APPENDIX. MATRICES OF SPIN-ORBIT INTERACTION

$$J=7/2:\qquad \begin{array}{c|ccc|} & {}^2G & {}^4F & {}^2F \\ {}^2G & -3/4 & (5/8)^{\frac{1}{2}} & (15/16)^{\frac{1}{2}} \\ {}^4F & (5/8)^{\frac{1}{2}} & 0 & -(3/8)^{\frac{1}{2}} \\ {}^2F & (15/16)^{\frac{1}{2}} & -(3/8)^{\frac{1}{2}} & 1/4 \end{array} \times \xi_{3d}, \tag{A1}$$

$$J=9/2:\qquad \begin{array}{c|ccc|} & {}^2H & {}^2G & {}^4F \\ {}^2H & -3/5 & (66/25)^{\frac{1}{2}} & 0 \\ {}^2G & (66/25)^{\frac{1}{2}} & 3/5 & (5/2)^{\frac{1}{2}} \\ {}^2F & 0 & (5/2)^{\frac{1}{2}} & 3/2 \end{array} \times \xi_{3d}, \tag{A2}$$

$$J=1/2:\qquad \begin{array}{c|cc|} & {}^4P & {}^2P \\ {}^4P & -5/6 & -(14/9)^{\frac{1}{2}} \\ {}^2P & -(14/9)^{\frac{1}{2}} & -2/3 \end{array} \times \xi_{3d}, \tag{A3}$$

$$J=3/2:\qquad \begin{array}{c|ccccc|} & {}^4F & {}^2D_a & {}^2D_b & {}^4P & {}^2P \\ {}^4F & -2 & -(21/10)^{\frac{1}{2}} & (5/2)^{\frac{1}{2}} & 0 & 0 \\ {}^2D_a & -(21/10)^{\frac{1}{2}} & -3/4 & (21/16)^{\frac{1}{2}} & (2/5)^{\frac{1}{2}} & -(7/8)^{\frac{1}{2}} \\ {}^2D_b & (5/2)^{\frac{1}{2}} & (21/16)^{\frac{1}{2}} & 1/4 & 0 & -(7/8)^{\frac{1}{2}} \\ {}^4P & 0 & (2/5)^{\frac{1}{2}} & 0 & -1/3 & -(35/9)^{\frac{1}{2}} \\ {}^2P & 0 & -(7/8)^{\frac{1}{2}} & -(7/8)^{\frac{1}{2}} & -(35/9)^{\frac{1}{2}} & 1/3 \end{array} \times \xi_{3d}. \tag{A4}$$

VI. ACKNOWLEDGMENTS

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Paramagnetic Resonance Spectrum of Trivalent Gadolinium in the Cubic Field of Calcium Fluoride*

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The paramagnetic resonance spectrum of Gd^{3+} in CaF_2 has been analyzed at 3 cm wavelength at room and liquid helium temperatures. The spectrum shows that the cubic symmetry is essentially preserved around the gadolinium ion. The fourth-order and sixth-order cubic field splitting parameter have been evaluated as $c=+0.0185\pm0.0005$ and $d=-0.0004\pm0.0002$ cm^{-1}, where the total ground-state splitting is $8c-2d$. The g factor is $g=1.991\pm0.002$. Various mechanisms causing the ground-state splitting of an S state in a cubic field are discussed. The preservation of cubic symmetry and the absence of association with vacancies or interstitial ions can be explained by a stabilization of the complex by the spherical charge distribution of the S ion and an effective strong crystalline field.

I. INTRODUCTION

TRIVALENT gadolinium has seven f electrons and a ground state of ${}^8S_{7/2}$. Its paramagnetic resonance spectrum has been extensively studied. The reason for this is in part the ease with which the spectrum can be obtained even at room temperature since the spin-lattice relaxation time is fairly long.[1] Among the single crystals studied are the ethylsulfate,[2,3] the double nitrate,[4] the anhydrous trichloride,[5] and the hydrated trichloride.[6] The paramagnetic resonance

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* Supported by the U. S. Atomic Energy Commission.

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[6] M. Weger, M.Sc. thesis, Jerusalem, 1956 (unpublished).

spectrum in these crystals shows a complicated fine structure. A theory which explains the spectrum has been developed by Elliott and Stevens[7] and Judd[8] for C_{3v} and C_{3h} symmetries. The spin Hamiltonian according to these authors can be written for these symmetries (i.e., for all the above salts except for the hydrated chloride which has a lower symmetry) as

$$\mathcal{H}=g\beta(H_xS_x+H_yS_y+H_zS_z)+B_2^0P_2^0+B_2^2P_2^2+B_4^0P_4^0+B_6^0P_6^0+B_6^6P_6^6, \quad (1)$$

where P_n^m are operators which have the same transformation properties as the corresponding spherical harmonics Y_n^m. The dominant term in all the crystals investigated is $B_2^0P_2^0$ which transforms like $3\cos^2\theta-1$. At zero field the S state of gadolinium is split by this trigonal field into four doublets with an approximate separation of $6B_2^0$, $12B_2^0$, and $24B_2^0$, respectively, i.e., in the ratio of 1:2:4.

