

Paramagnetic Resonance of Trivalent Manganese in Rutile (TiO₂)*

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An analysis has been made of the paramagnetic resonance spectrum of Mn³⁺, 3*d*⁴, in rutile. The spectrum at 4.2°K can be fitted to a spin Hamiltonian with $S=2$; $g_z=1.99(\pm 0.01)$; $g_{xy}=2.00(\pm 0.02)$; $D=-3.4$ cm⁻¹(±0.1); $|E|=0.116$ cm⁻¹(±0.001); $a=0.13$ cm⁻¹(±0.02); $|A_x|=84.5(\pm 2.0)\times 10^{-4}$ cm⁻¹; $|A_z|=52.8(\pm 0.5)\times 10^{-4}$ cm⁻¹; $|A_e|=80.6(\pm 1.0)\times 10^{-4}$ cm⁻¹. The quartic term a , previously observed only in the 3*d*⁵ group has now also been detected for 3*d*⁴. The value of a for Mn³⁺ exceeds that for Mn²⁺ and Fe³⁺ systems (3*d*⁵) by factors of 60 and 4, respectively. The constants g , D , and A are in good agreement with theory. From the hyperfine splitting data a value of 3.2 a.u.⁻³ was obtained for $\langle r^{-3} \rangle$; this is about 30% below that calculated for the free Mn³⁺ ion. The S -electron contribution to the hfs, κ , was derived to be +0.52. Mn³⁺ has large zero-field splittings (the outer splitting is 412 kMc/sec), fairly long relaxation times, and narrow resonance lines and may be an appropriate material for masers operating at submillimeter wavelengths.

INTRODUCTION

THE spectrum of Mn⁴⁺ in ¹TiO₂ (3*d*³ with $S=\frac{3}{2}$) is the only spectrum that is visible at room temperature. At and below 77°K, one additional manganese resonance line is readily observed at low magnetic fields. It consists of six hyperfine components with intensities comparable in strength to the weaker transitions in the Mn⁴⁺ spectrum. This resonance line was also observed by Andresen² who speculated that it was the $m=+\frac{5}{2}\rightarrow m=-\frac{5}{2}$ Kramers transition³ of the Mn²⁺ ion. Our measurements at lower frequencies showed that this additional line was not a Kramers-type doublet, but had a zero-field splitting of 3.8 kMc/sec. In further experiments, additional manganese resonance lines were observed and another zero-field splitting was found at 20.8 kMc/sec. From a study of the spectrum, it is concluded that the additional manganese lines are due to the presence of Mn³⁺ (3*d*⁴ with $S=2$).

It is the first time to our knowledge that Mn³⁺ has been observed in paramagnetic resonance. However, Cr²⁺ in CrSO₄·5H₂O, which is isoelectronic with Mn³⁺, has been reported.⁴ The authors interpreted the Cr²⁺ spectrum with $S=2$ using the following spin Hamiltonian:

$$H = \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + D(S_z^2 - 2) + E(S_x^2 - S_y^2).$$

However, for a spin value greater than $\frac{3}{2}$, terms containing S^4 must be added to the spin Hamiltonian.⁵ The presence of these terms is well established from the

reported work on the 3*d*⁵ ions Mn²⁺ and Fe³⁺, and is also found to be necessary in explaining the Mn³⁺ spectrum. The S^4 term that has been introduced for Mn³⁺ is that corresponding to cubic symmetry. Terms representing the deviation from cubic symmetry were not included because of the good fit obtained between theory and experiment using only the cubic term. This cubic term, represented as usual by the parameter a , has a value of 3.8 kMc/sec for Mn³⁺ in TiO₂. This value can be compared with a value of 1.1 kMc/sec for Fe³⁺ in ⁶TiO₂ and much smaller values for Mn²⁺ in Al₂O₃ and Mn²⁺ in MgO (see Table I). Since the a term is due to admixtures of higher crystal-field levels, the a term is small when the crystal field is small. Thus, one would expect larger a

TABLE I. The constants A and a in host crystals with near cubic oxygen surroundings.

