TABLE I. Magnitude and sign of a for Mn^{2+}, Fe^{3+}, and Gd^{3+} in various crystals.

Ion	Crystal	Cubic field symmetry	a in cm^{-1}	g	Reference
Mn^{2+}	$(NH_4)_2Zn(SO_4)\cdot 6H_2O$	Appr. octahedral	+0.0005	2.000 ±5	a
	$ZnSiF_6\cdot 6H_2O$	Appr. octahedral	+0.0007	2.000 ±5	a
	$Mg_3Bi_2(NO_3)_{12}\cdot 24H_2O$	Appr. octahedral	+0.0010	1.997 ±3	b
	MgO	Octahedral	+0.00186	2.0014±5	This paper
	ZnS	Tetrahedral	−0.00076	2.000	c
Fe^{3+}	$KAl(SeO_4)\cdot 12H_2O$	Appr. octahedral	−0.0127	2.003 ±3	d
	MgO	Octahedral	+0.0205	2.0037±7	This paper and e
Gd^{3+}	CaF_2	Fluorite	+0.0175	1.991 ±1	This paper

[a] B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).
[b] R. S. Trenam, Proc. Phys. Soc. (London) **A66**, 118 (1953).
[c] L. M. Matarrese and C. Kikuchi, Phys. Rev. **100**, 1243(A) (1955). (These authors have determined the sign of a in ZnS from hyperfine considerations.)
[d] B. Bleaney and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 1 (1954).
[e] W. Low, Bull. Am. Phys. Soc. Ser. II, **1**, 283 (1956). The cubic field splitting was erroneously reported there as $|3a|=548$. It should read 658 gauss.

structure of α ferric alum shows that each trivalent ion is surrounded by a nearly regular octahedron of six water molecules and the sign of a would be expected to be positive. Moreover, preliminary results[4] indicate that the sign of a in Gd^{3+} in the cubic field of CaF_2 (fluorite structure, D negative) is positive.

These differences in the sign of a for the various crystals, as well as the variations in the g factor—the g factor of Fe^{3+} being larger than g_e (that of the free electron) while the g factor of Mn^{2+} and Gd^{3+} is less—are at present puzzling. It is probable that a solution of this problem will depend on an accurate calculation of the various excited states (^4P, ^4D, ^4G, etc.). It is possible that departures from cubic symmetry like in the alums might change the order of some of the energy levels.

The author gratefully acknowledges friendly encouragement from Professor C. A. Hutchison, Jr.

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[4] W. Low (to be published).

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Paramagnetic Resonance Spectrum of Manganese in Cubic MgO and CaF_2†

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The paramagnetic resonance spectrum of manganese in cubic MgO and CaF_2 has been analyzed at wavelengths of one and three cm. The cubic field splitting in MgO is given by $3a=(+55.9\pm0.9)\times10^{-4}$ cm^{-1}. The twofold degenerate level lies lower than the fourfold degenerate level. The hyperfine structure constant is $A=(-81.0\pm0.2)\times10^{-4}$ cm^{-1}; $g=2.0014\pm0.0005$. The large cubic field splitting and the reduced hyperfine structure point towards considerable covalent bonding. Anomalous intensity ratios of the fine structure lines were observed. In CaF_2 the hyperfine structure constant has a value of $A=(95\pm1)\times10^{-4}$ cm^{-1}. The line width of 40 gauss even at very low concentration prevented any resolution of fine structure. The large line width is probably caused by the interaction of the magnetic electrons with the fluorine ions.

INTRODUCTION

THE paramagnetic resonance spectrum of manganese has a number of unusual and interesting features. Divalent manganese has five $3d$ electrons, a half-filled electron shell. The resultant angular momentum is therefore zero and the paramagnetism arises only from the electronic spins. Bethe[1] has shown from group theoretical reasoning that a cubic field removes the sixfold degeneracy of the $^6S_{5/2}$ ground state and splits it into a twofold and fourfold degenerate level. The mechanism responsible for this splitting is imperfectly understood. Van Vleck and Penney[2] have suggested that the splitting arises from the action of both the cubic field and spin-orbit interaction; each mechanism separately is unable to give any splitting to any order of approximation. The splitting of the S state can be viewed as being due to admixtures from higher states of the $3d^5$ configuration to the ground state. These higher excited states are in turn split by

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† This work was supported by the U. S. Atomic Energy Commission.

* On leave of absence from the Hebrew University, Jerusalem, Israel.

[1] H. Bethe, Ann. Physik **3**, 133 (1929).

[2] J. H. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1934).

the cubic field and spin-orbit interaction. The splitting is expected to be small as one has to go to a fifth-order perturbation before any splitting can be obtained.

Bleaney and Ingram[3] have investigated in detail the paramagnetic resonance spectrum of manganese in Tutton salts and in manganese fluosilicate. They show that the ^6S state is split mainly by the small deviations from cubic symmetry in these crystals. The levels are split into three doublets of relative separation 0.061 and 0.109 cm^{-1}. The splitting caused by the predominantly cubic field is small and approximately 0.002–0.003 cm^{-1}. Abragram and Pryce[4] have suggested that another mechanism of second order might cause this large splitting. The dipole-dipole interaction of the spin-magnetic moments of the various $3d$ electrons depends on the orientation. If the electron distribution deviates from spherical or cubic symmetry, the average dipole-dipole energy will differ for the various states of M.

It is quite obvious that in a perfect cubic field this mechanism would not be operative. The only source for the observed splitting would be that suggested by Van Vleck and Penney. It was of interest to study this splitting in good cubic-field single crystals, and to determine as well whether the twofold or fourfold degenerate level has lower energy.

