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Paramagnetic Resonance of the Fe^{3+} Ion in $CaWO_4$ (Strong Tetragonal Crystal Field)

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The paramagnetic resonance spectrum of Fe^{3+}, in the W site of a tetragonal $CaWO_4$ single crystal, has been measured at *X*- and *K*-band frequencies. Four resonance lines arising from a distortion are observed having an isotropic (0.5% anisotropy at *X*-band frequencies) *g* factor of 4.3. The hyperfine interaction of $^{57}Fe^{3+}$, in an isotopically enriched sample, is $|A'|=13.4\pm0.2\,(10^{-4}\,\text{cm}^{-1})$ with an effective field at the nucleus H_e of 146 kG. The epr results are interpreted in terms of a strong crystal field of tetragonal symmetry, which is large compared to the Zeeman energy, and which is consistent with the observed angular dependence and the assumed site symmetry.

I. INTRODUCTION

THE paramagnetic resonance spectra of ions with half-filled 3*d* shells are generally characterized by a *g* factor close to 2.0, ground-state crystal-field splittings of a few tenths of a wave number, and long spin-lattice relaxation times. A few exceptions were found in the complex cyanides[1–3] which have anisotropic *g* factors and extremely large crystal-field splittings. The exceptional behavior of these salts can be explained by assuming that the crystal field dominates over the Coulomb interaction in such a way that Hund's rule is violated. Further evidence for strong crystal-field effects upon *S*-state ions is found in haemoglobin derivatives[4] which contain Fe^{3+}. A doublet is observed ($S'=\frac{1}{2}$) having $g_{\parallel}=2$ and $g_{\perp}=6$. The *g*-value variation can be explained by means of a large crystal field which splits the $^6S_{5/2}$ ground state into three doublets separated by 1.0 cm^{-1} or more.[5] Similar results have been found recently for Fe^{3+} in $PbTi_3O$.[6] The origin of the large crystal field ($DS_z^2 \gg g\beta\mathbf{H}\cdot\mathbf{S}$) is not well understood. Also, epr experiments performed on glasses containing iron have revealed an intense resonance at $g=4.27$.[7] An interpretation of the isotropic *g* factor was again found in the effects of a large crystal field. Basic to this interpretation is the assumption that all fourth-order terms and the second-order axial term in the spin operators are negligible, the principal coupling of the spins to their surroundings being represented by a term of the form $E(S_x^2-S_y^2)\gg g\beta\mathbf{H}\cdot\mathbf{S}$.

The purpose of this paper is to report on the paramagnetic resonance spectra of the Fe^{3+} ion substituted in $CaWO_4$. $CaWO_4$ has the scheelite structure[8] and is made up of Ca ions and tungstate tetrahedra. Thus in principal, both Ca and W sites are available for substitutional impurity ions. Considerations such as ionic size and electrical neutrality would be expected to limit occupancy to either one or the other cation position.[9] Recently, however, it has been shown that Nd^{3+} ions can occupy either site, but the Fe^{3+} ion is found only in the extremely strong crystal-field environment of the tungsten site.[10]

The experimental procedure is described in Sec. II and the results in Sec. III. Section IV is devoted to the discussion and a theoretical interpretation of the results.

II. EXPERIMENTAL PROCEDURE

Single crystals of Fe^{3+} doped $CaWO_4$ were grown from raw material which was prepared by calcination (1100°C in an oxidizing atmosphere) of an intimate equimolar mixture of calcium carbonate and tungstic acid anhydride contained in a platinum vessel. Substitution for calcium or tungsten using an Fe_2O_3 dopant was completed prior to calcination according to the general formulas $Ca_{(1-x)}A_xWO_4$ and $CaW_{1-x}B_xO_{4-3/2x}$, respectively. A 5–10% excess of the unsubstituted cation was added in each experiment in order to avoid a deficiency of that cation. The crystals were grown by slow withdrawal of an oriented seed from a melt which was contained in an iridium crucible. The crystal was rotated 15–30 rpm and withdrawn at the rate of 0.25 to 1.0 in. per hour. It was found that when large amounts (greater than 0.1 mole %) of Fe were added, the crystal became occluded with black particles which caused cracking. This same result has been reported by Nassau.[9] All attempts to force Fe^{3+} ions into Ca sites failed. The maximum amount of substituted iron in a clear crystal amounted to about 60 ppm as determined by emission spectroscopy. The more heavily doped crystals, when viewed along the growth axis, had a radial iron concentration gradient. The central area was black while successive ring-like areas were lighter shades of gray and contained less Fe. Attempts to force large concentra-

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[1] J. M. Baker, B. Bleaney, and K. D. Roberts, Proc. Phys. Soc. (London) **B69**, 1205 (1956).