Host lattice	Ion	$A \times 10^4$ cm ⁻¹	$a \times 10^4$ cm ⁻¹	Reference
TiO ₂	Cr ³⁺	16.7 (Cr ⁶³)	0	a, b
	Mn ⁴⁺	72	0	c, d
	Mn ³⁺	82 and 53	(+) 1300	This paper
	Mn ²⁺	77		This paper
	Fe ³⁺		+370(±70)	e
Al ₂ O ₃	Cr ³⁺	17.0(±0.5)	0	f
	Mn ⁴⁺	70(±0.5)	0	g
	Mn ²⁺	-79.6(±0.5)	~+22	h
	Fe ³⁺		+224±4	i
MgO	Cr ³⁺	16.2	0	j
	Mn ²⁺	-81.0(±0.2)	+18.6(±0.3)	k
	Fe ³⁺		+205	l

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¹ H. G. Andresen, Phys. Rev. **120**, 1606 (1960).

² H. G. Andresen, J. Chem. Phys. **35**, 1090 (1961).

³ In a private communication, Professor W. Low and Mrs. R. Stahl Brada of the Hebrew University of Israel informed us that they also observed the additional manganese resonance line and attributed it to Mn³⁺.

⁴ K. Ono, S. Koide, H. Sekiyama, and H. Abe, Phys. Rev. **96**, 38 (1954).

⁵ B. Bleaney and R. S. Trenam, Proc. Roy. Soc. (London) **223**, 1 (1954).

^a See Ref. 8.

^b H. J. Gerritsen, First International Conference on Paramagnetic Resonance, Jerusalem, 1962 (to be published).

^c See Ref. 1.

^d See Ref. 2.

^e See Ref. 6.

^f J. E. Geusic, Phys. Rev. **102**, 1252 (1956).

^g S. Geschwind, P. Kisluk, M. P. Klein, J. P. Remeika, and D. L. Wood, Phys. Rev. **126**, 1684 (1962).

^h W. Low and J. T. Suss, Phys. Rev. **119**, 132 (1961).

ⁱ G. S. Bogle and H. F. Symmons, Proc. Phys. Soc. (London) **73**, 531 (1959); S. Geschwind, Phys. Rev. Letters **3**, 207 (1959).

^j W. Low, Phys. Rev. **105**, 801 (1957); J. E. Wertz and P. Ausins, *ibid.* **106**, 484 (1957).

^k W. Low, Phys. Rev. **105**, 793 (1957).

^l W. Low, Phys. Rev. **69**, 1169 (1956).

⁶ D. L. Carter and A. Okaya, Phys. Rev. **118** 1485 (1960).

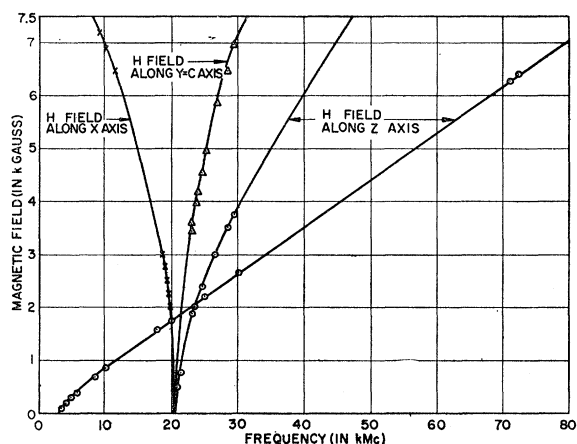


FIG. 1. Magnetic field vs frequency for Mn^{3+} in TiO_2 . Curves are theoretical and points are experimental at 4.2°K .

terms for trivalent ions than for divalent ions because an increase in charge increases the crystalline electric field. In reference to the spectrum of Cr^{2+} in $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$, it is not at all impossible that the a term was small compared to the other terms in the Hamiltonian and did not noticeably influence the observed spectrum.