The spectrum of Mn^{2+} is complicated by the fact that there is a large hyperfine structure caused by the nuclear spin of 5/2 of Mn^{55}. Indeed it turned out that in MgO:Mn the hyperfine structure splitting was larger than the splitting caused by the cubic field. In an S state hardly any hyperfine structure would normally be expected except for a very small (1×10^{-4} cm^{-1}) structure in crystals of very low symmetry. Abragram[5] has proposed that configurational interaction mixes into the ground state electron states having unpaired s electrons. It was, therefore, also of interest to measure the hyperfine structure in cubic fields.

In this paper the experimental results of manganese in cubic fields will be presented. In a later paper we shall present results of ferric ion in a cubic field. The results in this paper are notable in that the narrow line width enabled one to resolve the fine and hyperfine structure completely for various orientation of the crystalline field with respect to the magnetic field. The considerably larger fine structure splitting and the reduced hyperfine structure in MgO are explained as indication of covalent bonding. This will be contrasted with the results on CaF_2.

EXPERIMENTAL METHOD

The equipment was the standard apparatus for paramagnetic resonance absorption detection at the University of Chicago and only a brief description will be given here.

Measurements were made at wavelengths of 1.2 and 3.3 cm. At 1 cm, measurements could be made down to liquid helium temperatures. A TE_{011} circular reflection cavity was coaxially coupled to one branch of a magic T. The output was detected with 1N26 silicon crystal, amplified with a narrow-band amplifier and finally detected in a phase-sensitive detector and recorded as the first derivative of the absorption line. The klystron power supply was well stabilized and the frequency of the klystron stabilized on the absorption cavity. Magnetic field measurements were made with a rotating coil magnetometer which was periodically calibrated by proton resonance. Variations in the absolute measurements of the magnetic field in the region of 8000 gauss or higher were found to be of the order of ±5 gauss. Separations between adjacent lines of a few tens of gauss could be measured with an accuracy of about one gauss.

The three-cm apparatus is identical with that used by Hutchison and Noble[6] except for some minor adjustments. A rectangular full-wavelength cavity was in one arm of the magic T. The klystron frequency was stabilized by means of a modified Pound stabilizer. The output was detected by means of a Sperry bolometer. The second harmonic of the modulation frequency of the magnetic field was amplified in a very narrow band amplifier, detected by a phase detector and recorder. Detection of the second harmonic has some advantages. (1) It discriminates against slow changes in the slope of a wide line. One can, therefore, detect conveniently sharp lines superimposed on relatively wide absorption lines. (2) The line shape closely resembles that of the second derivative of the absorption line. Considerable increase in resolution is obtained. The disadvantage is that if a number of closely adjacent lines are present the superposition of these gives a somewhat complicated line shape.

The crystals were MgO single crystals obtained from Dr. G. R. Finlay, Norton Company. The concentration of Mn varied in different crystals from 0.001% to 0.1% by weight. Those with higher concentration showed a slightly pinkish tinge. The crystals contained various other impurities, in particular 0.005%–0.05% of Al and a little Si as well as Ca.

The calcium fluoride crystals were grown from the melt with varying concentrations of Mn of about 0.04%–0.5%. They were checked with x-rays to determine whether they are single crystals. It was found later that the introduction of a small amount of gadolinium (0.005%) could be used to determine whether one or more crystals were present. The fine structure spectrum of gadolinium proved to be a very convenient way to line up the crystal.

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[3] B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).

[4] A. Abragram and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 136 (1951).

[5] A. Abragram, Phys. Rev. **79**, 534 (1950).

[6] G. A. Noble, thesis, University of Chicago, 1955 (unpublished).

THEORY

The energy levels of the ${}^6S_{5/2}$ state have been calculated by Debye[7] and more fully by Kronig and Bouwkamp[8] for the case of cubic field potentials of the form $V=\sum_i C(x_i^4+y_i^4+z_i^4)$ where $C=(35/4)e/b^5$ in the case of an octahedral complex, and $C=-(70/9)e/b^5$ in the case of an 8-coordinated complex, where b is the distance between the paramagnetic ion and the diamagnetic neighbors.

The matrix elements involving the cubic potential as well as those of the spin-orbit coupling have been given by Penney and Schlapp.[9] The resultant 6×6 matrix can be diagonalized to give two levels, one twofold degenerate and the other fourfold degenerate, separated by a distance usually denoted by $3a$. If an external magnetic field is present the matrix does not factor in general for all directions of the crystalline axes with respect to the magnetic field. For large magnetic field $\beta H \gg a$, a power series expansion in $a/\beta H$ gives the values for the energy levels as[8]

$$\begin{aligned}
W_{\pm 1/2} &= \beta H + pa \pm (5/6)\phi(7-25\phi)a^2/\beta H_0 - (5/144)\phi(196-1635\phi+3125\phi^2)a^3/(\beta H_0)^2+\cdots,\\
W_{\pm 3/2} &= \pm 3\beta H - (3/2)pa \pm [(5/32)+(5/32)\phi(22-75\phi)]a^2/\beta H_0\\
&\quad +[(5/128)+(15/128)\phi(79-615\phi+1125\phi^2)]a^3/(\beta H_0)^2+\cdots,\\
W_{\pm 5/2} &= \pm 5\beta H + \tfrac{1}{2}pa \pm [(5/32)+(5/96)\phi(50-113\phi)]a^2/\beta H_0\\
&\quad +[-(5/128)-(25/1152)\phi(113-705\phi+1075\phi^2)]a^3/(\beta H_0)^2+\cdots. \qquad (1)
\end{aligned}$$