In addition to the fine structure the spectra show a small but detectable hyperfine structure caused by the spin of the odd isotopes 155 and 157. This hyperfine structure has determined the nuclear spin and the ratio of the magnetic moments of these isotopes.[9]

The S-state ions in general and the Gd^{3+} ion in particular are not well understood at present.[10] The central problem is the nature of the interaction which causes the ground-state splitting. Only a combination of a perturbation of the crystalline field and spin-orbit coupling can cause this splitting. There has been some conjecture regarding the splitting B_2^0 cause by the second order potential (in the $3d$ shell this is called in the usual nomenclature D, i.e., the axial field splitting).[7,8,11] There has been, however, no serious attempt to explain the splitting in a pure cubic field. This splitting has been observed previously only in ions of the $3d$ shell, for example in Mn^{2+} and Fe^{3+}. In the $4f$ shell the cubic field and spin-orbit coupling split the eightfold degenerate state into a twofold, fourfold, and another twofold level. We felt that an experimental investigation of this splitting a cubic field might aid a significant contribution to the understanding of the S state. The spectrum is easier to unravel as it has fewer parameters in the spin Hamiltonian. Moreover, it might well be the starting point for the investigation of other rare earth ions in cubic field symmetries.

There was another reason why the problem seems to be of interest to the author. For practical reason the trivalent gadolinium had to be imbedded in single crystals for CaF_2. In previous communications it has been shown that some trivalent ions can be substituted for divalent cations without disturbing appreciably the local cubic symmetry.[12,13] This was found for ions which have an effective S state in their ground state. Apparently the trivalent ions in an S state can stabilize the complex without the need of associated vacancies. It was worthwhile testing whether this would hold true for the gadolinium ion as well. This problem is more than of passing interest. Paramagnetic resonance is probably one of the most powerful tools of solid state which can determine the nature of vacancies, defects or charge compensations in single crystals. Many of the current theories of associated vacancies or defects can, therefore, directly be tested.

In Sec. 2 we shall develop the theory of the fine structure splitting of the gadolinium ion in a combined fourth and sixth order potential. In Sec. 3 we describe the experimental techniques and results. In Sec. 4 the significance of these results is discussed and a general review of the various problems of the S-state ions are presented.

II. THEORY

The crystalline potential acting on the magnetic electrons is usually expanded in a Taylor series about the center of the paramagnetic ion. For f electron it is sufficient to consider only the first two terms of this series (in a cubic field),

$$V=C(x^4+y^4+z^4-\tfrac{3}{5}r^4)+D|(x^6+y^6+z^6)+(15/4)(x^4y^2+x^2y^4+x^4z^2+x^2z^4+y^4z^2+y^2z^4)-(15/14)r^6|.$$

For calculating the matrix elements of V between states of various J_z it is more convenient to write the potential in terms of normalized tesseral harmonics, i.e.,

$$V=\frac{Z_ie^2r^4}{a_i^5}\left(\frac{4\pi}{9}\right)^{\frac{1}{2}}\left|(-28/9)Y_4^0+\left(\frac{2\times70^{\frac{1}{2}}}{9}\right)(Y_4^4+Y_4^{-4})\right|+\frac{Z_ie^2r^6}{a_i^7}\left(\frac{4\pi}{13}\right)^{\frac{1}{2}}\left|(16/9)Y_6^0+\left(\frac{8\times14^{\frac{1}{2}}}{9}\right)(Y_6^4+Y_6^{-4})\right|, \quad (2)$$

where

$$Y_n^m=\left|\frac{(2n+1)(n-|m|)!}{4(n+|m|)!}\right|^{\frac{1}{2}}P_n^{|m|}(\cos\theta)e^{im\phi},$$

r is the distance from the electron to any point of the cubic symmetry, and a is the distance from the surround-charges of the cube to the point of the cubic symmetry. This expansion is for the eightfold cubic coordination in which is assumed that the negative charges are point charges and are located at the corners of a cube. One significant fact is that the sixth- and fourth-order potential are of the opposite sign. The matrix elements for the crystalline field perturbation have been given

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[7] R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1953).

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by Penney and Schlapp[14] and their operator equivalent have been evaluated by Stevens.[15] Diagonalizing these matrices leads to the following energy values: 0 (twofold Γ_7), $5c+7d$ (fourfold Γ_8) and $8c-2d$ (twofold Γ_6). We have arbitrarily set the first level at zero. As c and d are of opposite sign it is seen that for positive c the fourfold degenerate level is lowered and the Γ_6 twofold level is raised by the sixth-order potential. c and d are numbers common to the various matrix elements and are proportional to the average value of $\langle r^4\rangle_{\text{Av}}$ and $\langle r^6\rangle_{\text{Av}}$, respectively. This energy level scheme is shown in Fig. 1 in which we assume that $d \ll c$ as found experimentally. Which twofold level is the lowest can only be decided by experiment.

