6})} \frac{\beta}{\beta_{n}} \sum_{M_{J}'} |\langle \Gamma_{6}, M_{J} | J_{Z} | \Gamma_{8}, M_{J}' \rangle|^{2}. \quad (5)$$

This additional term is of the same form as the last term in the spin Hamiltonian [Eq. (3)] and can be included by writing the last term as

$$(g_n' + g_n)\beta_n \mathbf{H} \cdot \mathbf{I}.$$
 (6)

For resonance transitions where the nuclear quantum

number does not change, the term [Eq. (6)] does not affect the position of the lines. However, it can be important where other transitions are observed. The correction term containing  $g_n'$  acts like a "pseudo-



FIG. 4. Ground-state energy levels of divalent holmium in  $CaF_2$ . The lines designating the  $\Delta m_I = 0$  and  $\Delta m_I = \pm 1$  transitions are not for a constant frequency.

<sup>6</sup> J. M. Baker and B. Bleaney, Proc. Phys. Soc. (London) A245, 156 (1958).

nuclear" g factor and if it is comparable with or larger than the nuclear g factor  $g_n$ , misleading results may be obtained. Although the general form of this correction term is anisotropic, it has been shown (see I) that in a cubic field the correction to a  $\Gamma_6$  or  $\Gamma_7$  state will be iso-

tropic if the Zeeman energy is small compared to the splitting to the nearest quartet state.

The third part of expression 4 arises from the hyperfine interaction alone. Expanding and again considering only the first quartet state, one gets

$$\sum_{f} \frac{|\langle i| a\mathbf{I} \cdot \mathbf{J} | f \rangle|^{2}}{E_{i} - E_{f}} = \frac{a^{2}}{E_{i} - E_{f}} \sum_{M_{J'}} \{\frac{1}{4} I \langle I + 1 \rangle [|\langle \Gamma_{6}, M_{J} | J_{-} | \Gamma_{8}, M_{J'} \rangle|^{2} + |\langle \Gamma_{6}, M_{J} | J_{+} | \Gamma_{8}, M_{J'} \rangle|^{2}] + \frac{1}{4} m_{I} [|\langle \Gamma_{6}, M_{J} | J_{-} | \Gamma_{8}, M_{J'} \rangle|^{2} - |\langle \Gamma_{6}, M_{J} | J_{+} | \Gamma_{8}, M_{J'} \rangle|^{2}] + m_{I}^{2} [|\langle \Gamma_{6}, M_{J} | J_{Z} | \Gamma_{8}, M_{J'} \rangle|^{2}] - \frac{1}{4} |\langle \Gamma_{6}, M_{J} | J_{-} | \Gamma_{8}, M_{J'} \rangle|^{2}] \}.$$
(7)

(9)

This equation gives rise to two kinds of correction terms, one quadratic in  $m_I$  and contributes a "pseudoquadrupole" interaction, the other is linear in  $m_I$  and contributes to the apparent magnetic hyperfine interaction. The term linear in  $m_I$  has an effect similar to that of the  $AS_zI_z$  term in the spin Hamiltonian and may produce an error when magnetic moments are calculated. From the coupling coefficients given by Polo,<sup>7</sup> the only nonzero matrix elements in Eq. (7) are given below:

$$\langle \Gamma_{8,\frac{3}{2}} | J_{+} | \Gamma_{6,\frac{1}{2}} \rangle = -C\sqrt{2} ,$$

$$\langle \Gamma_{8,-\frac{3}{2}} | J_{-} | \Gamma_{6}, -\frac{1}{2} \rangle = C\sqrt{2} ,$$

$$\langle \Gamma_{8,\frac{1}{2}} | J_{+} | \Gamma_{6}, -\frac{1}{2} \rangle = -C\sqrt{\frac{2}{3}} ,$$

$$\langle \Gamma_{8,-\frac{1}{2}} | J_{-} | \Gamma_{6,\frac{1}{2}} \rangle = C\sqrt{\frac{2}{3}} ,$$

$$\langle \Gamma_{8,\frac{1}{2}} | J_{z} | \Gamma_{6,\frac{1}{2}} \rangle = C\sqrt{\frac{2}{3}} ,$$

$$\langle \Gamma_{8,-\frac{1}{2}} | J_{z} | \Gamma_{6,-\frac{1}{2}} \rangle = C\sqrt{\frac{2}{3}} ,$$

$$\langle \Gamma_{8,-\frac{1}{2}} | J_{z} | \Gamma_{6,-\frac{1}{2}} \rangle = C\sqrt{\frac{2}{3}} ,$$

$$\langle \Gamma_{8,-\frac{1}{2}} | J_{z} | \Gamma_{6,-\frac{1}{2}} \rangle = C\sqrt{\frac{2}{3}} ,$$

where C is a constant to be calculated for a specific crystal field. Using the above relationships, the first term in Eq. (7) is a constant for all levels of the  $\Gamma_6$  state and can be neglected since we are only interested in energy differences. Also, it is easy to see that the coefficient of the  $m_1^2$  term is zero. Hence, in this particular case, because of fortuitous matrix elements the "pseudoquadrupole" interaction is zero. The remaining term in Eq. (7) can now be written as

where

$$\gamma = \frac{a^2}{2\left[E(\Gamma_8) - E(\Gamma_6)\right]} \left| \left< \Gamma_{6,\frac{1}{2}} \right| J_Z \left| \Gamma_{8,\frac{1}{2}} \right> \right|^2$$

 $\sum_{f} \frac{|\langle i| a\mathbf{I} \cdot \mathbf{J} | f \rangle^2}{E_i - E_f} = \mp \gamma m_I,$ 

and the minus sign is used for the  $|\Gamma_{6,\frac{1}{2}}\rangle$  state and the positive sign for the  $|\Gamma_{6},-\frac{1}{2}\rangle$  state.

A comparison of the magnitude of the second and third terms in Eq. (4) can now be made and one finds

$$\left|\frac{\sum_{f} 2\beta\Lambda H_{Z}\langle i | J_{Z} | f \rangle \langle f | a \mathbf{I} \cdot \mathbf{J} | i \rangle}{\sum_{f} |\langle i | a \mathbf{I} \cdot \mathbf{J} | f \rangle|^{2}}\right| = \frac{2a\Lambda\beta H_{Z}I_{Z}}{\frac{1}{2}a^{2}I_{Z}} = \frac{4\Lambda\beta H_{Z}}{a}.$$
(10)

<sup>7</sup> S. R. Polo (to be published).

From the approximate theory, it is easily shown that for  $H_z$  measured in kilogauss,  $\Lambda\beta/a\approx 2$ . Therefore, under the conditions of this experiment, the correction term which is linear in magnetic field ranges in magnitude from 8 to 40 times the field-independent term. Since the accuracy of the experiment does not warrant retaining both terms, only the term which is linear in field [Eq. (5)] is retained in the following analysis.