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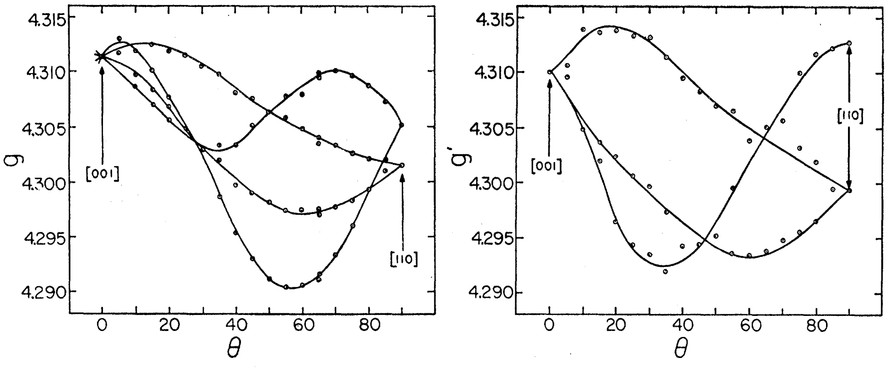
[8] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1949), Vol. 2, Chap. 8.

[9] K. Nassau and A. M. Broyer, J. Appl. Phys. **33**, 3064 (1962).

[10] R. W. Kedzie and M. Kestigian, Appl. Phys. Letters **3**, 86 (1963); **4**, 124 (1964).

FIG. 1(a). Angular dependence of the g' factor of Fe^{3+} in $CaWO_4$. Data obtained at room temperature (297°K) using a microwave frequency of 9.505 Gc/sec. The axis of rotation is the $[\bar{1}10]$ crystal axis, and the angle θ is measured in degrees from the [001] symmetry axis. (b) Same as Fig. 1(a), with the exception that the temperature has been reduced to 77°K and the frequency is 9.029 Gc/sec.



(a) (b)

tions of iron into W sites were unsuccessful, and a poorer quality crystal generally resulted which appeared to be more prone to thermal shock.

In all samples, Mn^{2+} impurities at concentrations less than 3 ppm were found. The presence of the Mn^{2+} impurity served a useful purpose, since it could be used to check crystal orientation. In addition, broadening of the outer fine-structure lines of the Mn were used to detect crystal strain in the Fe-doped crystals.[11]

The orientation of the crystal axes with respect to the applied field (H_0) was found to be extremely critical. After the orientation of the crystal axes had been determined by x-rays, the crystal was transferred to the microwave cavity. However, a series of minute readjustments were still required. The orientation was monitored by varying the angle between H_0 and the [001] direction. A single sharp line was observed when H_0 was parallel to both the [001] and $[00\bar{1}]$ directions. The single line split into four equal components when the angle between H_0 and the c axis was as small as 0.1 deg.

Epr spectra were obtained with Strand Labs spectrometers, models 602-A/X and 602-A/K, operating at X (9.1 Gc/sec and K (25.0 Gc/sec) band frequencies. The magnetic field was provided by means of a Harvey-Wells model L-128 electromagnet. It was modulated at a frequency of 6 kc/sec with 13½ in. diam, single-wire pancake coils driven by an H. H. Scott type 250 BRL power amplifier. The dc field was measured using a Harvey-Wells nmr precision gaussmeter. The majority of the experiments were performed at room temperature; however, temperatures as low as 1.5°K were used.

The klystron resonance frequency was measured by zero beating with the output from a Hewlett-Packard model 540 B transfer oscillator. The primary frequency of the oscillator was determined by means of a Hewlett-Packard electronic frequency counter, model 524 C.

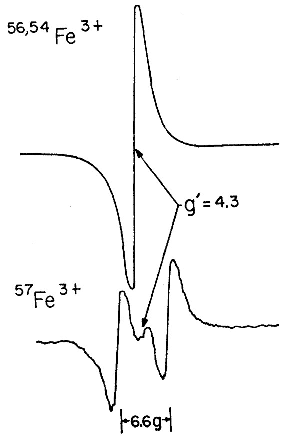
TABLE I. Dependence of g' upon orientation at X-band frequencies for samples of varying concentration.