If the a term in the Mn^{3+} spectrum would not have been included, the zero-field splitting Δ , of the $|+2\rangle \rightarrow |-2\rangle$ transition is predicted to occur at a frequency given by $\Delta = 3E^2/D = 0.3 \text{ kMc/sec}$. This is ten times smaller than the observed zero field. Because of the large effect of a on the zero-field splitting between the $|+2\rangle \rightarrow |-2\rangle$ transition, there is some doubt on the validity of deriving the constant E from the measured zero field splitting using the expression $\Delta = 3E^2/D$, as done by Tinkham⁷ for Fe^{2+} in ZnF_2 . Fe^{2+} is also a 5D ion, but with an orbital triplet lowest.

The resonance spectrum of $\text{ZnF}_2 : \text{Fe}^{2+}$ is analogous to that of $\text{TiO}_2 : \text{Mn}^{3+}$, with the exception that in the former case only the $|+2\rangle \rightarrow |-2\rangle$ transition was studied. Translating Tinkham's results into the parameters D and E , one finds that $D = -7.35 \text{ cm}^{-1}$ and $E = 0.70 \text{ cm}^{-1}$. If his assumption in neglecting the a term is correct, a zero-field splitting between the $|+1\rangle \rightarrow |-1\rangle$ states is expected to occur at $6E = 126 \text{ kMc/sec}$ for Fe^{2+} in ZnF_2 .

It appears that the relaxation time of Mn^{3+} is shorter than that of Mn^{4+} at 4.2°K and decreases rapidly with temperature. The rapid spin-lattice relaxation time causes the Mn^{3+} lines to broaden above 77°K , and the spectrum is not visible at room temperature.

In an experiment to reduce the Mn^{4+} ions to Mn^{3+} by γ irradiation, it was found that about 10% of the Mn^{4+} ions did convert but converted to Mn^{2+} . This spectrum was only observed when the irradiation took place at 77°K and the sample was not allowed to return to room temperature. Bringing the sample to room temperature converts the Mn^{2+} ions back to Mn^{4+} . The hyperfine

⁷ M. Tinkham, Proc. Roy. Soc. (London) **236**, 535 and 549 (1956).

splitting constant A of the Mn^{2+} spectrum is $77(\pm 2) \times 10^{-4} \text{ cm}^{-1}$. Preliminary measurements of the zero-field splittings are 1, 11, and 12 kMc/sec.

EXPERIMENTAL PROCEDURE

The spectrum was measured in the 2–70-kMc/sec region by using three spectrometers. No metal cavity was required since the crystal served as its own dielectric resonator,⁶ with Q values of the order of 30 000 at 4.2°K .

In the 2–8-kMc/sec frequency interval, a coaxial conductor was used with one of the ends shorted. The crystal was placed between the conductors near the shorted end and was made movable for matching purposes. In the 8–20-kMc/sec range, the crystal was placed inside an X band waveguide which was terminated by a tunable shorting plunger, the latter was used for obtaining proper matching conditions. In the 20–70-kMc/sec range, the same arrangement was used as for the 8–20-kMc/sec range except that K-band waveguide was used in place of the X-band guide. This improved the sensitivity and matching.

A stable oscillator was used at X-band frequencies. This source was doubled and tripled through the use of crystal harmonic generators. The relaxation times of Mn^{3+} were fast enough so that superheterodyne detection was not essential and straight detection with scope presentation was sufficient. The magnetic field was measured with a rotating coil gaussmeter, and a "Numar" proton resonance probe.