To apply the correction term, the Hamiltonian given by Eq. (3) is rewritten as

$$H = g\beta \mathbf{H} \cdot \mathbf{S} + A \mathbf{I} \cdot \mathbf{S} - (g_n' + g_n)\beta_n \mathbf{H} \cdot \mathbf{I}.$$
(11)

Since  $g_n$ , the nuclear g value, is found to be negligible compared to the experimentally determined constant,  $g_n'+g_n$ , the term in  $g_n$  can be neglected. Solving for the eigenenergies, one gets

$$E = -\frac{1}{4}A - (M+m)g_{n}'\beta_{n}H - M \\ \times \{ [g_{n}'\beta_{n}H + g\beta H + (M+m)A]^{2} \\ + [16 - (M+m)^{2}]A^{2} \}^{1/2}.$$
(12)

The opposite sign must be used in front of the square root term for the levels  $|-\frac{1}{2}, -\frac{7}{2}\rangle$  and  $|\frac{1}{2}, \frac{7}{2}\rangle$ . All of the 17 observed resonances given in Table I of I may now be fitted to Eq. (12) to an accuracy of 0.07% using the values g=-5.912 ( $g\beta=-0.2760\times10^{-3}$  cm<sup>-1</sup> G<sup>-1</sup>), A=-0.1307 cm<sup>-1</sup>,  $g_n'=+48$  ( $g_n'\beta_n=+1.2\times10^{-6}$  cm<sup>-1</sup> G<sup>-1</sup>). As discussed in I, one can calculate the energy above ground of the  $\Gamma_8^{(1)}$  state to a precision limited by  $g_n'$ . Using the values:  $\Lambda$  (the Lande g factor)=6/5, a=0.026 cm<sup>-1</sup> and the matrix element as 3.73, this energy is  $33\pm4$  cm<sup>-1</sup>. This agrees very well with a value of 33.8 cm<sup>-1</sup> obtained from optical experiments.<sup>8</sup> The good comparison between the observed separation of the  $\Gamma_8^{(1)}$  and  $\Gamma_6$  states and the value derived from  $g_n'$  supports the use of this correction term.

An analysis of the data given in Table II shows that the two resonances with an intensity of 20 belong to the  $\Gamma_6$  ground doublet which was discussed above. The lines with intensity of five belong to the thermally populated  $\Gamma_7$  state. The identification of the two weak lines with the  $\Gamma_7$  excited state was verified by comparing the observed field with the magnetic field calculated

<sup>&</sup>lt;sup>8</sup> H. A. Weakliem (private communication).

by using the g and A values for the  $\Gamma_7$  ground state in SrCl<sub>2</sub>. The energy above ground of the  $\Gamma_7$  state can be calculated using the equation

$$E(\Gamma_7) - E(\Gamma_6) = T \ln \left\{ \frac{A(\Gamma_6)}{A(\Gamma_7)} \left[ \frac{g(\Gamma_7)}{g(\Gamma_6)} \right]^2 \frac{\Delta\nu(\Gamma_6)}{\Delta\nu(\Gamma_7)} \right\}, \quad (13)$$

where A refers to the intensity, g is the g value,  $\Delta \nu$  is the linewidth, and T is the temperature. The above equation takes into account that the transition probabilities and magnetic fields are nearly equal for the two doublets. This is a very good approximation in this case. The derived value for the splitting above ground for the  $\Gamma_7$  state is  $29\pm4$  cm<sup>-1</sup>. This agrees with the value of 30.1 cm<sup>-1</sup> obtained from optical experiments.<sup>8</sup>

#### V. DIVALENT HOLMIUM IN SrF<sub>2</sub>

#### **Experimental Results**

The divalent resonance lines were observed at 4.2°K at both 26.958 and 9.471 Gc/sec in a crystal containing a total holmium concentration of 0.1%. The divalent holmium was obtained by  $\gamma$  irradiation and the resulting divalent concentration was about 0.002%. The spectrum is, as expected, isotropic and the fields at which resonant absorption occurs are similar to those for the CaF<sub>2</sub> lattice and are given in dissertation.<sup>9</sup> The linewidth at the lower frequency is 22 G (152 Mc/sec). In addition to the isotropic spectrum, an anisotropic holmium spectrum with intensities of about  $\frac{1}{10}$  the isotropic line was observed. The additional spectrum was seen before and after  $\gamma$  irradiation. These additional lines are stronger than the extraneous lines observed in the CaF<sub>2</sub> crystal, and are attributed to trivalent holmium in a crystal field of trigonal or tetragonal symmetry.

#### Theory

The data can be interpreted using the theory developed for CaF<sub>2</sub>. As in CaF<sub>2</sub>, the ground state is  $\Gamma_6$ from the g value. It is also found that all the data cannot be fitted without including the correction term, Eq. (4), which accounts for the mixing of the  $\Gamma_6$  ground doublet and the quartet state  $\Gamma_8^{(1)}$  by the hyperfine interaction.

All of the 17 observed resonances may be fitted to Eq. (12) to an accuracy of 0.1% using the values  $g=-5.916 (g\beta=-0.2762\times10^{-3} \text{ cm}^{-1} \text{ G}^{-1}) A=-0.1311 \text{ cm}^{-1}$ ,  $g_n'=+67 (g_n'\beta_n=+1.7\times10^{-6} \text{ cm}^{-1} \text{ G}^{-1})$ . The signs of the parameters were obtained as discussed for CaF<sub>2</sub>.

Although the exact value of the matrix element involved in Eq. (5) is unknown, the matrix element is nearly 3.7 in the entire range where  $\Gamma_6$  is lowest. The location of the  $\Gamma_8^{(1)}$  quartet state above the ground state is found to be  $23.8\pm4$  cm<sup>-1</sup> from  $g_n'$ . Optical data are not available. However, the SrF<sub>2</sub> lattice is larger than CaF<sub>2</sub> (see Table I) and a reduction in the crystal field is expected as one goes from CaF<sub>2</sub> to SrF<sub>2</sub>. This smaller crystal field suggests that the crystal-field split levels, if they do not cross each other, come closer together. On this basis, the derived splitting of  $23.8 \text{ cm}^{-1}$  in SrF<sub>2</sub> between the  $\Gamma_6$  and  $\Gamma_8^{(1)}$  is a reasonable value.

#### VI. DIVALENT HOLMIUM IN BaF2

Divalent resonance lines were identified at 4.2°K only at X-band frequencies after considerable difficulty. Several crystals of varying holmium concentrations were subjected to  $\gamma$  irradiation. These crystals exhibited no resonances which could be attributed to divalent holmium. After some crystals were baked in a barium atmosphere at 850°C for about one hour, two weak isotropic lines were observed. Because of the weak intensity of these lines and because of a strong anisotropic spectrum, the divalent lines were not identified at higher frequencies. The isotropic lines can be fitted to Eq. (12) to an accuracy of 0.3% using g = -5.91 $(g\beta = -0.276 \times 10^{-3} \text{ cm}^{-1} \text{ G}^{-1} \text{ and } A = -0.131 \text{ cm}^{-1}).$ This is the accuracy of the experiment. The reasonable fit of the data at two frequencies is strong evidence that the observed isotropic lines belong to divalent holmium. This means that the ground state is  $\Gamma_6$ . The poor accuracy prevented obtaining the "pseudo nuclear g factor,"  $g_n'$ .