Sample	Concentration	g' (001)	g' (110)
$^{56,54}Fe^{3+}$	60 ppm	4.312±0.004	4.308±0.004
$^{56,54}Fe^{3+}$	<3 ppm	4.313±0.004	4.309±0.004
$^{57}Fe^{3+}$	<3 ppm	4.311±0.004	4.308±0.004

III. EXPERIMENTAL RESULTS

It was initially believed that if trivalent iron was incorporated in the lattice, its paramagnetic resonance would be seen in the region $g=2$ at room temperature. Careful magnetic-field scans, at various angles, revealed only a $^{55}Mn^{2+}$ impurity. However, an intense line was found at $g'=4.3$. The angular dependence [Fig. 1(a)] shows that it is not a single line but splits into at least three components with a total anisotropy of about ½%. One line is observed when the spectrum is viewed with H_0 parallel to the [001] direction and two are viewed along the [110] direction. At 77°K [Fig. 1(b)] the spectrum is resolved into four components for which the percent anisotropy is the same as it was at room temperature. The g factor[12] was found to be independent of concentration at room temperature, as is shown in

FIG. 2. Comparison of the paramagnetic resonance spectra observed in a sample doped with naturally occurring $^{56,54}Fe^{3+}$ (upper curve), with that observed in a sample doped with isotopically enriched $^{57}Fe^{3+}$ (lower curve). The spectra were obtained at room temperature using a frequency of 9.5 Gc/sec and with the applied field (H_0) parallel to the crystallographic c axis.



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[11] In all crystals containing the ferric impurity, the $(\pm\frac{1}{2}\rightleftarrows\pm\frac{3}{2})$ and $(\pm\frac{3}{2}\rightleftarrows\pm\frac{5}{2})$ transitions of Mn^{2+} were severely strain-broadened. In some crystals, it was difficult to observe these lines when the applied field (H_0) was perpendicular to the [001] direction. Thirty lines were observable, however, when H_0 was rotated parallel to the c axis along which the linewidth decreased.

[12] The primed system (i.e., g' and A') will refer to the fictitious spin system in which $S=S'=\frac{1}{2}$.

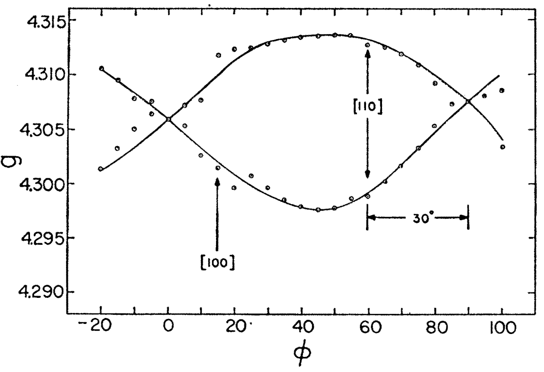

FIG. 3. Angular dependence of the g' factor for rotation of the applied field (H_0) in the (001) plane. Data obtained at room temperature using a microwave frequency of 9.501 Gc/sec. φ is the angle in degrees measured arbitrarily from the field (H_0) at which the two lines coalesce.

Table I, where g' (110) is calculated for the field midway between the two observed lines.

In order to check that the spectrum was due to Fe, a crystal containing ^{57}Fe was grown. The results are shown in Fig. 2. The single sharp line observed in crystals containing naturally occurring iron is split into a doublet when the ^{57}Fe concentration is enriched to 90%. The doublet separation is found to be 6.64 ±0.09 G from which we obtain a hyperfine constant $|A'|=13.4\pm0.2$ (10^{-4} cm^{-1}).

The angular dependence of the lines observed when the magnetic field is rotated in the (001) plane is shown in Fig. 3. Only two lines are seen which coalesce into one line every 90°. The angle between the [110] direction and the nearest position for which a single line is observed is 30°. The maximum g factor is found to be 4.314 and the minimum 4.298. Since it is difficult to resolve the lines at X band, except at low temperatures (77°K), the remainder of the experiments were performed at K-band frequencies. In Fig. 4, the angular dependence of the g factor is plotted at room temperature. The axis of rotation is the $[\bar{1}10]$ direction. The upper shaded area encloses the maximum and minimum values of the data obtained for the g factor at X-band frequencies. It is seen that the curves occur in pairs and that one curve of the pair can be transformed into the other by reflection about the [110] direction. One set of curves has a peak every 90° with a valley midway between peaks. The other two curves in Fig. 4 exhibit only one peak and valley every 180°.

The angular dependence of the g factor for a rotation of the magnetic field in a plane perpendicular to the [001] direction is shown in Fig. 5. Only two lines are observed which coalesce into one line every 90°. A slight asymmetry is noted in the curves; the minima occur 90°±12° from every maximum. The shaded portion indicates the regions of maximum and minimum excursions of the g factor at X-band frequencies.

A search for other lines—possibly due to other fine-structure transitions or to excited-state doublets—was made, but no other line which could definitely be assigned to the Fe ion was found.

IV. DISCUSSION

A. Valence State and Site Occupancy

We have found that the Fe^{3+} ion occupies a W site. The experimental data excludes the possibility that the resonances are due to the Fe^{2+} ion for several reasons, the most convincing of which is the fact that all doublets (and quartets, etc.) which arise from an even number of electrons must have $g_\perp=0$,[13] in sharp contradiction to our result of a first order allowed transition ($\Delta M_s=\pm1$) having $g_\perp=4.3$.