The energy levels of the $^8S_{7/2}$ state in a magnetic field have been calculated by Kittel and Luttinger[16] and more extensively by DeBoer and Van Lieshout.[17] These authors have used only the fourth-order potential. Generalizing these results to include the sixth-order potential we find that the energy levels are given for the 0, 0, 1 direction by[18]

$$\begin{aligned} E_{\pm 7/2} &= \tfrac{1}{2}(13c+5d\pm 3a) \\ &\qquad \pm\tfrac{1}{2}|(3c-9d-\tfrac{2}{3}a)^2+(140/9)a^2|^{\frac{1}{2}}, \\ E_{\pm 1/2} &= \tfrac{1}{2}(13c-5d\mp 3a) \\ &\qquad \mp\tfrac{1}{2}|(3c-9d+\tfrac{2}{3}a)^2+(140/9)a^2|^{\frac{1}{2}}, \\ E_{\pm 5/2} &= \tfrac{1}{2}(5c-7d\pm a)\pm\tfrac{1}{2}|(5c+7d-2a)^2+12a^2|^{\frac{1}{2}}, \\ E_{\pm 3/2} &= \tfrac{1}{2}(5c+7d\mp a)\pm\tfrac{1}{2}|(5c+7d+2a)^2+12a^2|^{\frac{1}{2}}, \end{aligned} \tag{3}$$

where $a=g\beta H$, $\beta=$ Bohr magneton, $H=$ magnetic field. For any other direction the matrix does not factor in general. For strong magnetic fields the energy levels can be expanded in a series. The magnetic dipole transitions ($\Delta M_j=\pm 1$) are given by

$$\begin{aligned} E_{\pm 7/2}\rightarrow E_{\pm 5/2} &= \beta g H_0 \pm\tfrac{1}{2}(10c+3d)p+\epsilon_1, \\ E_{\pm 5/2}\rightarrow E_{\pm 3/2} &= \beta g H_0 \mp\tfrac{1}{2}(5c+7d)p+\epsilon_2, \\ E_{\pm 3/2}\rightarrow E_{\pm 1/2} &= \beta g H_0 \mp\tfrac{1}{4}(12c-17d)p+\epsilon_3, \\ E_{1/2}\rightarrow E_{-1/2} &= \beta g H_0+\epsilon_4, \end{aligned} \tag{4}$$

where ϵ_1, ϵ_2, ϵ_3, ϵ_4 are terms in $c^2/\beta g H_0$, $d^2/\beta g H_0$, and $cd/\beta g H_0$; $p=(1-5\phi)$, $\phi=l^2m^2+m^2n^2+l^2n^2$ (l, m, n being the direction cosines between the magnetic field and the cubic axes), and $g=2.0023$.

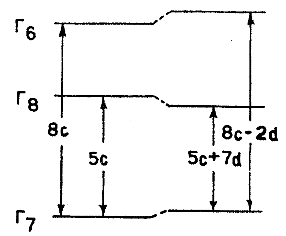

FIG. 1. The ground-state splitting of a $^8S_{7/2}$ state under the combined action of the fourth- and sixth-order potential. The left side indicates the splitting caused by the fourth-order potential only. The quantities c and d are factors proportional to the fourth- and sixth-order potential.

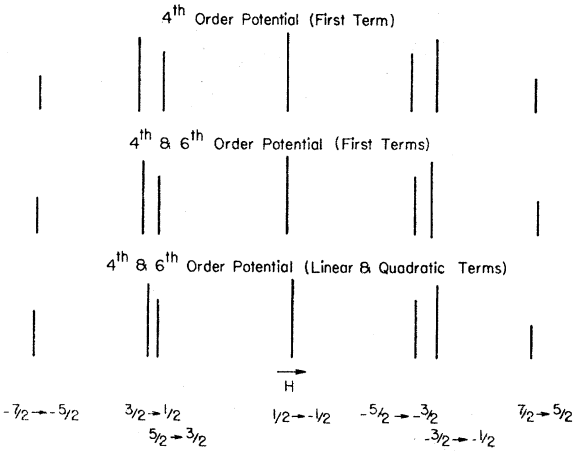

FIG. 2. Theoretical paramagnetic resonance spectrum of gadolinium in cubic fields. The top figure shows the influence of the predominant fourth-order potential. The middle figure indicates the influence of the first terms of the fourth- and sixth-order potential. The spectrum is still symmetrical in a plane about the $\frac{1}{2}\rightarrow -\frac{1}{2}$ transition. The lowest figure shows that this symmetry is destroyed if the higher correction terms are included.