The observed anisotropic spectrum was observed in all crystals before and after reduction treatments. This spectrum is much stronger than the anisotropic lines observed in SrF2 and CaF2. At X-band frequencies, this spectrum did not exhibit a clear set of eight lines due to the hyperfine structure of holmium. At frequencies near 27 Gc/sec, the spectrum cleared somewhat and two sets of eight lines were recognized and attributed to holmium. The two sets of eight hyperfine lines are intertwined and range from very low values in field to fields of about 3.5 kG. The lines are nearly equally spaced at high field and with spacings of approximately 600 and 550 G along the [110] direction for the two sets, respectively. The spectrum repeats at 60° intervals in the (111) plane. If these lines are described by a  $g_{11}$  and  $g_{1}$  using a spin  $S = \frac{1}{2}$  formalism, then  $g_{1} \simeq 0$  and the apparent value of  $g_{11}$  is about 14. This anisotropic spectrum is attributed to trivalent holmium in a crystal field of axial symmetry. A very anisotropic g value with  $g_1 \sim 0$  is common for trivalent rare earths in noncubic sites. The axial symmetry is probably caused by an interstitial fluorine in the nearestneighbor position along the cubic axes (see Fig. 1). Such a distortion would satisfy the observation in the (111) plane of three sites in the unit cell. However, the distortion could also be due to an interstitial fluorine in the next-nearest-neighbor position along the cube diagonal or an O<sup>2-</sup> ion replacing one of the fluorine ions on the cube edge.

<sup>&</sup>lt;sup>9</sup> E. S. Sabisky, thesis, University of Pennsylvania, 1965 (unpublished).

Frequency Gc	Observed field (G)	Transition hig notation	gh-field n	Observed for
9.458 9.458	1145.3 2331.0	$\begin{vmatrix} -\frac{1}{2}, -\frac{5}{2} \rangle \rightarrow \end{vmatrix} - \frac{1}{2}, -\frac{7}{2} \rangle \rightarrow \end{vmatrix}$	$\left  \frac{1}{2}, -\frac{7}{2} \right\rangle$ $\left  \frac{1}{2}, -\frac{7}{2} \right\rangle$	$\begin{array}{c} H_{DC} \bot H_{rf} \\ H_{DC} \bot H_{rf} \end{array}$
27.436	4418.4	$\left -\frac{1}{2},-\frac{7}{2}\right\rangle \rightarrow$	$ \frac{1}{2}, -\frac{7}{2}\rangle$	$H_{DC} \perp H_{rf}$
27.436	3696.6	$ -\frac{1}{2},-\frac{3}{2}\rangle \rightarrow$	$ \frac{1}{2}, -\frac{5}{2}\rangle$	$H_{DC} \perp H_{rf}$
27.436	3042.5	$ -\frac{1}{2},-\frac{3}{2}\rangle \rightarrow$	$ \frac{1}{2}, -\frac{3}{2}\rangle$	$H_{DC} \perp H_{rf}$
27.436	2472.7	$ -\frac{1}{2},-\frac{1}{2} angle ightarrow$	$ \frac{1}{2}, -\frac{1}{2}\rangle$	$H_{DC} \perp H_{rf}$
27.436	2000.1	$\left -\frac{1}{2}, \frac{1}{2}\right\rangle \rightarrow$	$\left \frac{1}{2}, \frac{1}{2}\right\rangle$	$H_{DC} \perp H_{rf}$
27.436	1624.8	$\left -\frac{1}{2}, \frac{3}{2}\right\rangle \rightarrow$	$\left \frac{1}{2}, \frac{3}{2}\right\rangle$	$H_{DC} \perp H_{rf}$
27.436	1335.9	$\left -\frac{1}{2}, \frac{5}{2}\right\rangle \rightarrow$	$\left \frac{1}{2}, \frac{5}{2}\right\rangle$	$H_{DC} \perp H_{rf}$
27.436	1116.3	$\left -\frac{1}{2}, \frac{7}{2}\right\rangle \rightarrow$	$\left \frac{1}{2}, \frac{7}{2}\right\rangle$	$H_{DC} \perp H_{rf}$
27.436	4013.7	$ -rac{1}{2},-rac{5}{2} angle ightarrow$	$\left \frac{1}{2},-\frac{7}{2}\right\rangle$	$H_{DC} \  H_{rf}$
27.436	3330.0	$ -\frac{1}{2},-\frac{3}{2} angle ightarrow$	$ \frac{1}{2}, -\frac{5}{2}\rangle$	$H_{DC} \  H_{rf}$
27.436	2722.1	$ -\frac{1}{2},-\frac{1}{2} angle ightarrow$	$ \frac{1}{2}, -\frac{3}{2}\rangle$	$H_{DC} \  H_{rf}$
27.436	2205.9	$ -\frac{1}{2}, \frac{1}{2} angle  ightarrow$	$\left \frac{1}{2},-\frac{1}{2}\right\rangle$	$H_{DC} \  H_{rf}$
27.436	1787.4	$\left -\frac{1}{2}, \frac{3}{2}\right\rangle \rightarrow$	$\left \frac{1}{2}, \frac{1}{2}\right\rangle$	$H_{DC} \  H_{rf}$
27.436	1460.9	$\left -\frac{1}{2}, \frac{5}{2}\right\rangle \rightarrow$	$\left \frac{1}{2}, \frac{3}{2}\right\rangle$	$H_{DC} \  H_{rf}$
27.436	1211.7	$\left -\frac{1}{2}, \frac{7}{2}\right\rangle \rightarrow$	$\left \frac{1}{2}, \frac{5}{2}\right\rangle$	$H_{DC} \  H_{rf}$
27.436	visible	$ -\frac{1}{2},-\frac{3}{2} angle ightarrow$	$\left \frac{1}{2},-\frac{7}{2}\right\rangle$	$H_{DC} \perp H_{rf}$
27.436	3038.5	$ -\frac{1}{2},-\frac{1}{2} angle ightarrow$	$ \frac{1}{2}, -\frac{5}{2}\rangle$	$H_{DC} \perp H_{rf}$
27.436	2449.2	$\left  -\frac{1}{2}, \frac{1}{2} \right\rangle \rightarrow$	$ \frac{1}{2}, -\frac{3}{2}\rangle$	$H_{DC} \perp H_{rf}$
27.436	1980.9	$\left -\frac{1}{2}, \frac{3}{2}\right\rangle \rightarrow$	$\left \frac{1}{2},-\frac{1}{2}\right\rangle$	$H_{DC} \perp H_{rf}$
27.436	1610.1	$\left -\frac{1}{2}, \frac{5}{2}\right\rangle \rightarrow$	$\left \frac{1}{2}, \frac{1}{2}\right\rangle$	$H_{DC} \perp H_{rf}$
27.436	visible	$\left -\frac{1}{2}, \frac{7}{2}\right\rangle \rightarrow$	$\left \frac{1}{2}, \frac{3}{2}\right\rangle$	$H_{DC} \perp H_{rf}$

TABLE III. Observed transitions for SrCl<sub>2</sub>:Ho<sup>2+</sup> at 4.2°K.

#### VII. DIVALENT HOLMIUM IN SrCl<sub>2</sub>

## **Experimental Results**

The ground-state spectrum was observed between 1.3 and 10°K at frequencies near 9 Gc/sec and 27 Gc/sec in a crystal containing a total holmium concentration of 0.1%. The divalent state was obtained by  $\gamma$  irradiation and approximately 5% was converted. The spectrum is isotropic and the fields at which resonant absorption occurs are given in Table III. The linewidth at the lower frequency is 1.8 G (14 Mc/sec) at 4.2°K and is temperature-dependent above 7°K. Some additional lines were also observed but they were at most 1/20 of the intensity of the isotropic spectrum. The spectrum of holmium in SrCl<sub>2</sub> is more like holmium in CaF<sub>2</sub> than SrF<sub>2</sub> or BaF<sub>2</sub> with respect to the intensity of the anisotropic spectrum.