EXPERIMENTAL RESULTS

The single crystals of rutile doped with manganese contained about 50 parts per million of manganese. It was concluded on the basis of intensity measurements, linewidths, and transition probabilities that the amount of trivalent and tetravalent manganese are comparable. The observed Mn^{3+} resonance lines are about an order of magnitude weaker than those of Mn^{4+} because the $|+2\rangle \rightarrow |-2\rangle$ transition due to the lowest lying energy levels is rather forbidden while the transitions between

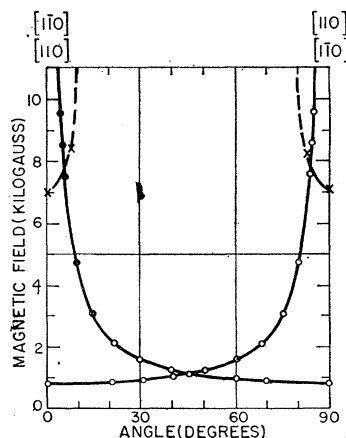


FIG. 2. Spectrum of Mn^{3+} in rutile at 4.2°K at 9615 Mc/sec in the (001) plane.

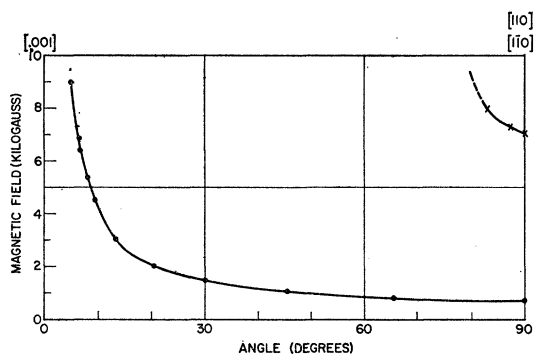


FIG. 3. Spectrum of Mn^{3+} at $4.2^\circ K$ at 9183 Mc/sec in the (110) plane.

$|+1\rangle \rightarrow |-1\rangle$ levels are about ten times wider than the Mn^{4+} lines. The Mn^{3+} ions enter substitutionally for the Ti^{4+} ions. This follows directly from the observed paramagnetic resonance spectra and the known symmetry of the substitutional site.

The two observed zero-field splittings are shown in Fig. 1. The centers of the six hyperfine lines are plotted along the magnetic y , z , and x axes. The c axis coincides with the y axis, while the magnetic x and z axes are parallel to the $[110]$ and $[1\bar{1}0]$ directions. Along the $[110]$ direction or equivalently along the $[1\bar{1}0]$ direction, two of the three magnetic axes are thus simultaneously observed. This is because rutile has two ions in the unit cell whose symmetry axes differ by a 90° rotation about the c axis.^{6,8}

Figures 2 and 3 show the observed spectrum in the (001) and (110) planes. The resonance lines which go

to the 3.8-kMc/sec zero-field splitting have a linewidth of approximately 2 G at $4.2^\circ K$ with an over-all width of 283 G for the six hfs lines. The resonance lines which go to the 20.8-kMc/sec zero-field splitting have a linewidth of about 20 G with total widths of 431 G (c axis), 453 G (x axis) and 283 G (z axis). Intensity measurements at $4.2^\circ K$ and $1.2^\circ K$ at 9 kMc/sec showed that the $|+2\rangle \rightarrow |-2\rangle$ energy levels are lowest. This means that the sign of D is negative. In addition the intensity ratio between the $|+1\rangle \rightarrow |-1\rangle$ transition and the $|+2\rangle \rightarrow |-2\rangle$ transition at different temperatures permitted a rough determination of D (see theoretical interpretation).