The transitions are given by (strong transitions $\Delta M=\pm 1$):

$$\begin{aligned}
M=\pm 1/2 \rightarrow -1/2:&\ g\beta H = g\beta H_0 + (a^2/g\beta H_0)[(10/3)\phi(7-25\phi)]+[a^4/(g\beta H_0)^3]\{\cdots\}+\cdots,\\
M=\pm 3/2 \rightarrow \pm 1/2:&\ g\beta H = g\beta H_0 \pm (5/2)pa - (a^2/g\beta H_0[(5/48)(3+178\phi-625\phi^2]+[a^4/(g\beta H_0)^3]\{\cdots\}+\cdots,\\
M=\pm 5/2 \rightarrow \pm 3/2:&\ g\beta H = g\beta H_0 \mp 2pa + (a^2/g\beta H_0)[(5/3)\phi(1-7\phi)]+[a^4/g\beta H_0)^3]\{\cdots\}+\cdots. \qquad (2)
\end{aligned}$$

The parameter $p=1-5\phi$ and $\phi=l^2m^2+m^2n^2+n^2l^2$, where l, m, n are the direction cosines of the magnetic field referred to the cubic axes of the crystal.

The series converges rapidly for the fields used at three or one cm (3000 or 8000 gauss), since $a^2/g\beta H$ is 0.13 and 0.05 gauss, respectively. The higher order terms in $a^4/(g\beta H)^3$ can be neglected. The energy level scheme is shown in Fig. 1 assuming the observed value of 18.6×10^{-4} cm^{-1} for a (a being positive).

The intensity of the lines is proportional to $S(S+1)-M(M-1)$. The expected spectrum, then, from Eq. (2) and Fig. 1 is a central line at approximately $g=2$ with relative intensity 9 flanked on either side by two lines at separations $(5/2)pa$ and $2pa$ and with relative intensities 8 and 5, respectively.

So far we have dealt only with electronic transitions. The total Hamiltonian including hyperfine structure interaction is given by

$$\begin{aligned}
\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S}+\tfrac{1}{6}a[S_x^4+S_y^4+S_z^4-\tfrac{1}{5}S(S+1)(3S^2-1)]\\
+A\mathbf{S}\cdot\mathbf{I}-\gamma\beta_N\mathbf{H}\cdot\mathbf{I}, \qquad (3)
\end{aligned}$$

where the first two terms give the fine structure energy levels of Eq. (1). The term $A\mathbf{I}\cdot\mathbf{S}$ represents the hyperfine structure interaction, and the term $\gamma\beta_N\mathbf{H}\cdot\mathbf{I}$ the interaction of the external magnetic field with the nuclear moment. The hyperfine structure constant A is written as

$$A=2\gamma\beta\beta_N\langle 1/r^3\rangle_{\text{Av}}k,$$

where γ = gyromagnetic ratio, β = Bohr magneton, β_N = the nuclear magneton, $\langle 1/r^3\rangle_{\text{Av}}$ is averaged over the $3d$ wave function, k is a numerical coefficient of the term $\mathbf{S}\cdot\mathbf{I}$ which occurs quite generally in paramagnetic resonance and which will be discussed later.

In the case of strong fields one has to add to Eq. (1) the following terms representing the contribution of the hyperfine structure to the energy levels:

$$\begin{aligned}
AMm+(A^2/2g\beta H_0)\{[M(I(I+1)-m^2]\\
-m[S(S+1)-M^2]\}+\text{terms in } A^3/(2g\beta H_0)^3. \qquad (4)
\end{aligned}$$

To the formulas giving the various electronic transi-

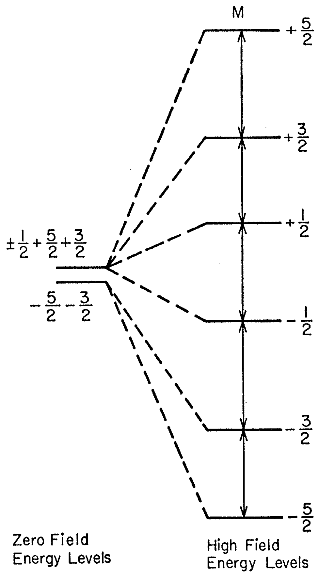

FIG. 1. Energy levels of the ${}^6S_{5/2}$ state in a cubic field with zero-field splitting $3a=+59$ gauss.

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[8] E. de L. Kronig and C. J. Bouwkamp, Physica **6**, 290 (1939).

[9] W. G. Penney and R. Schlapp, Phys. Rev. **41**, 194 (1932).

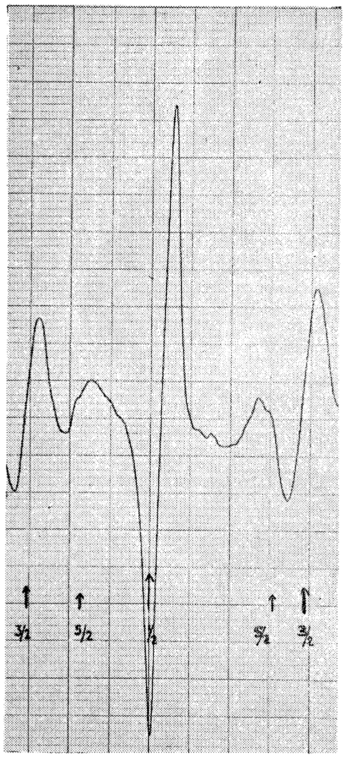

FIG. 2. Typical spectrum of the pentad $m=-5/2$. The transitions from left to right are $M=3/2\rightarrow 1/2$, $M=-5/2\rightarrow -3/2$, $M=1/2\rightarrow -1/2$, $M=5/2\rightarrow 3/2$, and $M=-3/2\rightarrow -1/2$.

tions, Eq. (2), one has to add

$$-Am-(A^2/2g\beta H_0)\{I(I+1)-m^2+m(2M-1)\}\\ -[A^3/4(g\beta H_0)^2]+\text{higher order terms,} \qquad (5)$$

where M and m are the magnetic quantum numbers of the electron and nuclear spin, respectively.