If the sixth-order contribution is negligible, then the fine structure spectrum shows seven lines, three on each side of the $\frac{1}{2}\rightarrow -\frac{1}{2}$ transition with relative separation of 10:5:6. If the sixth-order potential is taken into account, then to first-order expansion the spectrum is still symmetrical with respect to the $\frac{1}{2}\rightarrow -\frac{1}{2}$ transition and the 3 satellites on each side are separated in the ratio of $10c+3d:5c+7d:\frac{1}{2}(12c-17d)$. The second-order correction terms destroy this symmetry as the various levels are shifted differently. For example for the 0, 0, 1 direction these levels to second order are

$$\begin{aligned} E_{\pm 7/2}\rightarrow E_{\pm 5/2} &= g\beta H_0 \pm\tfrac{1}{2}(10c+5d)-\frac{5}{8}\frac{c^2}{g\beta H}, \\ E_{\pm 5/2}\rightarrow E_{\pm 3/2} &= g\beta H_0 \mp\tfrac{1}{2}(5c+7d), \\ E_{\pm 3/2}\rightarrow E_{\pm 1/2} &= g\beta H_0 \mp\tfrac{1}{2}(6c-7d)+\frac{5}{8}\frac{c^2}{g\beta H}, \\ E_{+1/2}\rightarrow E_{-1/2} &= g\beta H_0+\frac{35}{32}\left(\frac{c-3d}{g\beta H}\right)^2 g\beta H. \end{aligned} \tag{5}$$

Then quadratic terms in Eq. (5) are small but not negligible at 1 cm wavelength. The effect of these terms is illustrated in Fig. 2 for the 0, 0, 1 direction, as found also by experiment. They widen the (5/2→3/2) − (3/2→1/2) separation on one side and narrow this separation on the other side of the (1/2→−1/2) transition.

The angular variation of the fine structure of an

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[17] J. DeBoer and R. Van Lieshout, Physica **15**, 570 (1949).

[18] DeBoer and Van Lieshout have assumed that the Γ_6 level at zero, i.e., the reverse order of our level scheme. If we use their notation, then the levels are given by

$$\begin{aligned} W_{6,2} &= \tfrac{1}{2}(3c-9d)+3a\pm|16a^2+2a+\tfrac{1}{4}(3c-9d)^2|^{\frac{1}{2}}, \\ W_{8,4} &= \tfrac{1}{2}(11c-11d)+a\pm|16a^2+10a+\tfrac{1}{4}(5c+7d)^2|^{\frac{1}{2}}, \\ W_{7,5} &= \tfrac{1}{2}(11c-11d)-a\pm|16a^2-10a+\tfrac{1}{4}(5c+7d)^2|^{\frac{1}{2}}, \\ W_{3,1} &= \tfrac{1}{2}(3c-9d)-3a\pm|16a^2-2a+\tfrac{1}{4}(3c-9d)^2|^{\frac{1}{2}}. \end{aligned}$$

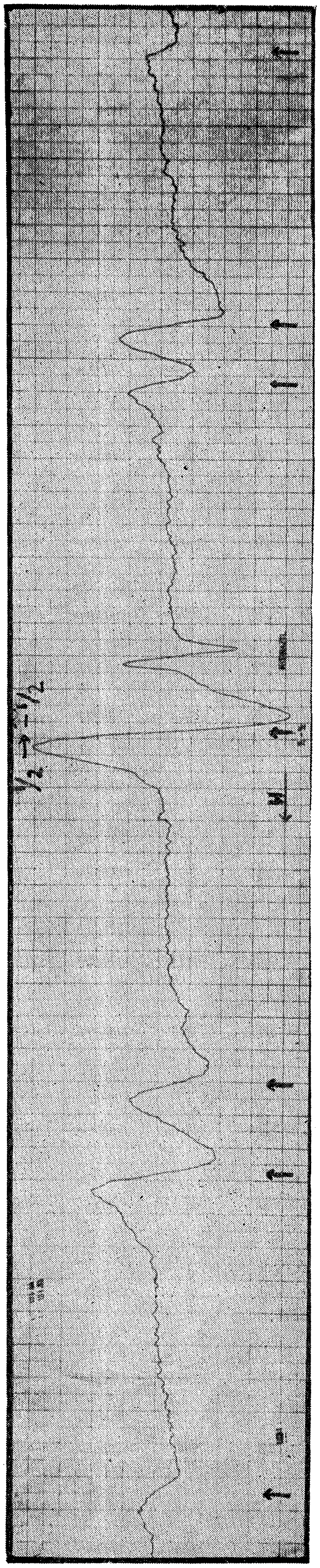

FIG. 3. The observed paramagnetic resonance spectrum near the (1, 0, 0) plane.

S-state spectrum for rotation about various planes has been discussed in detail for the Mn^{2+} ion by the author[19] and by Matarrese and Kikuchi.[20] The same formulas apply in the case of the gadolinium ion.