THEORETICAL INTERPRETATION

The data can be fitted using the spin Hamiltonian^{5,9}:

$$H = \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + D(S_z^2 - 2) \\ + E(S_x^2 - S_y^2) + \frac{1}{6}a\{S_x^4 + S_y^4 + S_z^4 - 10I^2/5\} \\ + A_x I_x S_x + A_y I_y S_y + A_z I_z S_z$$

with the constants $S=2$; $I=\frac{5}{2}$; $D=-3.4 \pm 0.1 \text{ cm}^{-1}$; $a=0.13 \pm 0.02 \text{ cm}^{-1}$; $|E|=0.116 \pm 0.001 \text{ cm}^{-1}$; $g_x=1.99 \pm 0.01$; $g_{x,y}=2.00 \pm 0.02$; $|A_x|=(84.5 \pm 2.0) \times 10^{-4} \text{ cm}^{-1}$; $|A_y|=(52.8 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}$; $|A_z|=(80.6 \pm 1.0) \times 10^{-4} \text{ cm}^{-1}$. From the small E/D ratio and also from the near equal values of the hfs constants A_x and A_y as contrasted to the value for the hfs constant A_z , it is concluded that the symmetry is nearly tetragonal, though the exact surroundings are orthorhombic.

Along the z axis, the energy values for the above Hamiltonian are obtained by setting the following determinant equal to zero.

$m_s \backslash m_s'$	2	1	0	-1	-2
2	$2D+0.1a+2G-W$	0	$E\sqrt{6}$	0	$0.5a$
1	0	$-D-0.4a+G-W$	0	$3E$	0
0	$E\sqrt{6}$	0	$-2D+0.6a-W$	0	$E\sqrt{6}$
-1	0	$3E$	0	$-D-0.4a-G-W$	0
-2	$0.5a$	0	$E\sqrt{6}$	0	$2D+0.1a-2G-W$

The hyperfine terms were omitted and G represents $\beta g_z H_z$. This 5×5 determinant factors into a 2×2 and a 3×3 . The solution of the 2×2 determinant results in $\nu_{\text{res}} = 2(G^2 + 9E^2)^{1/2}$. The zero field splitting is equal to $6E$ and observation of the zero-field splitting (20.8 kMc/sec) determines E , while the magnetic-field dependence may be used to obtain g_z . The addition of the diagonal⁹ term $(7/36)F\{S_x^4 - (31/7)S_z^2 + (72/35)\}$ to the above Hamiltonian representing the deviation from cubic symmetry would not influence the values of E and g_z . The F term would also hardly influence the $|+2\rangle \rightarrow |-2\rangle$ zero-field splitting if $D \gg E$ and F , as is the case.

The resonant frequencies along the other two mag-

netic axes can be obtained by use of the transformation formula given by Bleaney and Stevens.⁹ A first-order approximation of the lowest resonant frequencies is easily derived and the results are:

$$\nu_{x,y} = a; \quad \nu_x = 6E + 3G^2/D; \quad \nu_y = 6E - 3G^2/D.$$

These expressions explain the qualitative features of the experimental results. That is, resonances above 4 kMc/sec were not observed for the magnetic field along the x or y axis for the $|+2\rangle \rightarrow |-2\rangle$.

A sketch of the theoretical energy levels for frequency versus the magnetic field along the magnetic axes is given in Figs. 4(a), 4(b), 4(c). The curves were obtained by a numerical calculation on an IBM-650 computer.

⁸ H. J. Gerritsen, S. E. Harrison, H. R. Lewis, and J. P. Wittke, Phys. Rev. Letters 2, 153 (1959).

⁹ B. Bleaney and K. W. M. Stevens, Repts. Progr. Phys. 16, 138 (1953).