Bleaney and Hayes[14] have found that an isotropic g factor of 4.3 arises due to a small quantity of Fe$^+$ ions in a site of cubic symmetry in a single crystal of NaF. CaWO$_4$ crystallizes in the scheelite structure having a unit cell-space group $C_{4h}^6(I4_1/a)$; hence the site symmetry is not higher than tetragonal. But the strongest argument against Fe$^+$ and in favor of Fe^{3+} is perhaps the extreme sharpness of the resonance, even at room temperature, indicating the presence of an S-state ion. Thus, we conclude that the resonance is due to Fe^{3+}.

The CaWO$_4$ structure is such that it contains two different sites for substitutional positive impurity ions, the eight-coordinated sites of Ca and the tetrahedral sites of the W ion. The Fe^{3+} ion is small, having an ionic radius of about 0.65 Å, compared to about 0.62 Å for W^{6+}, and about 1.00 Å for Ca^{2+}. The Ca site requires only one additional unit of negative charge per Fe ion, while the W site requires three units of positive charge, which makes the Ca site the more probable substitutional site from the charge-compensation point of view. It is most likely, however, that the Fe ion does not occupy an oxygen excess or deficient site, but rather, that charge compensation occurs remotely after the impurity is grown into the crystal. Thus, it appears that site occupancy cannot be determined in this case on the basis of factors such as charge compensation and ionic size alone, but will also depend upon the chemical bonding and the kinetics of crystal growth.

The strength of the crystalline electrostatic field for divalent and trivalent S-state ions (Mn^{2+},Gd^{3+}) in the Ca site is known.[15] The magnitude of the crystal-field splitting is greater for the trivalent ion but smaller than the Zeeman energy. The ratio of the axial-splitting parameter D(Gd)/D(Mn) is 6.7, and in both cases,

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[13] J. S. Griffith, Phys. Rev. **132**, 316 (1963). A forbidden transition ($\Delta M_s=\pm2$) due to an orbital singlet ground state of Fe^{2+} ($S=2$) is also excluded by resonance experiments which show that the signals vanish for $\mathbf{h}_{rf}\|\mathbf{H}_0$. Thus, the transition probability is proportional to the square of the matrix elements of S_x and the matrix elements of S_z are zero.

[14] B. Bleaney and W. Hayes, Proc. Phys. Soc. (London) **B70**, 626 (1957).

[15] C. F. Hempstead and K. D. Bowers, Phys. Rev. **118**, 131 (1960).

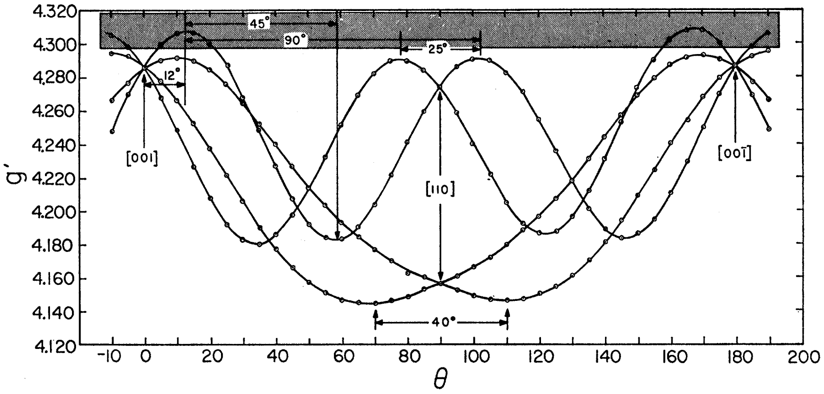

FIG. 4. Angular dependence of the g' factor observed at a frequency of 25.035 Gc/sec and room temperature. The axis of rotation is the [1̄10] direction, and θ is the angle measured in degrees from the [001] crystallographic direction.

$2S+1$ fine-structure transitions are observed. Similar results are found in Al_2O_3.[16]

Comparing $CaWO_4$ with other host materials, we conclude that the ratio of $D(\mathrm{Fe})/D(\mathrm{Mn})$ for the tetragonal tungstate lattice could not be much larger than 10. Thus, the axial-splitting parameter for the Fe^{3+} ion in the Ca site will not be greater than about 1400 (10^{-4}) cm^{-1} (less than the Zeeman energy), since $D(\mathrm{Mn})$ in $CaWO_4$ (Ca site) is ~ -140 (10^{-4}) cm^{-1}. If this is the case, a g factor of 2 and $2S+1$ fine-structure transitions would be observed in the epr spectrum. Since such a spectrum is absent, we conclude that there is no observable amount of Fe^{3+} in the Ca site.