Using a 0.02% holmium-doped SrCl<sub>2</sub> crystal in which the holmium was completely reduced to the divalent

TABLE IV. Observed transitions for  $SrCl_2{:}Ho^{2+}$  at 25°K at 9.26 Gc.

Observed field (kG)	Linewidth Mc	Transition	Intensity	Energy level
1.01		$\left -\frac{1}{2},-\frac{7}{2}\right\rangle \rightarrow \left -\frac{1}{2},-\frac{5}{2}\right\rangle$		$\Gamma_6$
1.18		$\left -\frac{1}{2},-\frac{5}{2}\right\rangle \rightarrow \left -\frac{1}{2},-\frac{7}{2}\right\rangle$		$\Gamma_7$
2.49	711	$\left -\frac{1}{2},-\frac{7}{2}\right\rangle \rightarrow \left \frac{1}{2},-\frac{7}{2}\right\rangle$	52	$\Gamma_6$
2.30	833	$\begin{vmatrix} \frac{1}{2}, -\frac{7}{2} \end{pmatrix} \rightarrow \begin{vmatrix} -\frac{1}{2}, -\frac{7}{2} \end{vmatrix}$	220	$\Gamma_7$

state by the electrolysis-reduction technique,<sup>10</sup> the excited state  $\Gamma_6$  was observed at temperatures above 14°K. Table IV gives the fields at which resonant absorption occurs for both the ground-state doublet  $\Gamma_7$  and the excited state  $\Gamma_6$ .

#### Theory

The theory for the ground state is very similar to that developed for the ground state of divalent holmium in CaF<sub>2</sub>. As in CaF<sub>2</sub>, the approximate Hamiltonian is not sufficient to satisfy the observed data. However, contrary to finding the  $\Gamma_6$  doublet as the ground state in CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub>, the ground state in SrCl<sub>2</sub> is identified as the  $\Gamma_7$  doublet from the *g* value. Therefore, in Fig. 3, the ratio of the crystal-field parameters changed in such a manner as we went from CaF<sub>2</sub> to SrCl<sub>2</sub> that a crossing of the  $\Gamma_6$  and  $\Gamma_7$  states occurred. Table III shows that in addition to the three kinds of transitions seen in CaF<sub>2</sub> and SrF<sub>2</sub>, six transitions have been observed which correspond to a change of the spin quantum number and a change by 2 in the nuclear quantum number.

The discrepancy between the observed data and the theory developed for  $CaF_2$  can again be resolved by properly accounting for the mixing of the  $\Gamma_7$  ground state with the nearby  $\Gamma_8^{(1)}$  quartet state by the hyperfine interaction. The correction term is identical to Eq. (4), except that  $\Gamma_6$  is replaced by  $\Gamma_7$  as the ground state. As in CaF<sub>2</sub>, the correction term linear in magnetic field need only be retained. The correction term is identical to Eq. (5) except that  $\Gamma_7$  replaces  $\Gamma_6$ . As found for CaF<sub>2</sub>, the coefficient of the  $m_I^2$  term in Eq. (7) can be shown to be zero by using the coupling coefficients as tabulated by Polo.<sup>7,9</sup>

To apply the correction term, the Hamiltonian can be written as given by Eq. (11) The eigenenergies are

$$E = -\frac{1}{4}A - (M+m)g_{n}'\beta_{n}H + M\{[g_{n}'\beta_{n}H + g\beta H + (M+m)A^{2}]^{2} + [16 - (M+m)A^{2}]\}^{1/2}.$$
(14)

This equation is identical to Eq. (12) with the exception of a change in sign in front of the square root term because of the signs of g and A. The term including  $g_n$ was again neglected. All of the 21 observed resonances in Table III may now be fitted to Eq. (14) to an accuracy of 0.05% using the values g=+6.751 ( $g\beta=+0.3152$  $\times 10^{-3}$  cm<sup>-1</sup> G<sup>-1</sup>) A=+0.1478 cm<sup>-1</sup>,  $g_n'=+43$  ( $g_n'\beta_n$  $=+1.1\times 10^{-6}$  cm<sup>-1</sup> G<sup>-1</sup>). The signs of the above parameters were determined as in CaF<sub>2</sub>. These parameters fit the resonant absorption data at temperatures of 1.3, 4.2, and 10°K within the experimental error of 0.05%. Therefore, there is no measurable temperaturedependent g value between 1.3 and 10°K. It should be noted that the error although within 0.05% was not

<sup>&</sup>lt;sup>10</sup> H. Guggenhiem and J. V. Kane, Appl. Phys. Letters 4, 172 (1964); F. Fong, J. Chem. Phys. 41, 245 (1964); see also Ref. 9.

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Host	Ground state	g	$A  (\rm cm^{-1})$	$g_n'$ Pseudonuclear $g$ -factor	Separation of $\Gamma_8$ and ground state (cm <sup>-1</sup> )	Separation of excited doublet and ground state (cm <sup>-1</sup> )
CaF <sub>2</sub>	$\Gamma_6$	$-5.912 \pm 0.005$	$-0.1307 \pm 0.0002$	$+48\pm4$	33.0±4.0	$\Gamma_7:29\pm4$
$SrF_2$	$\Gamma_6$	$-5.916{\pm}0.005$	$-0.1311 \pm 0.0003$	$+67\pm6$	$23.8 {\pm} 4.0$	•••
$BaF_2$	$\Gamma_6$	-5.91	-0.131	•••	•••	•••
$SrCl_2$	$\Gamma_7$	$+6.751 \pm 0.003$	$+0.1478 \pm 0.00015$	$+43\pm3$	$29.0 \pm 3.0$	$\Gamma_6:23\pm3$

TABLE V. Experimental and derived parameters for Ho2+

random. This implies that the field-independent correction term along with other correction terms must be examined if more accuracy is desired.

The exact value of the matrix element involved in Eq. (5) depends on the ratio of the crystal-field parameters. However, in the entire range where the  $\Gamma_7$  state is lowest, the matrix element is between 2.9 and 3.6 for X = -0.6 and X = 0, respectively, in the notation of Lea, Leask, and Wolf (see Fig. 3). Thus, one can calculate the energy above the  $\Gamma_7$  ground state of the  $\Gamma_8^{(1)}$ state to a precision limited by  $g_n'$ . Using the values  $\Lambda$ (the Landé g factor)=6/5, a=A(6/34)=0.0261 cm<sup>-1</sup> and taking the matrix element as 3.3 (corresponds to X = -0.4), this energy is 29.0 $\pm$ 3.0 cm<sup>-1</sup>. Divalent rare earths in SrCl<sub>2</sub> are just being studied by optical techniques and no appropriate crystal-field splittings are available for comparison purposes.

An analysis of the data given in Table IV shows that two of the four resonance lines belong to the  $\Gamma_7$  groundstate doublet which was discussed above. The remaining two resonance lines belong to the thermally populated  $\Gamma_6$  state which can easily be verified by using the constants evaluated for the  $\Gamma_6$  ground state in CaF<sub>2</sub>. The energy above ground of the  $\Gamma_6$  state can be calculated using Eq. (13) after  $\Gamma_6$  and  $\Gamma_7$  are interchanged. The derived value for the splitting above ground of the  $\Gamma_6$  state is  $23\pm3$  cm<sup>-1</sup>. It also has been observed<sup>9</sup> that the non-temperature-dependent part of the linewidth of the  $\Gamma_6$  excited state is about 20 times larger than the width of the ground state  $\Gamma_7$ . The majority of the broadening is due to phonon emission and will be discussed in another paper.