III. EXPERIMENTAL TECHNIQUE AND RESULTS

Single crystals of CaF_2 containing less than 0.05% of gadolinium by weight were grown for this experiment. The oven was a conventional induction furnace. The CaF_2 powder was mixed with GdF_3 and about 0.5% of PbF_2 powder and placed in a graphite crucible. The crucible was inside an Alundum tube which was sealed at both ends. Dried helium gas could be introduced from the top and escaped through a small opening at the bottom of the Alundum tube. The furnace was slowly heated by the induction furnace until the PbF_2 boiled off. PbF_2 acts as a scavenger and removes the moisture. This is important, for if any water is present the resulting crystals have a milky color. This is presumably caused by the reaction of the CaF_2 with water vapor or with oxygen giving CaO. Stockbarger[21] claims that CaF_2 reacts strongly with water vapor at temperatures in excess of 100°C and that this rate increases rapidly with increasing temperature. The dried helium helped considerably in producing clearer crystals and possibly prevented any excess of oxygen ions in these crystals. It is to be noted that the ionic radii of $O^{=}$ and F^{-} are approximately the same and one can therefore expect the CaO to form solid solutions with CaF_2.

The whole furnace was permitted to fall through the coil of the induction furnace at a rate of $1\text{–}1\frac{1}{2}''$ per hour. The furnace was operated at 1450°C. Usually the first trial gave already satisfactory crystals for paramagnetic resonance work. Some crystals looked like one single crystal but on investigation by x-rays or by paramagnetic resonance revealed that they consisted of several crystals with small misalignments of a few degrees of one with respect of another. It usually proved possible to cleave off one section of the crystal consisting of one single crystal.

Measurements were made at 1.2 cm wavelength and at room temperature. A typical spectrum is shown in Fig. 3. Here the crystal was mounted along the 1, 0, 0 axis. It is seen that the spectrum consists of seven lines only indicating only one ion per unit cell. The separation of the components from the central $\frac{1}{2} \rightarrow -\frac{1}{2}$ line is approximately in the ratio of 10:6:5:1:5:6:10. All this are strong indications that the crystal symmetry around the Gd^{3+} ion is predominantly cubic and that c is much larger than d.

The angular variation of the fine structure was examined in a number of planes notably in the (0,0,1) and (0,1,1) planes. Figure 4 shows the measured angular dependence of the fine structure as the magnetic

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field is rotated about the (0,0,1) plane. The crystal was mounted in the (0,0,1) plane within 3° [the natural cleavage planes are (1,1,1) for CaF_2]. The spectrum conforms closely to that expected from a cubic crystal. The fine structure is seen to collapse at about 31° and 58° from the (1,0,0) plane. The spectrum is slightly asymmetrical, i.e., the separation of the transitions $(-3/2 \rightarrow -1/2)-(-5/2 \rightarrow -3/2)$ is larger than the $(+3/2 \rightarrow 1/2)-(5/2 \rightarrow 3/2)$ (low-field components). Similarly, the separation of the $7/2 \rightarrow 5/2$ line from the central $1/2 \rightarrow 1/2$ line (high-field separation) is slightly smaller than the corresponding low-field separation. This can be accounted for only if c and d have opposite signs in Eq. (5). We give here already the absolute signs of these transitions in anticipation of results to be discussed subsequently. A close inspection reveals that the spectrum is also not quite symmetrical with respect to a plane at 45° as would be predicted by theory. We feel that this is caused by the slight misalignment of the crystal. Even a small variation of about 2–3° in the alignment have a large effect on the fine structure spectrum, since the splitting is so large.

The spectrum permits the evaluation of the following parameters: $g=1.991\pm0.002$, $c=+0.0185\pm0.0005\ \mathrm{cm}^{-1}$, $d=-0.0004\pm0.0002\ \mathrm{cm}^{-1}$ at $T=290°\mathrm{K}$ and at 1.25 cm wavelength.† The absolute sign of c was determined from intensity measurements at liquid helium temperatures. We have also made a qualitative measurement of the fine structure at liquid helium temperature and found that c is increased by a few percent compared with the value at room temperature.

All crystals showed in addition a weak spectrum which varied in a manner as if an axial field were present. The axes of this field seemed to be along the cubic axes of the crystal. In Fig. 3 some of these weak lines can be seen. As this spectrum was not of interest in the present connection, we shall not discuss this in detail.

The theoretical intensity of the fine structure components $M=-7/2:M=3/2:M=5/2:M=1/2:M=-5/2:M=-3/2:M=+7/2$ is 7:15:12:16:12:15:7. The experimental intensity ratios are difficult to measure as the line width varies for the different components as seen in Fig. 3 and the amplitude, therefore, depends on the depth of the field modulation. The measured amplitudes are (measured from low to high fields) 2:6.5:4:16:5:7.7:2.5. The integrated intensity ratio of the $1/2 \rightarrow -1/2$ to the $3/2 \rightarrow -1/2$ transitions is approximately 16:10 instead of the theoretical 16:15.