B. Spin Hamiltonian Analysis

1. Fine Structure

Castner *et al.*[7] have shown, on the basis of their work with Fe^{3+} in glasses, that an isotropic g factor of 4.3 can arise from a crystal field of the form

$$\mathcal{H}_E = E(S_x^2 - S_y^2)\,,$$

which is much larger than the Zeeman energy. This type of crystal field can be shown, on the basis of a point-charge model, to arise from certain *special* severe distortions of oxygen tetrahedra. For example, Slichter[17] has proposed a mechanism which would give rise to $\mathcal{H}_E$ (if fourth-order terms can be neglected). In his model the Fe^{3+} ion, which is at the center of an oxygen tetrahedron, is distorted by twisting the oxygens above the basal plane clockwise, and the oxygens below the basal plane counterclockwise (using the symmetry axis as the screw axis). This distortion would tend to bring the oxygen atoms together in pairs 180° apart when viewed along the symmetry axis. It should be noted that a distortion which makes the upper and lower edges of the tetrahedron nonorthogonal must maintain the angle (θ_0) subtended at the Fe ion by the upper and lower pairs of oxygens equal to $\cos^{-1}(\frac{2}{3})$. If this is not the case, the spin Hamiltonian will have a D term. Since the WO_4 tetrahedron does not have $\theta=\theta_0$ we would expect a D term even with such a distortion.

An even more convincing argument against such an explanation in our case is provided by the low-temperature experiments. The isotropic line arising from $\mathcal{H}_E$ is due to an excited state. The observed "excited" doublet must be several degrees above the ground-state doublet, and, for this reason, a decrease in the Boltzmann factor should be observable at K-band frequencies where $h\nu/k = 1.2$°K when the temperature is reduced below

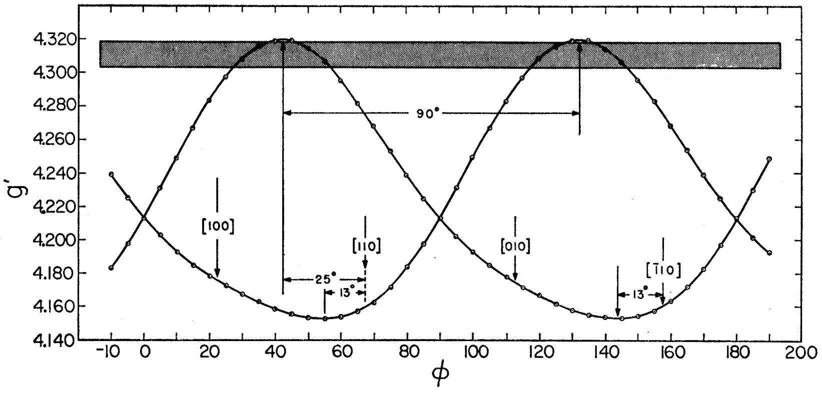

FIG. 5. Angular dependence of the g' factor for rotation of the applied field (H_0) in the (001) plane. Data obtained at room temperature using a frequency of 25.080 Gc/sec. φ is the angle in degrees measured arbitrarily from the field (H_0) at which the two lines coalesce.

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[16] W. Low and J. T. Suss, Phys. Rev. **119**, 132 (1960); L. S. Korneinko and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **33**, 805 (1957) [English transl.: Soviet Phys.—JETP **6**, 620 (1958)]; G. S. Bogle and H. F. Symmons, Proc. Phys. Soc. (London) **73**, 531 (1959).

[17] W. P. Slichter (private communication).

4.2°K. No decrease in the intensity of the spectrum was observed at temperatures as low as 1.5°K. We conclude, therefore, that the resonance line does not arise from $\mathcal{H}_E$.

It is easily shown that no other choice of only second-order terms leads to an isotropic g of the correct value. Therefore, we assume that fourth-order terms also are present. It is reasonable to investigate a spin Hamiltonian which has the same symmetry as the undistorted W site first (or Ca site), namely S_4 symmetry.[18] This choice considerably narrows the possibilities.