## VIII. DISCUSSION

Table V gives the experimental values of the g value, the magnetic hyperfine constant A, and the derived separation of the first quartet,  $\Gamma_8^{(1)}$ , state from the ground state for divalent holmium in the various cubic hosts.

#### A. Ground State of Ho<sup>2+</sup>

The ground state of  $Ho^{2+}$  in  $CaF_2$  is identified as  $\Gamma_6$ from the g value and from Fig. 3 the  $\Gamma_6$  state is lowest for X < -0.45. From intensity measurements at 25°K, the  $\Gamma_7$  state was found to lie below the  $\Gamma_8^{(1)}$  state which is in agreement with the optical measurements of Weakliem.<sup>8</sup> To fit the optical data, Weakliem uses a value for  $B_4/B_6 = -5.1$  [notation of Eq. (1)] or  $(B_4/B_6)_{\text{LLW}} = -219$ . This corresponds to X = -0.49. As one goes to the larger lattices, the expectation is that  $B_4/B_6$  should increase, since

$$\frac{B_4}{B_6} \propto \frac{R^2}{\langle r^6 \rangle / \langle r^4 \rangle}$$

where  $\langle r^n \rangle$  is the integral of  $r^n$  over the 4f radial density,  $\langle R^n \rangle$  is an equivalent parameter relating the distance between the rare-earth ion and the nearby diamagnetic ions, and R should increase with the lattice while the variation in  $\langle r^n \rangle$  from lattice to lattice is expected to be small. The experimental results for  $SrF_2$  and  $BaF_2$  show that the  $\Gamma_6$  state is lowest which is not in disagreement with theoretical prediction. The reduction of the  $\Gamma_8^{(1)}$  state splitting in SrF<sub>2</sub> from that in  $CaF_2$  is also expected since the larger  $SrF_2$  lattice implies a reduction in the crystalline field. However, the experimental data for Ho<sup>2+</sup> in the fluoride hosts are not sufficient to denote changes in the  $B_4/B_6$  ratio. But for Dy<sup>2+</sup> in the three fluorite hosts, Kiss<sup>11</sup> has shown that a constant value of the  $B_4/B_6$  ratio can be used to fit the observed optical splittings. Kiss has also shown that the value of  $B_4$  goes more like  $1/R^2$  than  $1/R^5$ expected from the point-charge model. The optical results for  $Dy^{2+}$  in the fluorite hosts indicate that the point-charge model is suspected. As Table V shows, the ground state for  $Ho^{2+}$  in  $SrCl_2$  is the  $\Gamma_7$  state in contrast to a  $\Gamma_6$  state for the three fluorite hosts. Thus the ratio of  $B_4/B_6$  has decreased (see Fig. 3) even though the SrCl<sub>2</sub> lattice is larger than any of the three fluorite hosts. The point-charge model predicts an increase in the  $B_4/B_6$  ratio rather than the observed decrease. The relative positions of the  $\Gamma_6$  and  $\Gamma_8^{(1)}$  states for  $SrCl_2$ bracket the  $B_4/B_6$  ratio between -3.5 (X = -0.4) and -4.4 (X = -0.45). The anomaly in the variation of the  $B_4/B_6$  ratio may in part be due to the fact that the rareearth ion is replacing cations of different ionic radii and some effective distance to the neighboring ligands must be used. Undoubtedly the size of the cations is important. However, the problem of an adequate description of  $\langle R^n \rangle$  remains.

For the case of Er<sup>3+</sup> in CaF<sub>2</sub>, Baker, Hayes, and Jones<sup>12</sup> found that the ground state is a  $\Gamma_7$  doublet in

 <sup>&</sup>lt;sup>11</sup> Z. J. Kiss, Phys. Rev. 137, A1749 (1965).
 <sup>12</sup> J. M. Baker, W. Hayes, and D. A. Jones, Proc. Phys. Soc. (London) 73, 942 (1959).

(16)

contrast to a  $\Gamma_6$  for Ho<sup>2+</sup> in CaF<sub>2</sub>. Elliott and Stevens<sup>13</sup> suggested the formula  $\langle r^n \rangle \propto (Z-55)^{-n/4}$  for  $\langle r^n \rangle$ , which is in fairly close agreement with the  $\langle r^n \rangle$  values calculated by Freeman and Watson<sup>14</sup> using a Hartree-Fock method. Using the relationship  $B_4/B_6 \propto R^2(Z-55)^{1/2}$ , the ratio of  $(Z-55)^{1/2}$  in going from Ho<sup>2+</sup> to Er<sup>3+</sup> is about  $(12/10)^{1/2}$  and therefore  $B_4/B_6$  is expected to increase by a small amount. However, one expects R to decrease in going from Ho<sup>2+</sup> to Er<sup>3+</sup> since the fluorines see a change in the charge from 2 to 3. This decrease in R is probably larger than the slight increase due to Z. This will decrease the value of |X| in Fig. 3 in agreement with the observed changes in the ground state for Er<sup>3+</sup>. A similar result was found using optical measurements for the isoelectronic pair  $Tm^{2+15}$  and  $Yb^{3+16}$  in CaF<sub>2</sub>. Thus, the ratio of  $B_4/B_6$  is found to be larger for the divalent ion than the isoelectronic trivalent ion. The "pseudo" correct and incorrect predictions of the variation of  $B_4/B_6$  cast doubt on the adequacy of the point-charge model in relating the  $B_4$  and  $B_6$  constants to more fundamental parameters. In addition to the complications of covalency and the breakdown of Russell-Saunders coupling, the rare-earth ions have 5s and 5p shells which are outside the 4f shell. A slight distortion of these shells by the lattice will be important because of their effect on the crystal field and the shielding or antishielding of the 4f shell. Thus, it appears that while the constants  $B_4$  and  $B_6$  are useful and meaningful for calculating such things as crystalfield splittings their interpretation in terms of more physical parameters is not clear.

## B. q Value

From Table V, it is seen that the ground state for Ho<sup>2+</sup> in the fluorite hosts is  $\Gamma_6$  doublet. The experimental g value is less than the uncorrected theoretical value of -6.00 by 1.5%. This is outside the experimental error and is difficult to explain. Judd and Lindgren<sup>17</sup> show that the corrections due to relativistic effects, etc. for Ho atoms reduces the g value by about 0.4%. A departure from L-S coupling will mix in the  ${}^{2}K_{15/2}$  state which is approximately 20 000 cm<sup>-1</sup> above the ground state. Assuming a spin-orbit constant of 2000 cm<sup>-1</sup> and using the matrix element calculated by Judd and Loudon<sup>18</sup> this correction is only 0.2%. One might expect that the remainder of the discrepancy could be due to: (a) a mixing of the  ${}^{4}I_{13/2}$  state into the ground state by the crystal field; (b) a small axial distortion; or (c) a thirdorder Zeeman effect due to mixing of the  $\Gamma_8^{(1)}$  state with the  $\Gamma_6$  state. In order to check the contribution of (a) to the g value, the ground-state wave function for the  $\Gamma_6$ 

state must be rewritten as  $\alpha_0 \psi(15/2,\Gamma_6) + \alpha_1 \psi(13/2,\Gamma_6)$ , where  $\alpha_1$  is determined by the crystal field and  $\alpha_0$  is obtained by normalization. The g value for the  $\Gamma_6$ ground state is then given by

$$g' = 2 \langle \alpha_0 \psi (15/2, \Gamma_6) + \alpha_1 \psi (13/2, \Gamma_6) | L_z + 2S_z | \alpha_0 \psi (15/2, \Gamma_6) + \alpha_1 \psi (13/2, \Gamma_6) \rangle.$$
(15)