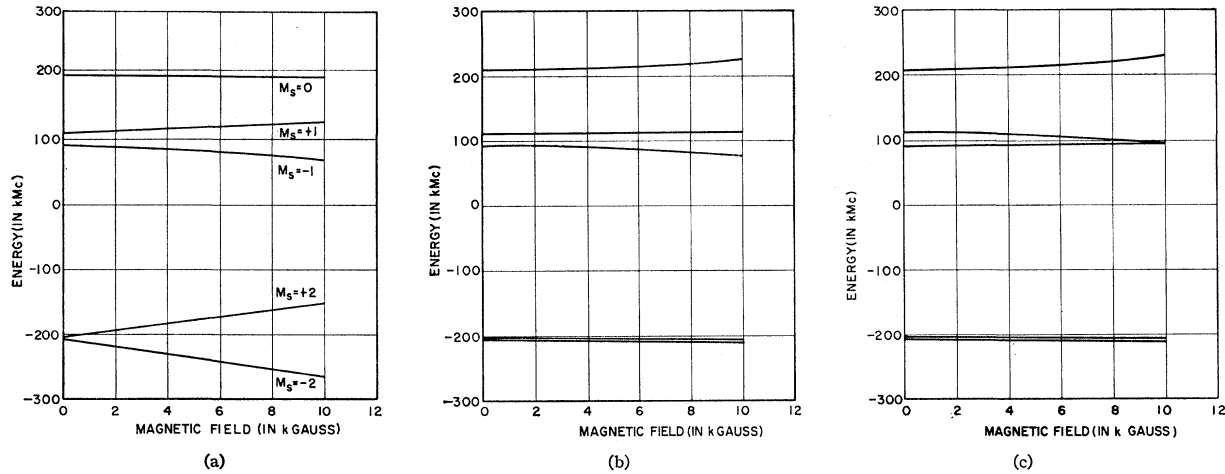


FIG. 4. (a) Theoretical energy levels of Mn^{3+} in TiO_2 for the magnetic field along the Z axis. Constants used are $D = -103$ kMc/sec; $|E| = 3.47$ kMc/sec; $a = +3.8$ kMc/sec; $g = 1.99$. (b) Theoretical energy levels of Mn^{3+} in TiO_2 for the magnetic field along the Y axis. Constants used are $D = -103$ kMc/sec; $|E| = 3.47$ kMc/sec; $a = +3.8$ kMc/sec; $g = 2.00$. (c) Theoretical energy levels of Mn^{3+} in TiO_2 for the magnetic field along the X axis. Constants used are $D = -103$ kMc/sec; $|E| = 3.47$ kMc/sec; $a = +3.8$ kMc/sec; $g = 2.00$.

The constants used in the calculation of the energy levels as given in the figures were $D = -103$ kMc/sec and $a = +3.8$ kMc. This gives a very good agreement with the experimental results, as can be seen from Fig. 1. However, the values $D = -112$ kMc/sec and $a = -3.2$ kMc/sec give an almost equally good fit with the experimental results. Cross combinations of the D and a values give poor agreement with experiments. In order to decide between the two possibilities without having to resort to very high frequencies, relative intensity measurements were obtained between a hyperfine component of the $|+2\rangle \rightarrow |-2\rangle$ and one of the hyperfine components of the $|+1\rangle \rightarrow |-1\rangle$ transitions. In order to obtain a simple expression for the relative intensities an orientation was chosen such that these two hyperfine components nearly coincided. This orientation was at 27 kMc/sec with a field of 2.8 kG along the z axis, $[110]$, at 27, 4.2, and 1.7°K. At 1.7°K, the $|+1\rangle \rightarrow |-1\rangle$ transition could not be detected because the levels are almost totally depopulated. If we define the relative intensity ratio at temperature T as $R(T) = A(|+2\rangle \rightarrow |-2\rangle) / A(|+1\rangle \rightarrow |-1\rangle)$ the experimental result is $R(4.2)/R(27) = 17 \pm 5$. The expected value of the relative intensity ratio can be calculated using the expression $R(T) = \exp(h\nu_{13}/kT)$, where ν_{13} represents the distance between the $|-2\rangle$ and $|-1\rangle$ energy levels. Using the above expression, the calculated value for $R(4.2)/R(27)$ using $D = -103$ kMc/sec and $a = +3.8$ kMc/sec is 19.5. For $D = -112$ kMc/sec and $a = -3.2$ kMc/sec, $R(4.2)/R(27)$ is 26.5. The results of the experiment though perhaps not decisive are in favor of $D = -103$ kMc/sec and $a = +3.8$ kMc/sec. In order to get a more conclusive result, an electron paramagnetic resonance (EPR) experiment at higher frequencies must be performed.