For low or intermediate fields the energy levels are relatively complicated, as $g\beta H_0$ is in these two cases of the order of $3a$ and A, respectively, in the case of manganese. An experiment at intermediate fields in MgO:Mn is contemplated.

The ground state of manganese is S and no hyperfine structure would be expected. Configuration interaction may result in admixture of states of the type $3s3d^54s$ to the $3d^5$ ground state.[4,5] Unpaired s electrons are very potent in giving a large contribution to the hyperfine structure splitting because of the Fermi term[10] $2\gamma\beta\beta_N[\frac{1}{3}(8\pi)\psi^2(0)]\mathbf{S}\cdot\mathbf{I}$ and only a small admixture of such states could account for the hyperfine structure. In a more detailed calculation Abragram *et al.*[11] find, using a modified Hartree-Fock self-consistent wave function of the cuprous ion, that the admixture is of the right sign but about ten times smaller than the experimental value. They conclude that an explanation of the s-electron effect in paramagnetic resonance spectra must still be regarded as an open question. It may be worthwhile to recalculate the admixture using the recent Hartree[12,13] wave function for Mn^{2+}.

EXPERIMENTAL RESULTS

A. Manganese in Magnesium Oxide

1. *Observed Spectrum*

The spectrum consists of 6 groups of 5 lines. The hyperfine structure constant A is, therefore, larger than the ground state splitting $3a$. For any orientation of the cubic axes the $M=\pm 3/2\rightarrow \pm 1/2$ transition was at approximate distance of $(5/2)pa$ and the $M=\pm 5/2\rightarrow \pm 3/2$ transition at $2pa$, i.e., in the approximate ratio of 5:4 from the central $1/2\rightarrow -1/2$ transition. A typical group ($m=-5/2$) is shown in Fig. 2. To determine the parameters a and A more carefully, the spectrum was examined in a number of planes. In particular, the angular variation of the spectrum when the crystal was mounted along one of the cleavage planes (001) was investigated with care. When one works at 1 cm, the second-order terms in $a^2/g\beta H_0$ are minimized but still have to be corrected for.

The $M=\pm 3/2\rightarrow \pm 1/2$ transitions can be written from Eqs. (2) and (5) as

$$M=+3/2\rightarrow -1/2:\ g\beta H=g\beta H_0-Am-(A^2/2g\beta H_0)\\ \times(35-m^2+2m)+\epsilon_2+(5/2)pa,$$

$$M=-3/2\rightarrow -1/2:\ g\beta H=g\beta H_0-Am-(A^2/2g\beta H_0)\\ \times(35-m^2-2m)+\epsilon_2-(5/2)pa, \qquad (6)$$

where ϵ_2 are terms in $a^2/g\beta H_0$. The separation between these two transitions is given by

$$\Delta(g\beta H)=5pa-(A^2/g\beta H_0)(2m). \qquad (6a)$$

Measuring this separation for $m=+5/2$ and for

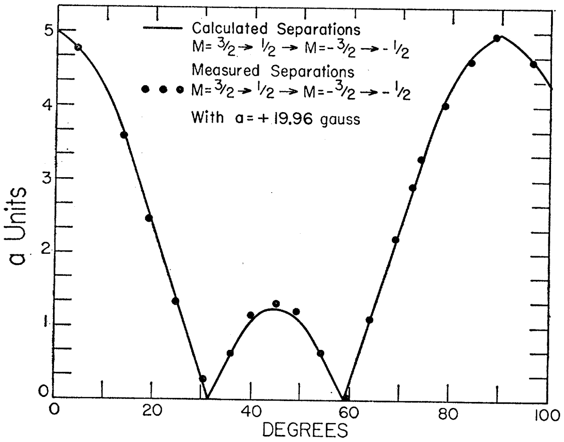

FIG. 3. Average separation $\langle\Delta(g\beta H)\rangle_{Av}$ for the M, m transitions $(3/2, 5/2)\rightarrow(-3/2, 5/2)$ and $(3/2, -5/2)\rightarrow(-3/2, -5/2)$. The theoretical line is drawn for $5pa$. The measured points fitted this line with $a=19.96$ gauss.

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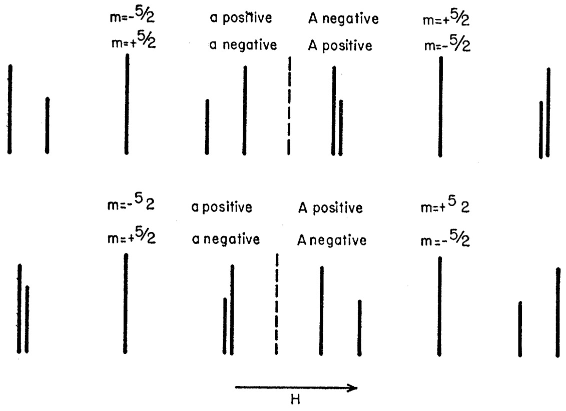

FIG. 4. Spectrum of the fine structure for $m=5/2$ and $m=-5/2$. The upper diagram shows the spectrum when A and a have opposite signs. The dotted line indicates the omission from the diagram of the pentads $m=\pm3/2$ and $m=\pm1/2$. The lower diagram shows the spectrum when A and a have the same sign. The spectrum is drawn to scale for $5A^2/g\beta H_0=4.55$ gauss. Note that the $M=\pm3/2\rightarrow\pm1/2$ and $M=\pm5/2\rightarrow\pm3/2$ transitions fall nearly together at high fields when a/A is negative and at low fields when a/A is positive. The first case is the one which is found experimentally.