IV. DISCUSSION

We shall divide the discussion of these results into two sections: (1) The significance of the S state for the theory of paramagnetic resonance spectra and (2) the significance to the theories of vacancies and defects in the solid state.

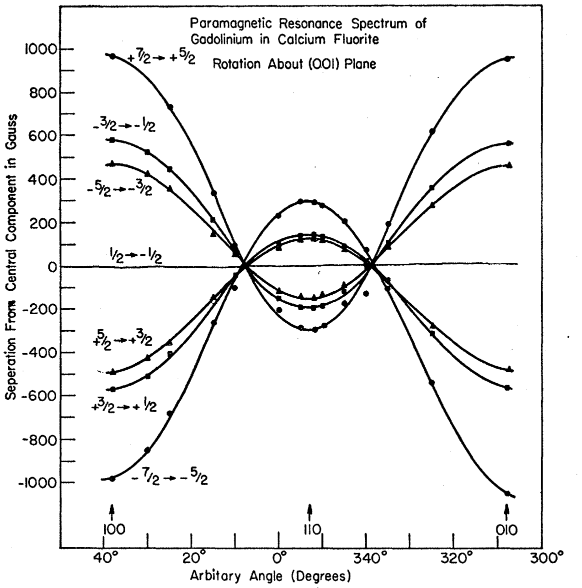

FIG. 4. Angular variation of the fine structure lines as the magnetic field is rotated about the (0,0,1) plane.

(1) We shall give here a short review of the various problems encountered in the theory of the S state in paramagnetic resonance. Most of this material can be found in scattered literature on spectra of Gd^{3+}, Mn^{2+}, Fe^{3+}, and Cm^{3+}. The main problem is the nature of the splitting of the ground state. The eightfold degeneracy of the ground state can only be removed by the simultaneous action of the crystal field and the spin coupling. The latter mixes in higher excited states to the ground state. The next higher levels in the case of gadolinium are the ${}^6P_{7/2}$ and ${}^6D_{7/2}$ at about 30–31 000 cm^{-1} and 36 000 cm^{-1}, respectively. The spin-orbit coupling is of the order of 1500 cm^{-1}. It is, therefore, seen that any mechanism involving spin-orbit coupling perturbation to a high power will yield very small splittings of the ground state.

Judd[8] has pointed out that there is no correlation between the observed parameters B_n^m and the various potential parameters V_n^m which appear in an expansion of the potential energy. This in itself is not so surprising as the parameters B_n^m involve the spin-orbit coupling constant as well as the potential constants to a high power. Moreover, there may be more than one perturbation which is operative. The resultant of the various perturbations will determine the sign and the magnitude of the various coefficients B_n^m. This makes the problem of course very complicated as we would have to consider each splitting parameter B_n^m separately, for each given crystalline symmetry and probably even for each individual crystal. In crystals of C_{3v} and C_{3h} symmetry the B_2^0 term is the most important, and so far has

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† *Note added in proof.*—C. Ryter [Helv. Phys. Acta **30**, 354 (1957)] has independently measured the paramagnetic resonance spectrum of gadolinium in natural crystals of CaF_2. His results are $8c-2d=0.1491\pm0.0008\ \mathrm{cm}^{-1}$ and $(5c+7d)/(8c-2d)=0.596\pm0.002$. These results are in very good agreement with those reported here, 0.1488 and 0.596, respectively.

received considerable attention. This parameter differs from crystal and is strongly temperature-dependent in the region between room and liquid air temperatures. The same has been found to hold true for the curium spectrum which has $5f^7$ electrons.[22] The other coefficients are also temperature dependent, though not to such an extent. Another fact which is indicative of the complexity of the problem is the fact that the $B_4{}^0$ coefficient may have either positive (lathanum trichloride) or negative sign (ethyl sulfate).

In the case of the cubic field splitting there are probably also a number of mechanisms operative. In general all these mechanisms must involve a splitting of the ${}^6P$ state as this is the only state which is connected by spin-orbit coupling with the ground state ${}^8S$. It is worthwhile in this connection to list the significant matrix elements which are different from zero in a general cubic field:

$$\begin{aligned}&\langle {}^8S_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^6P_{7/2}\rangle\neq 0,\\ &\langle {}^6P_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^6D_{7/2}\rangle\neq 0,\\ &\langle {}^6P_{7/2}|V|{}^6G_{7/2}\rangle\neq 0,\\ &\langle {}^6D_{7/2}|V|{}^6G_{7/2}\rangle\neq 0,\\ &\langle {}^8S_{7/2}|V|{}^8S_{7/2}\rangle=0,\\ &\langle {}^6P_{7/2}|V|{}^6P_{7/2}\rangle=0,\\ &\langle {}^6P_{7/2}|V|{}^6D_{7/2}\rangle=0,\\ &\langle {}^6X_{7/2}|V|{}^8S_{7/2}\rangle=0,\\ &X={}^6P_{7/2},\ {}^6D_{7/2}\cdots.\end{aligned}\tag{6}$$