DISCUSSION OF RESULTS

The ground state for Mn^{3+} is 5D . This state splits in the strong mainly octahedral field¹⁰ of the six surrounding oxygen ions into an orbital triplet 5T_2 and an orbital doublet 5E . The 5E state has the lower energy. The situation is analogous to Cu^{2+} ($3d^9$) with respect to the orbital energies. In this case, the situation can be described as a hole in the $3d$ filled shell, while Mn^{3+} ($3d^4$) represents a hole in the half-filled shell. The hole has the lower energy when it is in the doublet states where its wave functions are directed toward the O^{2-} ions. In the triplet states, the wave functions for the hole avoid the O^{2-} ions. The two levels into which the doublet E splits can be denoted by A_1 and B_1 . As in the case of Cu^{2+} , the wave function for A_1 is $\psi(A_1) = (3z^2 - r^2)/r^2$ and the g values are $g_{11} = 2$, $g_1 = 2 - 6\lambda/\Delta$. For B_1 , the wave function is $\psi(B_1) = (x^2 - y^2)/r^2$ and the g values are $g_{11} = 2 - 8\lambda/\Delta$ and $g_1 = 2 - 2\lambda/\Delta$. It was observed that Cu^{2+} in TiO_2 has g values¹¹ and hyperfine splitting constants corresponding to B_1 , indicating that the oxygens along the z axis ($[110]$ direction) are moved outwards. This is in agreement with other observations on Cu^{2+} in nearly octahedral surroundings⁹ and is believed to be its natural Jahn-Teller tendency.

One might expect that an analogous argument holds for Mn^{3+} . In this case, the g values cannot be used as deciding factors since both g_z and $g_{x,y}$ are very nearly 2.00. The two states, 5A_1 and 5B_1 , into which the 5E doublet splits in a tetragonal field have not only different g values, but differ also in the sign of D and in the hyperfine constants as can be seen in Table II.

Here $\lambda =$ spin-orbit constant, Δ is the splitting be-

¹⁰ J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, New York, 1962), p. 352.

¹¹ H. J. Gerritsen and E. S. Sabisky, *Phys. Rev.* **125**, 1853 (1962).

TABLE II. A comparison of the theoretical results for the states 5A_1 and 5B_1 with experimental values.

5A_1	5B_1	Observed
$g_{11}=2$	$g_{11}=2-8\lambda/\Delta$	1.99 ± 0.01
$g_1=2-6\lambda/\Delta$	$g_1=2-2\lambda/\Delta$	2.00 ± 0.02
$D=+3(\lambda^2/\Delta+4\lambda^2/3E+\rho)$	$D=-3(\lambda^2/\Delta+4\lambda^2/3E+\rho)$	-3.4 cm^{-1}
$A=2\beta\beta_n\gamma\langle r^{-3}\rangle(-1/7-\kappa)$	$A=2\beta\beta_n\gamma\langle r^{-3}\rangle(+1/7-\kappa)$	$\pm 53\times 10^{-4}\text{ cm}^{-1}$
$B=2\beta\beta_n\gamma\langle r^{-3}\rangle(+1/14-\kappa)$	$B=2\beta\beta_n\gamma\langle r^{-3}\rangle(-1/14-\kappa)$	$\pm 83\times 10^{-4}\text{ cm}^{-1}$
$\psi=(3z^2-r^2)/r^2\equiv Y_2^0$	$\psi=(x^2-y^2)/r^2\equiv \sqrt{\frac{1}{2}}(Y_2^2+Y_2^{-2})$	

tween the doublet and triplet, and E is the separation between the 5E (ground state) which belongs to the t_2^3 e configuration and the next higher state, 3H , which belongs to the t_2^4 configuration.