We are thus led to the spin Hamiltonian

$$\mathcal{H}=\mathcal{H}_c+g\beta\mathbf{H}\cdot\mathbf{S}+A\mathbf{I}\cdot\mathbf{S}. \tag{1}$$

Here $\mathcal{H}_c$ contains the crystal-field terms.

$$\mathcal{H}_c=D\{S_z^2-1/3S(S+1)\} \\ +(a/6)\{T_{40}+(5/14)^{1/2}(T_{40}+T_{4-4})\}+(F/9)T_{40}, \tag{2}$$

where T_{4m} are the components of a fourth-rank spherical-tensor operator:

$$T_{40}=1/20\{35S_z^4-[30S(S+1)-25]S_z^2 \\ +3S(S+1)(S^2+S-2)\}, \tag{3}$$

$$T_{4\pm4}=1/20(35/2)^{1/2}\{S_x\pm iS_y\}^4. \tag{4}$$

In defining our coefficients we have followed the convention of Bleaney and Trenam.[19] Thus, it can be shown that

$$\{T_{40}+(5/14)^{1/2}(T_{40}+T_{44})\} \\ =\{S_x^4+S_y^4+S_z^4-\tfrac{1}{5}S(S+1)(3S^2+3S-1)\}, \tag{5}$$

where the z axis is the [001] crystal axis and the x and y axes are not necessarily crystal axes. If the site symmetry were tetragonal rather than the lower symmetry S_4, the x and y would indeed be crystal axes. The D and F terms in Eq. (2) are second- and fourth-order axial crystal-field terms having tetragonal symmetry. Thus, $\mathcal{H}_c$ has tetragonal symmetry about the [001] crystal axis. We have not included a small term in $\mathcal{H}_c$, however, due to a distortion (which is responsible for the four resonance lines and the slight deviation from tetragonal symmetry evident in the angular-dependent data). If the site distortion preserved tetragonal symmetry, the resonance spectra observed for H_0, rotated in the (001) plane, would have a period of $\frac{1}{2}\pi$, in contrast with the experimental results shown in Fig. 5.

Since $g'\neq2$ and is very nearly independent of the experimental frequency, we must assume that $\mathcal{H}_c$ is much larger than the Zeeman and hyperfine terms. Therefore, we diagonalize $\mathcal{H}_c$ first. It follows easily from the tetragonal symmetry of $\mathcal{H}_c$ that the states $m_s=\pm\frac{1}{2}$ are eigenfunctions of $\mathcal{H}_c$ and the states $m_s=\pm\frac{5}{2}$ only mix with the states $m_s=\mp\frac{3}{2}$. Furthermore, time-inversion symmetry implies that $(\mathcal{H}_c)_{-m,-m'}=(-)^{m'-m}(\mathcal{H}_c)_{m,m'}{}^*$ so that in our case $\mathcal{H}_c$ factors into two identical matrices $\mathbf{h}$:

$$\mathcal{H}_c=\left|\begin{array}{c:c} \mathbf{h} & 0 \\ \hdashline 0 & \mathbf{h} \end{array}\right|. \tag{6}$$

It is found that the $\mathbf{h}$ matrix is given by

$$6\mathbf{h}=\begin{array}{|c|c|c|c|} \hline & |+\frac{5}{2}\rangle & |-\frac{3}{2}\rangle & |+\frac{1}{2}\rangle \\ \hline |+\frac{5}{2}\rangle & 20D+3a+2F & 3\sqrt{5}a & 0 \\ \hline |-\frac{3}{2}\rangle & 3\sqrt{5}a & -4D-9a-6F & 0 \\ \hline |+\frac{1}{2}\rangle & 0 & 0 & -16D+6a+4F \\ \hline \end{array}, \tag{7}$$

in which the labeling of the columns is appropriate to the left-half of $\mathcal{H}_c$ while the columns for the right half are obtained by changing the sign of $m_s(|m_s\rangle\rightarrow|-m_s\rangle)$. In a strong crystal field, the $|\pm\frac{1}{2}\rangle$ doublet has $g_{\parallel}=2$, $g_{\perp}=6$, and, for this reason, is not responsible for the epr spectrum. Hence, we have considered a state (unnormalized) of the form $\psi=|\frac{5}{2}\rangle+\alpha|-\frac{3}{2}\rangle$. If we require the Kramers doublet to have $g_{\parallel}=g_{\perp}$, only the following possibilities are found:

1. $\alpha=\pm\sqrt{5}$. These states have $g=10/3$, not in agreement with the experimental value of 4.3. (We note that $|\frac{5}{2}\rangle-\sqrt{5}|-\frac{3}{2}\rangle$ is a partner of the E'' representation of the octahedral double group 0* and hence must lead to an isotropic g value.)

2. $\alpha=\pm(5/9)^{1/2}$. In this case $g=30/7=4.28$, which agrees with our observed values. However, for $\psi^{\pm}=|\frac{5}{2}\rangle\pm\sqrt{5/9}|-\frac{3}{2}\rangle$ to be an eigenfunction of $\mathbf{h}$, the following relation must be satisfied:

$$6D+3a\mp a+2F=0. \tag{8}$$

This is an accidental relationship between the second- and fourth-order terms which does not follow from the symmetry, but which is required for isotropy.