Expanding and neglecting the term in  $\alpha_1^2$ , one finds

$$g = 2\alpha_0^2 \langle \psi(15/2,\Gamma_6) | L_z + 2S_z | \psi(15/2,\Gamma_6) \rangle$$

and

$$\Delta g = 4\alpha_0 \alpha_1 \langle \psi(15/2, \Gamma_6) | L_z + 2S_z | \psi(13/2, \Gamma_6) \rangle. \quad (17)$$

The g value defined by Eq. (16) is the g value for the unperturbed  $\Gamma_6$  ground state with  $\alpha_0 = 1$ . Using the wave functions given by Polo<sup>7</sup> and others,  $\Delta g$  is identically zero for this case and the contribution of (a) is negligible. Nor can the effect be due to an axial field since any significant contribution of the axial field must cause a detectable anisotropy. Finally, the third-order Zeeman effect is negligible in this case. From Weakliem,8 the ground-state wave function for the  $|15/2,\Gamma_6\rangle$  state in CaF<sub>2</sub> is

$$\psi'(15/2,\Gamma_6) = 0.985/0.9853\psi(15/2,\Gamma_6) + 0.025/0.9853\psi(13/2,\Gamma_6)$$

where  $\psi$  without the prime denotes the wave functions of the unperturbed states. Thus,  $\alpha_0^2$  is very nearly one, and g' of Eq. (15) is the g value of the unperturbed  $\Gamma_6$  ground state to order  $\alpha_1^2$ . Therefore, the major portion of the discrepancy ( $\sim 0.9\%$ ) is not accounted for.

For the SrCl<sub>2</sub> host, the ground state is  $\Gamma_7$  and the experimental g value of 6.751 differs from the uncorrected theoretical value of +6.8 by 0.049 or 0.7%. However, in contrast to the fluorite hosts, the mixing of the  ${}^{4}I_{13/2}$  state into the ground state by the crystal field is not zero.

Since the  ${}^{4}I_{13/2}$  state contains two  $\Gamma_{7}$  states, Eq. (17) must be extended and is given to order  $\alpha_1^2$ ,  $\alpha_2^2$  by

$$\Delta g = 4\alpha_0 \alpha_1 \langle \psi(15/2, \Gamma_7) | L_z + 2S_z | \psi(13/2, \Gamma_7^{(1)}) \rangle + 4\alpha_0 \alpha_2 \langle \psi(15/2, \Gamma_7) | L_z + 2S_z | \psi(13/2, \Gamma_7^{(2)}) \rangle, \quad (18)$$

where  $\psi(13/2,\Gamma_7^{(1)})$  and  $\psi(13/2,\Gamma_7^{(2)})$  represent the two wave functions for the two  $\Gamma_7$  states of the  ${}^4I_{13/2}$  multiplet. Optical data are not available and the  $B_4$  and  $B_6$ constants will be estimated from the data in this paper. A good estimate of the  $B_4/B_6$  ratio is -3.6 which corresponds to X = -0.4 for the ground-state multiplet. In order to obtain the wave functions for the two  $\Gamma_7$ states in the  ${}^{4}I_{13/2}$  multiplet from the published data of LLW, the value of X' for the excited state must be computed. Using a value of X = -0.4 for the J = 15/2state, X' is calculated to be -0.64 for the J=13/2state. The pertinent wave functions can be obtained from LLW.  $B_4$  for CaF<sub>2</sub> is 2275 cm<sup>-1</sup> from optical measurements, while  $B_4$  for  $SrCl_2$  is estimated from the

<sup>13</sup> R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) A218, 553 (1953).

 <sup>&</sup>lt;sup>14</sup> A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).
 <sup>15</sup> Z. J. Kiss, Phys. Rev. 127, 718 (1962).
 <sup>16</sup> W. Low, Phys. Rev. 118, 1608 (1960).

<sup>&</sup>lt;sup>17</sup> B. R. Judd and I. Lindgren, Phys. Rev. **122**, 1802 (1961). <sup>18</sup> B. R. Judd and R. Loudon, Proc. Roy. Soc. (London) A251,

<sup>127 (1959).</sup> 

data in this paper to be 830 cm<sup>-1</sup>. Using splittings of 5520 cm<sup>-1</sup> and 5750 cm<sup>-1</sup> for the  $\Gamma_7^{(1)}$  and  $\Gamma_7^{(2)}$  states, one finds that  $\alpha_0 = 0.9993$ ,  $\alpha_1 = 0.019$ , and  $\alpha_2 = 0.031$ . The corrected ground-state wave function for the  $|15/2,\Gamma_7\rangle$  state in SrCl<sub>2</sub> is

$$\psi'(15/2,\Gamma_7) = 0.9993\psi(15/2,\Gamma_7) + 0.019\psi(13/2,\Gamma_7^{(1)}) + 0.031\psi(13/2,\Gamma_7^{(2)}),$$

where  $\psi$  without the prime denotes the wave functions of the unperturbed states. From Eqs. (16) and (17) the calculated g value is 6.790 + 0.061 = 6.851. The difference between the calculated and experimental g values is  $\Delta g = 0.100$  or 1.4%. A more accurate calculation must await better values of  $B_4$  and  $B_6$  from optical measurements. However, the estimated correction shows that as found in the fluorite crystals a discrepancy exists in the g value of the order of 1.5%. As previously discussed, it is possible to account for only 0.6% of the discrepancy.

It is common to relate such differences in the gvalue to the presence of covalent bonding. If this is done in the notation of Bleaney<sup>19</sup> and Low,<sup>20</sup> a value of (1-k)=0.022 is derived for Ho<sup>2+</sup> in CaF<sub>2</sub>, where k is the orbital k factor. For comparison, (1-k) = 0.009 for Tm<sup>2+</sup> in CaF<sub>2</sub><sup>19</sup> while  $(1-k)\sim 0.2$  for ions in the 3-d group.<sup>21</sup> It is naive to assume that covalency does not exist and that the static crystal-field model is an adequate description for the iron and rare-earth group ions. We know that such factors as covalency play a dominant role in the iron-group ions and a much smaller role for the rare-earth group ions where direct ligand overlaps are indeed much smaller. That a small covalent term does exist for the rare-earth ions is in line with the Endor measurements of the fluorine hyperfine structure in the Eu<sup>2+</sup> spectrum in CaF<sub>2</sub> by Baker and Williams<sup>22</sup> which reveal a small contact interaction. However, since in the rare earths one is dealing with small effects, one cannot simply assume that covalency is the dominant factor in all cases and that the amount of covalency can be obtained by relating the difference between an experimental g value and theoretical values with at times added questionable corrections. It recently has been suggested that the orbit-lattice interaction may have a measurable effect on the g value. The orbit-lattice interaction does play an important role in spin-lattice relaxation and after all, the actual state of a crystal is not static as the point-charge model assumes but each lattice ion undergoes small thermal oscillations about its equilibrium position. Inoue<sup>23</sup> using an appropriate model showed that the expected correction to the

ground-state g value for  $Ho^{2+}$  and  $Tm^{2+}$  in  $CaF_2$  is  $\Delta g = +0.10$  and -0.01, respectively. The observed values of  $\Delta g$  are +0.088 and -0.03 for Ho<sup>2+</sup> and Tm<sup>2+</sup>, respectively. While such calculations are difficult to make and some of the assumptions are questionable, the predicted magnitude of the g shift implies that the orbit-lattice interaction cannot be simply ignored for the rare-earth ions. In order to resolve the importance of the orbit-lattice interaction in the g shift, g-value measurements must be made over a large temperature range since a temperature dependence of  $T^4$  is predicted from the calculations of Inoue.<sup>24</sup> Temperature-dependent measurements were made in SrCl<sub>2</sub>, but primarily because of linewidth broadening and partly due to poorquality crystals at the time, accurate measurements could only be made between 1.5 and 10°K. As previously stated, no change in the g value was observed within the experimental accuracy of 0.05%. Inoue's calculations predict that one has to go to temperatures near 30°K before the temperature-dependent part of the g shift becomes measurable.