$m=-5/2$ (or any $\pm m$), we get

$$\langle\Delta(g\beta H)\rangle_{\text{Av}}=5pa. \tag{7}$$

It is seen that this average separation is independent of the hyperfine structure constant and second-order effects in $a^2/g\beta H_0$. In practice it was found that the $m=\pm5/2$ transitions could be measured more carefully than the other $\pm m$ transitions because these transitions only overlap in part with the adjacent transitions.

The angular variation in the 100 plane is given explicitly by

$$p=\tfrac{1}{8}(35\cos^4\theta-30\cos^2\theta+3+5\sin^4\theta\cos4\psi), \tag{8}$$

and for completeness' sake only the $3/2-1/2$ transition will be given here as

$$\begin{aligned}g\beta H={}&g\beta H_0\pm\frac{5}{16}a(35\cos^4\theta-30\cos^2\theta+3+5\sin^4\theta\cos4\psi)\\&-\frac{a^2}{g\beta H_0}\left\{\frac{5}{48}\left[3+178\left(\frac{1}{8}-\frac{1}{40}(35\cos^4\theta\right.\right.\right.\\&\left.-30\cos^2\theta+5\sin^4\theta\cos4\psi)\right)\\&-625\left(\frac{1}{8}-\frac{1}{40}(35\cos^4\theta-30\cos^2\theta\right.\\&\left.\left.\left.+5\sin^4\theta\cos4\psi)\right)^2\right]\right\}-Am-\frac{A^2}{2g\beta H_0}\\&\times\{I(I+1)-m^2+m(2M-1)\}-\frac{A^3}{4(g\beta H_0)^2},\end{aligned} \tag{9}$$

where θ is the angle which the [001] axis makes with the external field and ψ the meridian plane. For $\psi=0$, i.e., if the crystal is mounted so that one of the crystal axes is perpendicular to the external field, the spectrum is repeated for every 90° and is symmetrical about $\theta=45°$. The fine structure collapses if higher order terms and hyperfine structure terms are neglected when $35\cos^4\theta-30\cos^2\theta+3+5\sin^4\theta=0$ or approximately $\theta=31°43'$ and $58°17'$. Between these two angles p becomes negative and the order of the level reverses itself. At 45° the spectrum has a second maximum with $p=-0.25$.

Figure 3 shows the experimental spectrum of $\langle\bar{\Delta}(g\beta H)\rangle$ for $M=\pm3/2\rightarrow\pm1/2$ and $m=\pm5/2$. Since we measure the average separation of similar M transitions, we have plotted Δ as always positive. It is seen that the agreement is fairly satisfactory if one chooses $a=+19.96\pm0.3$ gauss. The main uncertainty is due to small but persistent deviations at angles between 20–70°. It is possible that these deviations are shifts in the positions of these line shapes due to the superposition of the $5/2-3/2$ transitions which at these angles falls very close to the $3/2-1/2$ transitions. These deviations have been taken into consideration in estimating the error in a.

The hyperfine structure constant is best measured for $M=1/2\rightarrow-1/2$ transitions because the line width is very narrow (see discussion of line width). The separation of $m=5/2\rightarrow m=-5/2$ is $5A-5A^3/4(g\beta H_0)^2$. Measurement at 1.2 cm yield a value of 86.9±0.5 gauss and at 3 cm a value of 86.7±0.2 gauss.

2. *Measurement of the Sign of a and A*

Inspection of Eq. (2) shows that for *positive* p the transition $M=3/2\rightarrow1/2$ falls at a higher field than the central $1/2\rightarrow-1/2$ transition if a is positive and conversely if a is negative. From Eq. (5) it is seen that for negative A, transitions with m positive fall at higher magnetic fields than with m negative. Equation (6a) shows that the separation $\Delta(g\beta H_0)$ between $M=3/2\rightarrow1/2$ to $M=-3/2\rightarrow-1/2$ is larger at low fields than the same separation at high field by $(A^2/2g\beta H_0)(4m)$ if A and a have opposite sign. If A and a have the same sign, then this separation is smaller at low fields. The opposite holds true for the $M=+5/2\rightarrow3/2$ to $M=-5/2\rightarrow-3/2$ separation. The various possibilities are shown in Fig. 4 for the $m=\pm5/2$. Experimentally it is found that the low-field separation $\Delta(g\beta H_0)$ for $|m|=5/2$ is larger by about 4.5±0.1 gauss $\sim5A^2/g\beta H_0$ than the high-field separation. Moreover, at high field the $\pm5/2\rightarrow\pm3/2$ and $\pm3/2\rightarrow\pm1/2$ transitions nearly coincide. A and a have, therefore, opposite signs.

From the paramagnetic resonance spectrum alone only the relative sign of A and a can be found. In order to determine the absolute sign an additional experiment is necessary. There are a number of possibilities.