If Eq. (8) is satisfied, the normalized eigenfunctions of $\mathbf{h}$ are

$$\psi_1^{\pm}=(9/14)^{1/2}|\tfrac{5}{2}\rangle\pm(5/14)^{1/2}|-\tfrac{3}{2}\rangle, \quad (g_{\parallel}=g_{\perp}=30/7), \\ \psi_2^{\pm}=(5/14)^{1/2}|\tfrac{5}{2}\rangle\mp(9/14)^{1/2}|-\tfrac{3}{2}\rangle, \\ (g_{\parallel}=2/7,\ g_{\perp}=30/7), \tag{9} \\ \psi_{1/2}=|\tfrac{1}{2}\rangle, \quad (g_{\parallel}=2,\ g_{\perp}=6),$$

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[18] No terms of odd order in the spin operators are present in the fine-structure Hamiltonian when we are dealing with an odd number of electrons. However, it is easily seen that any fine-structure spin Hamiltonian, containing only terms of even order, which is invariant under S_4, is also invariant under the larger tetragonal group. Hence, we generally refer to the tetragonal symmetry of the site, even though this is somewhat incorrect.

[19] B. Bleaney and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 1 (1954).

and the eigenvalues are

$$\lambda_1^{\pm}=-D\left\{-\frac{10}{3}+\frac{2K+3\pm5}{2K+3\mp1}\right\},$$

$$\lambda_2^{\pm}=-D\left\{\frac{2}{3}-\frac{6K+9\pm5}{2K+3\mp1}\right\},\tag{10}$$

$$\lambda_{1/2}^{\pm}=-D\left\{\frac{8}{3}+\frac{4K+6}{2K+3\mp1}\right\},$$

where $K=F/a$ is a measure of the fourth-order axial term in comparison with the cubic fourth-order terms. For a crystal field having tetrahedral (or cubic, or octahedral) symmetry, $K=0$. A point-charge calculation of the crystal field assuming equal charges at the positions of the four oxygen ions surrounding the tungsten site yields $K\cong1.21$. The eigenvalues, Eq. (10), have been plotted as a function of K in Figs. 6 and 7. The dashed line is a plot of the parameter $f\equiv F/9D$, which compares the fourth-order and second-order axial terms. Using Eq. (8)

$$f^{\pm}=(-2K/6K+9\mp3).\tag{11}$$

Referring to Fig. 6, it is seen that for $K>-5/7$, the value of λ_1^+ lies between λ_2^+ and $\lambda_{1/2}^+$, whereas the low-temperature experiments indicate that the isotropic resonance is due to the lowest doublet. In addition, for $-\frac{3}{2}<K<-5/7$ $|f^+|$ is much larger than would be expected on a physical basis, while for $K<-\frac{3}{2}$ $|f^+|$ deviates considerably from the value calculated from the point-charge model. On the other hand, it is seen in Fig. 7 that for $D<0$, λ_1^- is the lowest eigenvalue at a value of K, which agrees well with that calculated from the point-charge model and, in addition, $|f^-|$ is not unreasonably large. Hence, we have chosen the lower sign in Eqs. (8)–(11) to explain our results even though the higher energy doublets have not been observed and thus the correctness of this choice has not been verified directly. It is perhaps interesting to note, however, that by making this choice we arrive at the identical wave function used by Castner *et al.*[7] in interpreting their results on glasses.

A search for the other doublets was made, but they were not observed even though they would be populated at room temperature. It is possible to explain their absence as being due to strain broadening, for as we noted previously,[11] the crystal is severely strained, but it appears that a very special type of strain must be invoked. For example, the presence of a large random "E" term (of which ψ_1^- is an eigenfunction), but the absence of randomness in the D, a, or F terms will broaden all the doublets except the ground doublet. In this case, the broadening of the $|\frac{1}{2}\rangle\rightleftarrows|-\frac{1}{2}\rangle$ doublet is still expected to be small and the resonance line should probably be observed when the applied field is parallel to the Z axis. However, it should be noted that even small deviations of the quantity on the right of Eq. (8) from zero will cause substantial broadening of the ground doublet, since the g tensor is very sensitive to this relation.

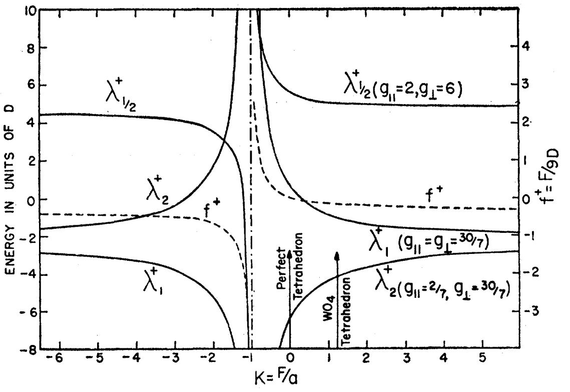

FIG. 6. The eigenvalues, $\lambda_{1/2}^+$, λ_1^+, λ_2^+, (left-hand ordinate) and the parameter f^+ (right-hand ordinate) are plotted as a function of the parameter K. The two arrows designate the values of K calculated from a point-charge model for a perfect tetrahedron and for the WO$_4$ tetrahedron.