Inspection of these matrix elements permits the construction of several mechanisms in addition to the fifth-order process (quartic in the spin-orbit coupling and linear in the crystalline potential) proposed by Pryce,[23] for example,

$$\langle {}^8S_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^6P_{7/2}\rangle\langle {}^6P_{7/2}|V|{}^6G_{7/2}\rangle \times\langle {}^6G_{7/2}|V|{}^6P_{7/2}\rangle\langle {}^6P_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^8S_{7/2}\rangle,\tag{7a}$$

$$\langle {}^8S_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^6P_{7/2}\rangle\langle {}^6P_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^6D_{7/2}\rangle \times\langle {}^6D_{7/2}|V|{}^6G_{7/2}\rangle\langle {}^6G_{7/2}|V|{}^6P_{7/2}\rangle \times\langle {}^6P_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^8S_{7/2}\rangle,\tag{7b}$$

$$\langle {}^8S_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^6P_{7/2}\rangle\langle {}^6P_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^6D_{7/2}\rangle \times\langle {}^6D_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^6F_{7/2}\rangle\langle {}^6F_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^6G_{7/2}\rangle \times\langle {}^6G_{7/2}|V|{}^6P_{7/2}\rangle\langle {}^6P_{7/2}|\mathbf{L}\cdot\mathbf{S}|{}^8S_{7/2}\rangle.\tag{7c}$$

Other perturbations of higher order can easily be constructed but are probably of even smaller magnitude. It is to be noted that the first two proposed mechanisms [(7a) and (7b)] are quadratic in the crystalline field potential while Pryce's mechanism is linear. Similar perturbations can be constructed for noncubic fields except that in general there will be many more matrix elements than given by (6), and correspondingly many more combinations which result in perturbations of comparable magnitudes.

These considerations can now be applied to the experimental results of the S-state ions in cubic fields. The value of $8c=0.148\ \mathrm{cm}^{-1}$ shows that there exists a large splitting of the ground state. This splitting in $\mathrm{CaF_2}$ is of the same order of magnitude as the second order splitting $B_2{}^0$ in ethyl sulfate and lanthanum chloride. One may expect that the crystalline field of Gd in $\mathrm{CaF_2}$ is somewhat stronger than in crystals of C_{3v} or C_{3h} symmetry because of the attraction of the excess charge on the fluorine ions. The small temperature dependence of the splitting is some indication that the mechanism responsible for the splitting is linear in the potential. A perturbation involving V to a high power would give a strong temperature dependence. On the other hand, it is quite possible that the excess charge on the gadolinium ion stabilizes the complex to such an extent that the interactomic distances change only to a very slight extent with temperature.

In the case of the ${}^6S_{5/2}$ state, i.e., Fe^{3+} and Mn^{2+} in MgO, the cubic field splitting parameter $3a=3c=0.0615$ and $0.00558\ \mathrm{cm}^{-1}$, respectively.[10] From the optical data we estimate that ratio of the spin-orbit coupling to the third power is approximately 3. The strength of the crystalline field of Fe^{3+} is about twice that of Mn^{2+}.[24] The excited energy levels of the free ions ${}^4G$ and ${}^4P$ are at 32 000 and 35 000 cm^{-1} for Fe^{3+} and about 27 000 and 29 000 cm^{-1} for Mn^{2+}. In a crystal the levels of the Fe^{3+} are probably lowered by several thousand cm^{-1} because of the strong covalent bonding in trivalent ions.[25,26] The ratio of about 11:1 in the ground-state splitting of these two ions is not unreasonable according to the first mechanism (7a). However, Pryce's mechanism may be of the same order of magnitude. This possibly may explain the puzzle of the difference in sign of the cubic field splitting parameter of Fe^{3+} in ferric alums (negative) and in MgO (positive). The sign of the cubic field splitting will depend on which of the two mechanisms predominates as they are of opposite sign.

It is also of interest to note that all g factors of Gd^{3+} or Eu^{2+} are approximately 1.991, always less than the free electron spin (2.0023). Apparently the contribution of the ${}^6P_{7/2}$ state to the ground state reduces the value of the g factor.

(2) The results are of interest to the theories of vacancies and defects in ionic crystals. As gadolinium is trivalent, some mechanism must be found to maintain the neutrality of the crystal. If gadolinium goes into substitutional solid solution one would expect either positive vacancies or negative-ion interstitials to be present. The negative-ion interstitials could be F^- or O^{2-} ions. The vacancies could obviously be Ca^{2+} ions.