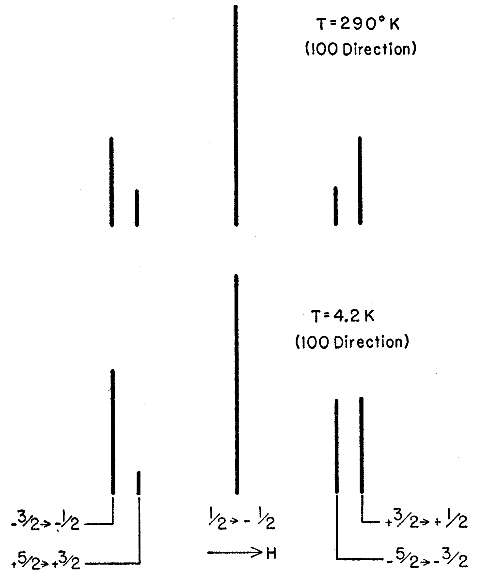

FIG. 5. Ratio of the observed relative intensities of the fine structure lines for $m=-5/2$ at $T=290$°K and 4.2°K. The two lines with increase intensities in the lower figure are the $M=-3/2\rightarrow-1/2$ and $M=-5/2\rightarrow-3/2$ transitions.

(*a*) *Measurement of the susceptibility or specific heat at very low temperatures.*—At extremely low temperatures the twofold- and fourfold-degenerate levels are not equally populated. The entropy at absolute zero will be either $R\ln 4$ or $R\ln 2$ according as the fourfold- or twofold-degenerate level has lower energy. The partition function is given by $Z=2(2+e^{-3a/kT})$ and will differ according as a is positive or negative. This leads to different susceptibilities or magnetic specific heats at the low-temperature end. This will, however, be complicated in the case of manganese by the hyperfine structure which will split the energy levels further.

At temperatures low compared with $3a/k$, this leads to a contribution to the specific heat at zero field:

$$\begin{aligned} CT^2/R &= 2a^2+\tfrac{1}{3}A^2[S(S+1)(I+1)] \\ &= 2a^2+(1225/48)A^2 \\ &= 2.55\times10^{-4}\ \mathrm{deg}^2. \end{aligned} \tag{10}$$

(*b*) *Anisotropy in susceptibility.*—If the crystalline symmetry is less than cubic, a measurement of the anisotropy of the susceptibility can determine the sign of one of the parameters. In the case of axial symmetry Bleaney and Ingram[3] give the following formulas:

$$\begin{aligned} \chi_{\parallel} &= Ng_{\parallel}^2[S(S+1)/3kT][1-(32/15)D/kT], \\ \chi_{\perp} &= Ng_{\perp}^2[S(S+1)/3kT][1+(16/3)D/kT]. \end{aligned} \tag{11}$$

If $g_{\parallel}=g_{\perp}$, the direction of the anisotropy gives the sign of D, the initial splitting in an axial field. This method cannot be used for a cubic field as there is no anisotropy in the susceptibility.

(*c*) *Measurement of the relative intensity of the absorption lines at low temperatures.*—Since the relative populations of the various levels differ at low temperatures, the intensities of the absorption lines will be different for the various electronic transitions. The $M=-5/2$ and $M=-3/2$ levels will be more populated at low temperatures and high magnetic fields (see Fig. 1). Absorption lines originating from these levels will be more intense than these from $M=+5/2$ or $M=+3/2$. The experimental results are shown in Fig. 5. The lower curve gives the intensity of the lines at 4.2°K as measured from the oscilloscope. As discussed before (for positive p), the transition $M=3/2\rightarrow1/2$ will fall at higher fields, and that of $M=5/2\rightarrow3/2$ at lower field than the central $M=1/2-1/2$ transition, if a is positive. Figure 5 shows this to be so, and, therefore, a is positive and A is negative. The double degenerate level has lower energy (as shown in Fig. 1).

3. *Determination of the g Factor*

The g factor was measured both at 1 and 3 cm. In both cases the six hyperfine structure lines of the electronic transition $M=1/2\rightarrow-1/2$ were measured near $\phi=0$ to avoid the necessity of making second-order corrections. The magnetic field near $g=2$ was calibrated with the organic free radical α,α-diphenylpicryl hydrazyl (2.0037). Allowing a liberal error of 4 gauss between the extremes of the hyperfine lines, we find $g=2.0016\pm0.001$ at 1 cm (rotating coil measurement). Proton resonance measurement at 3 cm yield a value of 2.0014 ± 0.0005. The results are summarized in Table I.

4. *Line Width and Intensity*

The theoretical ratios of the intensity for the pentad in Fig. 2 are 8:5:9:5:8. The measured intensities are approximately (at $T=290$°K) 3.6(±0.4):1.5(±0.3):9:1.5(±0.3):3.6(±0.4). This ratio varied only slightly with the percentage of manganese in the crystal. There is some indication that at lower temperatures the relative intensities of the two satellites are slightly but not significantly higher. The lines were very narrow with the $M=1/2\rightarrow-1/2$ transition about $1\frac{1}{2}$ gauss or less, the $M=\pm3/2\rightarrow\pm1/2$ transitions wider, and the $M=\pm5/2\rightarrow\pm3/2$ transitions wider still with approximately 3 gauss between points of maximum slope.[14] It

TABLE I. Constants of manganese in MgO and CaF$_2$ in units of 10^{-4} cm^{-1}.

Crystal	Wave-length	Tempera-ture	Hyperfine structure constant	a	g
MgO	1.2 cm	290°K	-81.2 ± 0.5	18.65 ± 0.3	2.0016 ± 0.001
		70°K	-81.3 ± 0.5		2.0015 ± 0.001
	3.2 cm	290°K	-81.0 ± 0.2		2.0014 ± 0.0005
CaF$_2$	1.2 cm	290°K	95.4 ± 1		2.0013 ± 0.001
		4.2°K	94.5 ± 1		2.0012 ± 0.001

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[14] In the preliminary note [W. Low, Phys. Rev. **101**, 1827 (1956)] a typographical error should be corrected. The line width of Mn^{2+} and V^{2+} is ~2 gauss and not 4 gauss as stated. The statement that deviations from cubic symmetry were found is wrong.

was found that more accurate measurement of intensity could be obtained when the spectrum was observed on the oscilloscope. A typical picture is shown in Fig. 6. Measurements with the lock-in detector depended somewhat on the depth of the modulation, as the line width differed for the various transitions. It was difficult to measure the integrated intensity, but it is quite obvious from Figs. 2 and 6 that it differs considerably from the theoretical estimate. Wertz *et al.*[15] find that the fourth hyperfine line counting from the low-field side ($m=+1/2$) shows unusually large variations of intensity relative to the other five. We have not detected such variations in any of our good crystals.