Covalency and the orbit-lattice interaction are reasonable explanations for the small g shift measured in rare-earth ions. Whether either effect dominates in a particular case cannot be answered at the present time and must await more experimental and theoretical work. Proof of the effect of lattice vibrations must undoubtedly come from temperature-dependent measurements of the g value. Ho<sup>2+</sup> in CaF<sub>2</sub> or in SrCl<sub>2</sub> are not suitable for such measurements since at about 30°K it has a linewidth of 1000 Mc/sec. Tm<sup>2+</sup> in SrCl<sub>2</sub> or CaF<sub>2</sub> appears to be the best possible choice. It has the disadvantage of a smaller g discrepancy than Ho<sup>2+</sup>, but linewidth broadening does not occur until about 40°K. Also, paramagnetic resonance absorption of Tm<sup>2+</sup> in CaF<sub>2</sub> has been observed in the excited  $J = \frac{5}{2}$  multiplet.<sup>25</sup> This state is 8966 cm<sup>-1</sup> above ground and was populated by optical pumping. The excited multiplet  ${}^{4}F_{5/2}$  differs only in the J value from the ground multiplet  ${}^{4}F_{7/2}$  and the configuration of the crystal-field split states within each J multiplet are similar. Thus, one might expect different amounts of covalent bonding in the two Jstates, since J is changed, but the influence of the zero point lattice vibrations is expected to be very similar in the two states. It is a difficult experiment in terms of accuracy but one that should be pursued.

## C. Magnetic Hyperfine Constant

The hyperfine interaction,  $a\mathbf{I}\cdot\mathbf{J}$ , of <sup>165</sup>Ho I (4 $f^{11}6s^2$ ,  ${}^{4}I_{15/2}$ ) has been measured by Goodman et al.,<sup>26</sup> who find  $a = 800.583 \pm 0.003$  Mc/sec while the experimental value of a for Ho<sup>2+</sup> from Table VI is 0.0261 cm<sup>-1</sup> or  $783\pm1$ Mc/sec. Judd and Lindgren<sup>17</sup> give calculated values of

 <sup>&</sup>lt;sup>19</sup> B. Bleaney, Proceedings of the 1963 Conference on Quantum Electronics, Paris (Columbia University Press, New York, 1964).
 <sup>20</sup> W. Low and R. S. Rubins, Phys. Rev. 131, 2527 (1963).
 <sup>21</sup> W. Low, Paramagnetic Resonance in Solids (Academic Press Inc., New York, 1960). This reference contains a summary on couplet handling for increase resonance).

 <sup>&</sup>lt;sup>22</sup> J. M. Baker and F. I. B. Williams, Proc. Roy. Soc. (London)
 A267, 283 (1962).

<sup>&</sup>lt;sup>28</sup> M. Inoue, Phys. Rev. Letters 11, 196 (1963).

<sup>&</sup>lt;sup>24</sup> M. Inoue, thesis, Harvard University, 1963 (unpublished).
<sup>25</sup> E. S. Sabisky and C. H. Anderson (unpublished).
<sup>26</sup> L. S. Goodman, H. Kopfermann, and K. Schlupmann, Naturwiss. 49, 101 (1962).

Host	$A \ \mathrm{cm}^{-1} \ \mathrm{Experiment}$	$a cm^{-1}$ Uncorrected	Crystal-field corrections cm <sup>-1</sup>	Core polarization $a_{\sigma} \operatorname{cm}^{-1}$	a <sup>a</sup> Mc/sec Corrected	Ratio to Ho atom
$CaF_2$ SrCl <sub>2</sub>	$-0.1307{\pm}0.0002 \\+0.1478{\pm}0.00015$	+0.0261 +0.0261	$0 \\ +0.0004$	-0.00046 -0.00046 <sup>b</sup>	797 809	0.996 1.011

TABLE VI. Magnetic-hyperfine constant for ground state of Ho<sup>2+</sup> in CaF<sub>2</sub> and SrCl<sub>2</sub>.

• For HoI atom =800.58 Mc/sec. Calculated values for  $\frac{\langle r^{-3} \rangle \text{ for Ho IV}}{\langle r^{-3} \rangle \text{ for Ho I}} = \frac{9.32}{8.87} = 1.05.$ 

<sup>b</sup> Including admixtures with J = 13/2 state increases  $a_c$  to -0.00048.

 $\langle r^{-3} \rangle$  of 8.87 atomic units (a.u.) and 9.32 a.u. for Ho I and Ho IV, respectively. This would suggest that *a* for Ho<sup>2+</sup> should be larger than for Ho I while the observed value is 2.1% smaller. This discrepancy could be due to : (a) mixing of  $\Gamma_8^{(1)}$  state with the ground state by hyperfine interaction; (b) mixing of the  ${}^{4}I_{13/2}$  state into the ground state by the crystal field; or (c) the effect of core polarization.

The contribution of (a) can be estimated by evaluating that part of the hyperfine correction term [Eq. (4)] which was shown to contribute to an apparent magnetic hyperfine interaction [Eq. (9)]. If this is done, it is found that the correction is approximately the experimental error and will be neglected.

The effect of (b) is more difficult to estimate. One must examine the general expression for the magnetic interaction between the electrons and the nucleus given by Fermi.<sup>27</sup> The interaction, neglecting the term for s electrons, is

$$2\beta\beta_n\mu_n/I\langle 1/r^3\rangle \mathbf{N}\cdot\mathbf{I},\qquad(19)$$

where  $\mathbf{N} = \sum \{\mathbf{l}_i - \mathbf{s}_i + (3(\mathbf{r}_i \cdot \mathbf{s}_i)\mathbf{r}_i/r_i^2)\}$ , and  $\beta_N$  is the nuclear magneton,  $\mu_N$  the value of the nuclear magnetic moment in nuclear magnetons, and *I* the nuclear spin. From the Wigner-Eckart theorem, the matrix elements of the operator **N** can be replaced by a factor times *J* only within a manifold of constant *J* states. Elliott and Stevens<sup>13</sup> have computed the matrix elements of the operator *N* with the next excited state by using operator equivalents and assuming that Russell-Saunders coupling holds. An expression for *a* which includes the mixing with the next spin-orbit multiplet is

$$a = a' \left[ \alpha_0^2 + \frac{\langle 15/2 ||N|| 13/2 \rangle}{\langle 15/2 ||N|| 15/2 \rangle} \times \frac{\Delta g}{2 \langle 15/2 ||\Lambda|| 13/2 \rangle \langle 15/2, \Gamma, \frac{1}{2} |J_z| 15/2, \Gamma, \frac{1}{2} \rangle} \right], \quad (20)$$

where a' is the corrected hyperfine constant due to mixing and a is the hyperfine constant if the ground state is unperturbed. a is given by

$$\frac{\frac{1}{2}A}{\langle 15/2,\Gamma,\frac{1}{2}|J_z|15/2,\Gamma,\frac{1}{2}\rangle};$$

<sup>27</sup> E. Fermi, Z. Physik 60, 320 (1930).