2. *Hyperfine Structure*

The hyperfine interaction $A\mathbf{I}\cdot\mathbf{S}$ has been included in the Hamiltonian, Eq. (1), because it was measured in a crystal containing an enrichment of the ^{57}Fe $(I=\frac{1}{2})$ isotope. The results are shown in Fig. 2. It must be noted at this point that the spin Hamiltonian given by Eq. (1) describes the total spin-$\frac{5}{2}$ manifold which has $g=2$, whereas the spin Hamiltonian for the doublet which is observed experimentally is given by

$$\mathcal{H}_d=g'\beta\mathbf{H}\cdot\mathbf{S}'+A'\mathbf{I}\cdot\mathbf{S}',\tag{12}$$

where $S'=I=\frac{1}{2}$, $g'=4.3$, and the hyperfine interaction constants in Eqs. (12) and (1) are related by

$$A=gA'/g'.\tag{13}$$

Equation (13) is obtained by equating the hyperfine

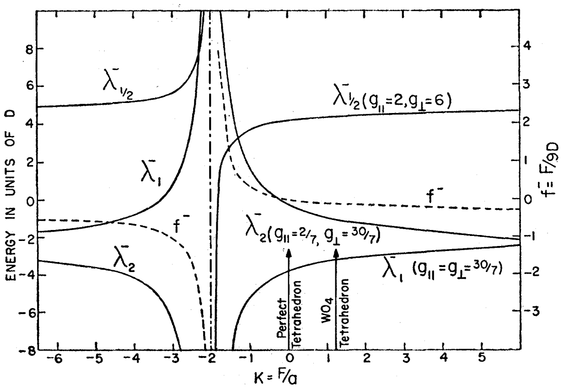

FIG. 7. The eigenvalues, $\lambda_{1/2}^-$, λ_1^-, λ_2^-, (left-hand ordinate) and the parameter f^- (right-hand ordinate) are plotted as a function of K.

splittings in Eq. (12) with those in Eq. (1). The effective field at the nucleus when the electrons are in the state $\psi_1^{\pm}$ is then

$$H_e(\psi_1^{\pm})=A'/4\mu=146\ \mathrm{kG}\,, \qquad (14)$$

and the effective field when the electrons are in the (unstationary) state $|\frac{5}{2}\rangle$ is

$$H_e(|\tfrac{5}{2}\rangle)=5A/4\mu=340\ \mathrm{kG}. \qquad (15)$$

This last value is the same as that found in FeF_2 but lower than the values found in other materials which range from 390–540 kG.[20] This is probably due to the strong covalent character of the W site.

V. CONCLUSION

The paramagnetic resonance spectrum of Fe^{3+} substituted in the W site has been observed in $CaWO_4$ single crystals. The spectrum consists of four narrow, equally intense resonance lines having an approximately isotropic g factor of 4.3. We have interpreted the spectrum assuming an electrostatic crystal field much larger than the Zeeman energy consistent with the symmetry of a Ca or W site. The g value follows from the form of the spin Hamiltonian if a specific and not unreasonable relationship is satisfied between the coefficients of the crystal-field terms. No additional resonances due to excited states were observed at room temperature, although we are not able to give an entirely satisfactory explanation for their absence.

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Phonon-Assisted Optical Absorption in an Electric Field*

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Expressions are derived for the optical absorption coefficient due to indirect interband transitions in a solid in a uniform electric field. The results are expressed in terms of Airy-function integrals which are evaluated numerically. As an example, the results are applied to indirect optical absorption in silicon.

1. INTRODUCTION

THE theory of direct optical transitions in solids in electric fields has been developed by Franz,[1] Keldysh,[2] Callaway,[3] and Tharmalingam,[4] and has been tested experimentally in several materials.[5]

Recently, experiments have been reported on phonon-assisted (indirect) optical absorption of silicon[6] and germanium[7] in high electric fields. In this paper, we develop the theory of the influence of electric fields on such indirect optical transitions in solids, following the general formalism of Tharmalingam.[4] We use the effective-mass approximation with tensor effective masses and assume weak Coulomb interaction between electrons and holes. The results are quite general, being applicable to insulators and semiconductors of large dielectric constant, wherever the effective-mass approximation is useful. In particular, we discuss the application of the theory to silicon.

2. THEORY

For a single valence-band maximum (say, at $\mathbf{k}=0$), a conduction-band minimum at $\mathbf{K}_0$, and one phonon

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