The difference between the theoretical and experimental line intensities will be discussed more fully in a forthcoming paper[16] on $MgO:Fe^{3+}$ in which these variations are even more pronounced. These differences are probably caused by the defects in the crystal structure.

B. Manganese in CaF_2

The spectrum consists of 6 broad lines with $A=101.1\pm1$ gauss and $g=2.0013\pm0.001$ at $T=4.2°K$, and $A=102\pm1$ gauss and $g=2.0012\pm0.001$ at $T=290°K$. The line width did not change appreciably at low temperatures or at low concentrations, and no fine structure could be resolved. The minimum line width of the 6 hyperfine lines was 40±4 gauss between points of maximum slope. No significant changes were observed in the line width for various angular variations of the magnetic field with respect to the crystal axes. It may be significant that the spectrum of gadolinium in one of the crystals showed a minimum line width of about 15 gauss for the $M=1/2\rightarrow-1/2$ transition.

DISCUSSION

The measurements reported in this paper carry a number of interesting implications with it. The ground state splitting is shown to correspond to that of a cubic field, leaving the twofold-degenerate level lowest. This is in agreement with the results by Bleaney and Ingram[3] as well as those by Trenam[17] on magnesium bismuth nitrate. However, a comparison with their values of a as well as those recently found by Matarrese and Kikuchi[18] on cubic ZnS ($a\sim7.7\times10^{-4}$ cm^{-1}) shows that the cubic field splitting in MgO is larger by about a factor of two. This points to a very strong crystalline field interaction. Possibly this might be caused by the relatively large ionic radius of Mn^{2+} of about 0.90 A,[19] which would make it a misfit in the crystal of MgO (the radius of Mg^{2+} is about 0.78 A).

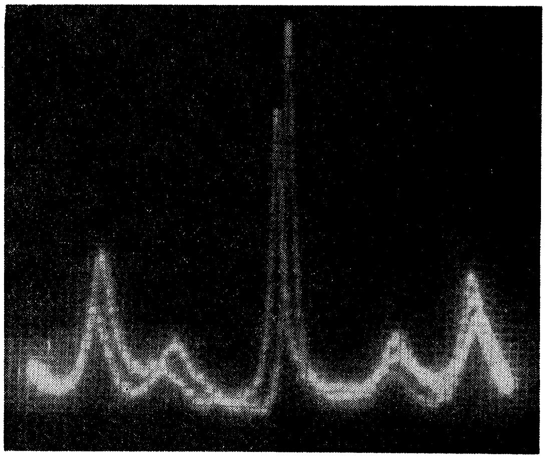

FIG. 6. Absorption spectrum of MgO:Mn at a temperature 70°K. The central line is much narrower than the other four fine structure lines.

Owen[20] and Stevens[21] have discussed the influence of covalent bonding on the paramagnetic resonance spectra of the hydrated iron group. In the case of manganese which has a $(d\epsilon)^3(d\gamma)^2$ configuration these considerations show that the $d\epsilon$ electrons will move into the orbits of the adjacent oxygen ions ($2p_\pi$ orbits) and form π bonding and the $d\gamma$ electrons will interact with the $2p_\sigma$ and $2s$ electrons of the oxygen ions and form σ bonding. Independent evidence for the existence of σ bonding from the paramagnetic and optical absorption spectrum of Ni^{2+} in MgO as well as the existence of π bonding from the paramagnetic spectrum of Cr^{3+}, V^{2+}, and Fe^{2+} will be presented in a separate paper.[22] The effect of the π and σ bonding is very similar to an increase in the crystal field strength, and increases the cubic field splitting.

Evidence for covalent bonding in MgO:Mn is also furnished from the hyperfine structure constant. Our results show that in the strongly ionic crystal CaF_2:Mn A is $\sim95\times10^{-4}$ cm^{-1} whereas in MgO A is about 81 $\times10^{-4}$ cm^{-1}, a reduction of about 15%. Van Wieringen[23] has presented considerable evidence of the existence of a correlation between the reduction of the hyperfine structure and the amount of covalent bonding. According to him one may infer that in MgO:Mn there is about 20% covalent bonding.

The ratio of the hyperfine structure caused by configurational interaction is approximately constant for similar environments. In MgO the ratio of $A_{Mn^{2+}}/A_{V^{2+}}=1.09\pm0.01$ whereas in Tutton salts this ratio is about 1.06 ± 0.03.[24] In MgO the ratio of $A_{Cr^{3+}}/A_{V^{2+}}$ is 4.67

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[24] The data are taken from K. D. Bowers and J. Owen, Repts. Progr. Phys. **18**, 304 (1955).