 $\Delta g$  is defined by Eq. (17) or (18);  $\Gamma$  is either  $\Gamma_6$  or  $\Gamma_7$ , whichever is being computed; and from Elliott,<sup>13</sup>  $\langle 15/2 ||N|| 13/2 \rangle = -83/(3^2 \times 5^2 \times \sqrt{14})$ ,  $\langle 15/2 ||N|| 15/2 \rangle$  $= (2^4 \times 11)/(3^2 \times 5^2)$  and  $\langle 15/2 ||\Lambda|| 13/2 \rangle = 2/5\sqrt{14}$ . For the fluorite hosts,  $\Delta g = 0$ ;  $\alpha_0^2 \sim 1.0$ , a' = a, there is no correction. For SrCl<sub>2</sub>,  $\Delta g = 0.061$ ,  $\alpha_0^2 = 0.9986$ , and a' = a(1.014) = 0.0265 cm<sup>-1</sup>, or an increase in the hyperfine constant of 1.4% due to the mixing of the  ${}^4I_{13/2}$  multiplet by the crystal field.

Core polarization arises in atoms in which one or more electrons belonging to outer shells are unpaired in spin direction. Core electrons with spin parallel to that of the unpaired electrons experience exchange forces different from those of core electrons of opposite spin. This exchange polarization results in nonzero values at the nucleus of the charge density for each pair of *s* electrons. Following the suggestion of Freeman and Watson<sup>14</sup> and Bleaney,<sup>28</sup> that is, that the core polarization per unit of electron spin is constant, a value of  $a_c = -14.0$  Mc/sec is obtained for Ho<sup>2+</sup> using a nuclear moment of +4.03.

The corrections to the hyperfine constant a are shown in Table VI. It is seen that a for the fluorite hosts is is very close to the experimental value for the Ho atoms, while a for  $SrCl_2$  is larger by 1.1%. The important thing to note is that leaving out the correction for core polarization, the *a* values differ by about 1.5%. The three effects which would influence a are: core polarization, zero-point lattice vibrations, and covalent bonding. The assumption of the same core polarization for a rare-earth ion independent of the lattice is questionable when the 5s electrons are included in this effect. For the influence of zero-point lattice vibrations, one could calculate a for CaF2 using Inoue's<sup>23</sup> results. In this case, the correction to a would be about 0.0004 cm<sup>-1</sup> or the order of 1.5%. The correction for SrCl<sub>2</sub> is expected to be larger since  $SrCl_2$  has a smaller Debye temperature and hence would then tend to shift the values farther apart. The effect of covalent bonding is difficult to estimate. All this points out the difficulty of obtaining good values of  $\langle r^{-3} \rangle$  from spin resonance data. To check the effect of lattice vibrations on the *a* value, the work of Bessent and Hayes<sup>29</sup> on the electron nuclear double resonance of Tm<sup>2+</sup> in CaF<sub>2</sub> should be extended to include

 <sup>&</sup>lt;sup>28</sup> B. Bleaney, J. Phys. Soc. (Japan) 17, Suppl. B-1, 435 (1962).
 <sup>29</sup> R. G. Bessent and W. Hayes, Proc. Roy. Soc. (London) A285, 430 (1965).

temperature-dependent measurements of the hyperfine constant A.

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# Electrodynamic Study of Josephson Tunneling in Superconducting Junctions

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We have performed a quantitative electrodynamic experiment on a Josephson oxide tunneling junction. Using a current source at 30 Mc/sec, we have verified the time dependence of the Josephson equation,  $j=j_0 \sin \left[\gamma_l-\gamma_r-(2e/\hbar)\int \mathbf{A}\cdot \mathbf{d}\mathbf{I}\right]$ , where  $(\partial/\partial t)\left[\gamma_l-\gamma_r-(2e/\hbar)\int i^r \mathbf{A}\cdot \mathbf{d}\mathbf{I}\right]=-(2eV/\hbar)$ . Thus the limiting voltage is shown to obey the quantum relationship,  $2eV = \hbar\omega$ . Measurements were made completely in the coherent state showing the diffraction nature of the junction as a function of applied magnetic field. The Josephson (parametric) inductance of the junction was directly observed and is in good agreement with the theory.

## INTRODUCTION

OSEPHSON<sup>1</sup> first predicted that a sufficiently thin tunneling junction between two superconductors would support a lossless tunneling current. He concluded that the current would be dc at zero voltage difference but that an alternating supercurrent would flow at finite voltages. Anderson<sup>2</sup> and Josephson<sup>3</sup> extended and interpreted the initial prediction in terms of the quantum phase difference of the superconducting order parameter or wave function at the two sides of the junction.

Experimental verification of the dc Josephson effect has been provided by a number of separate experiments<sup>4-7</sup> which elucidated the stationary quantumwave interference properties of superconducting circuits containing one or more Josephson junctions. The Josephson ac effect has been observed via detection in the junction itself by Shapiro<sup>8</sup> and others.<sup>9,10</sup> While the

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<sup>3</sup> B. D. Josephson, Rev. Mod. Phys. 36, 216 (1964). <sup>4</sup> P. W. Anderson and J. M. Rowell, Phys. Rev. Letters 10, 230

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D. D. Coon and M. D. Fiske. Phys. Rev. 138 A744 (1965)

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one approach of attempting to generate ac with the application of a dc voltage across the junction was under way in several laboratories, we chose to investigate the Josephson ac effect dynamically by a different experimental approach, namely, to observe the dynamic characteristics of a Josephson junction under the influence of a radio-frequency current source. This investigation is reported here with quantitative measurements of the quantum voltage, the Josephson inductance, and the superconducting phase difference in the coherent state averaged over the surface of the junction.

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#### THEORY

The fundamental equations relating to the Josephson effect express the phase-dependent part of the binding or coherence energy per unit area and the supercurrent density for weakly coupled superconductors as

 $E(\mathbf{r},t) = E_0 \cos \left[ \gamma_l - \gamma_r - \frac{2e}{r} \int_{-\infty}^{\infty} \mathbf{A} \cdot \mathbf{d} \mathbf{l} \right],$ 

and

$$L \quad \hbar J_i \quad J$$

(1)

$$j(\mathbf{r},t) = j_0 \sin\left[\gamma_l - \gamma_r - \frac{2\epsilon}{\hbar} \int_l \mathbf{A} \cdot \mathbf{d}\mathbf{I}\right], \qquad (2)$$

where  $[\gamma_l - \gamma_r - (2e/\hbar) \int_l^r A \cdot dl]$  is the gauge-invariant phase difference across the junction. We will explicitly concern ourselves with oxide junctions and use the coordinate definitions of Fig. 1. The phase difference  $[\gamma_{l} - \gamma_{r} - (2e/\hbar) \int_{l}^{r} \mathbf{A} \cdot \mathbf{dl}]$  will be a function of  $(\mathbf{r},t)$