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The experimental evidence supports that F^- interstitials are present in CaF_2 with solid solutions of trivalent rare earth ions. This evidence comes from three sources. (a) Zintl and Urgoard[27] have inferred from x-ray lattice constant measurements that YF_3 goes into solid solution up to 45 mole percent and that YF_3 introduces F^- interstitials. (b) Conductivity measurements by Ure[28] on CaF_2:YF_3 single crystals show that the predominant defect is the anti-Frenkel defect consisting of negative-ion vacancies and negative-ion interstitials. (c) Paramagnetic resonance measurements by Llewellyn *et al.*[29] on CaF_2 containing U^{3+} and Nd^{3+} show that there are three magnetic ions with axial symmetry about one of the cubic axes. They interpret their results as indicating that the trivalent ion replaces the divalent calcium ion and an excess F^- ion is at the body center of the adjacent cube of the fluorine ions. This reduces the symmetry from cubic to tetragonal axes along the three cubic axes. From the hyperfine structure of the fluorine ion they infer that the ninth fluorine ion actually is drawn closer to the trivalent uranium ion. Because of this the four fluorines between U^{3+} and the F^- interstitial will be pushed out somewhat.

Our results can be interpreted only to indicate that the cubic symmetry is essentiallly preserved. The question, therefore, arises why the spectrum of Gd^{3+} is different than those of other rare earth ions. There are a number of possibilities. One possibility may be connected with the different methods which these crystals have been grown. Another is that all the evidence presented above is on single crystals containing more than 0.1% of the rare earth ions whereas our measurements were made on crystals containing less 0.05% by weight of gadolinium. We have proposed a a different explanation.[13] The *S*-state ions with their spherical charge density may well stabilize the complex of the surrounding fluorine ions. The excess charge draw in symmetrically the eight fluorine ions, setting up stronger crystalline fields and shielding the trivalent ions from the potentials of any compensating charged ions. The interaction between such ions and the trivalent charge would be then very small. Considerable evidence for this mechanism has been accumulated, in particular for Fe^{3+} ($^6S_{5/2}$) and Cr^{3+} (an effective *S* state). We find that for these ions in MgO the cubic symmetry is preserved for small concentration of these impurity ions.[12,13] Recently results by Shaltiel and the author[30] on ThO_2 containing gadolinium ions have shown that in this crystal, which has the same fluorite crystal structure as CaF_2, the cubic symmetry is preserved as well.

The large line width of about 18 gauss for the $1/2 \rightarrow -1/2$ transition is probably caused by a number of reasons. The surrounding eight fluorine ions will result in a line width of a few gauss. Llewellyn[29] finds that the line width for Nd^{3+} in CaF_2 is less than 8 gauss. If our explanation of the stabilization of the complex $Gd^{3+}F_8^-$ is correct, we would expect a larger line width because of the stronger crystalline field and the resulting overlap of the $4f$ wave functions on the fluorine ions. More likely is the explanation that the compensating ions have a second-order effect which manifests itself in a broadening of the lines. This will affect the $5/2 \rightarrow 3/2$ and $3/2 \rightarrow 1/2$ transitions more than the $1/2 \rightarrow -1/2$ transition and, therefore, explain the larger line width and smaller intensity of the satellites.

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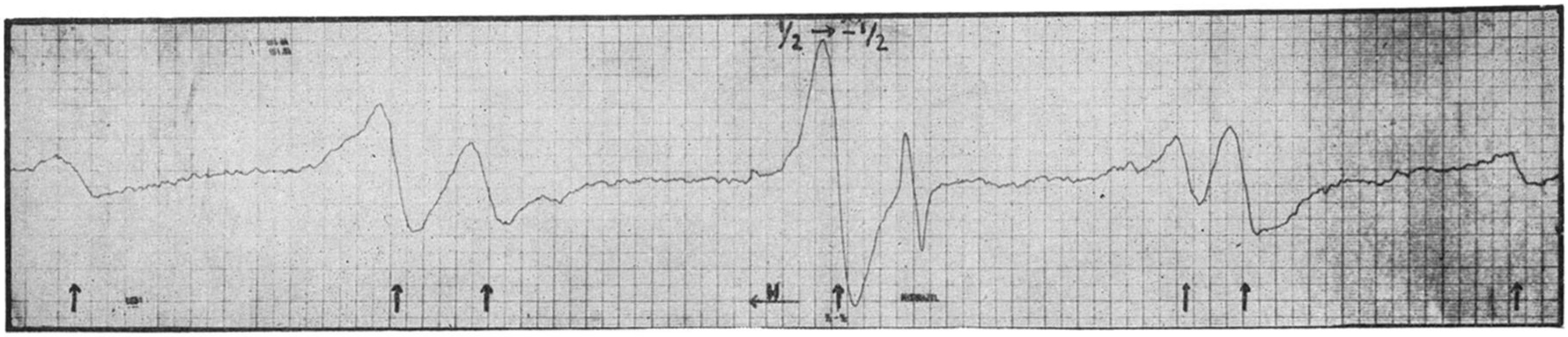

FIG. 3. The observed paramagnetic resonance spectrum near the (1, 0, 0) plane.