±0.1[25] and for $(NH_4)_2Zn(SO_4)_2:V^{2+}$ and $KAl(SeO_4)_2 \cdot 12D_2O:Cr^{3+}$ this ratio is 4.76±0.3.[24] In V^{2+} and in Cr^{3+}, as in Mn^{2+}, the source of the hyperfine structure is presumably unpaired s-electron states mixed in by configurational interaction. This seems to point to a surprising constancy of $k\langle 1/r^3\rangle_{\mathrm{Av}}$ in all these salts for similar environments, as well as to similar causes of reduction of the hyperfine structure constants. As V^{2+} and Cr^{3+} have only $(d\epsilon)^3$ electrons, the reduction of the hyperfine structure constant in these ions, and, therefore in Mn^{2+} as well, must be primarily caused by π bonding.[25]

The spectrum of $CaF_2:Mn$ showed a very large line width which probably prevented the observation of any fine structure. The large line width may have its origin in the interaction of the manganese ion with the surrounding fluorine ions. Tinkham[26,27] found that in $ZnF_2:Mn$ each hyperfine line is split into 15 "super-hyperfine lines." He explains this structure as being caused by the interaction of the magnetic electrons with the surrounding six fluorine atoms. The manganese ion in CaF_2 (fluorite structure) is surrounded by eight fluorine atoms. If such a mechanism should be assumed, each hyperfine line for each electronic transition should be split into 9 components with relative intensities 1:8:11:40:80:100:80:40:11:8:1. The total number of lines would be 45 instead of 5 and spread over $\pm(5/2)pa \pm m_F A_F$, where $m_F = 4, 3, \cdots, -4$ and A_F is the hyperfine structure constant caused by the interactions with the fluorine atoms. As the line width is nearly independent of angular variations, one can infer that $m_F A_F > (5/2)pa$. This enables one to estimate that A_F is approximately 20 gauss, and that the five $3d$ electrons spend less than 1% of the time on each fluorine atom. This is in agreement with the results found by Tinkham. The hyperfine structure constant of 101 gauss is very close to that found by him for ZnF_2, $A=102$ gauss. These two facts indicate that both crystals can be considered as predominantly ionic.

The g factor in $MgO:Mn$ and in $CaF_2:Mn$ seems to be less than that of the free electron (2.0023) and definitely less than that of Fe^3 ($g=2.0037$). There have been indications of similar differences in g factors in Tutton salts[3] and in Fe alum.[28] These deviations are not understood at present, and probably have their origin in the amount of coupling with the excited states ^4P, ^4D, ^4F, and ^4G.

A theoretical calculation of a and possibly of g depends on the detailed calculation of the excited states of the $(3d)^5$ configuration in the solid state. This may prove to be very difficult. The lowest excited state is ^4G which has matrix elements with ^4P and the much higher lying ^4F. Similarly ^4D has matrix elements with ^4F but not with ^4P or with ^4G. Presumably the ^4G level is split by the cubic field, which in turn in conjunction with spin orbit coupling may split the ^4P level. The latter may contribute to the splitting of the $^6S_{5/2}$ ground state.

In order to establish the order of the excited energy levels, the absorption spectrum of $MgO:Mn$ was scanned from 28 500 A to 2500 A. No significant absorption was found which could unambiguously be assigned to manganese and not to other impurities present in these crystals. As all the excited states have lower multiplicities, the transitions are forbidden, and only weak absorption lines corresponding to a quartet-sextet transition would be expected.

Wertz and Vivo[29] report an absorption band at 26 000 A. We observe absorption lines at 27 200 A and a weaker line at 25 800 A. They correlate this band with a paramagnetic resonance line at $g=2.003$ and assume tentatively that it is caused by oxygen ions. We have observed these two lines even when the paramagnetic resonance line could not be detected.

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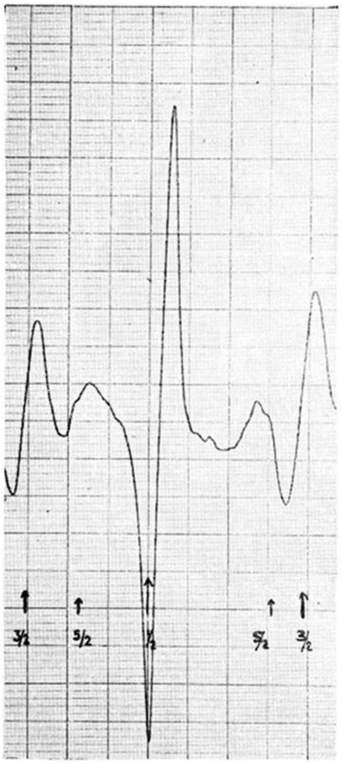

FIG. 2. Typical spectrum of the pentad $m=-5/2$. The transitions from left to right are $M=3/2\rightarrow 1/2$, $M=-5/2\rightarrow -3/2$, $M=1/2\rightarrow -1/2$, $M=5/2\rightarrow 3/2$, and $M=-3/2\rightarrow -1/2$.

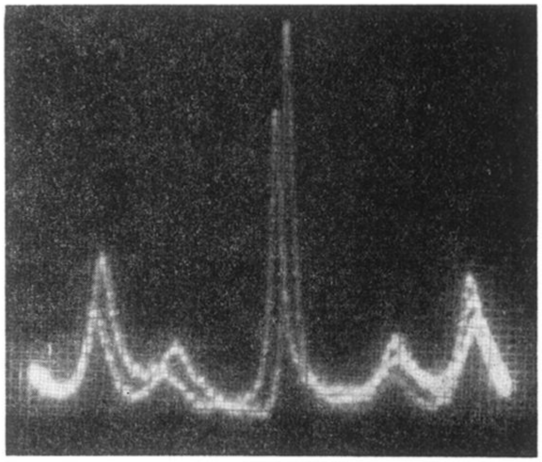

FIG. 6. Absorption spectrum of MgO:Mn at a temperature 70°K. The central line is much narrower than the other four fine structure lines.