The 3H state splits in a cubic field to give a 3T_1 state which is separated from the ground state by $E=5B+5C-\Delta$. For $E<0$, the 3H state would become the ground state. This would result in a spin (S) = 1, in contrast to the observed value of $S=2$. Therefore, one can conclude that E is positive. A rough estimate of E can be made as follows: The free-ion values are taken as $B=965\text{ cm}^{-1}$ and $C=4450\text{ cm}^{-1}$ from Griffith¹⁰ according to Tanabe and Sugano's work. Since the Mn^{3+} ion in rutile is surrounded by six O^{2-} ions, the free-ion values will be reduced by 71% in accordance with Jørgensen.¹² Assume Δ for Mn^{3+} is $16\,800\text{ cm}^{-1}$ since Δ for V^{3+} , Cr^{3+} , Fe^{3+} , and Co^{3+} in similar surroundings¹⁰ are $17\,800\text{ cm}^{-1}$, $17\,500\text{ cm}^{-1}$, $13\,600\text{ cm}^{-1}$, and $18\,100\text{ cm}^{-1}$. This leads to a value for E of 2820 cm^{-1} .

The spin orbit constant λ for the free-ion Mn^{3+} is 85 cm^{-1} and reduced by the factor 71%, λ becomes 60 cm^{-1} . From Table II for the state 5B_1 with the above values for E , Δ , and λ , the calculated value for D is -5.6 cm^{-1} if we neglect the ρ term. This value for D of -5.6 cm^{-1} is not too far away from the experimental value of -3.4 cm^{-1} considering the approximations that were required in obtaining values for E , λ , and Δ , the sensitivity of the result to E and the neglect of the rhombic component in the field.

HYPERFINE SPLITTING

From Table II, the expressions¹³ for the anisotropic hyperfine splitting for the state 5B_1 are:

$$A=2\beta\beta_n\gamma\langle r^{-3}\rangle(-\kappa+1/7)\equiv P(-\kappa+1/7)$$

$$= \pm 53\times 10^{-4}\text{ cm}^{-1}$$

and

$$B=2\beta\beta_n\gamma\langle r^{-3}\rangle(-\kappa-1/14)\equiv P(-\kappa-1/14)$$

$$= \pm 83\times 10^{-4}\text{ cm}^{-1}.$$

If A and B have the same signs, one gets $P=\pm 140\times 10^{-4}\text{ cm}^{-1}$ and $\kappa=+0.52$. If A and B have opposite signs, $P=\pm 630\times 10^{-4}\text{ cm}^{-1}$ and $\kappa=+0.06$. Since $P=(2\beta\mu_n/|I|)\langle r^{-3}\rangle$, one finds that $\langle r^{-3}\rangle=3.2\text{ (a.u.)}^{-3}$

¹² C. K. Jørgensen, Discussions Faraday Soc. 26, 110 (1958).

¹³ A. Abragam and M. H. L. Pryce, Proc. Royal Soc. (London) 206, 135 (1951).

for $|P|=140\times 10^{-4}\text{ cm}^{-1}$ and $\langle r^{-3}\rangle=14\text{ (a.u.)}^{-3}$ for $|P|=630\times 10^{-4}\text{ cm}^{-1}$. Dr. Weakliem of RCA Laboratories calculated $\langle r^{-3}\rangle$ for Mn^{3+} using the free-ion wave functions of Watson¹⁴ and got a value for $\langle r^{-3}\rangle$ of 4.7. Therefore, on this basis, the solution giving the values $|P|=630\times 10^{-4}\text{ cm}^{-1}$ and $\kappa=+0.06$ is rejected. Also, the value of $\kappa=+0.52$ derived for Mn^{3+} is more consistent with the values of¹⁵ $\kappa=0.56$ or 0.42 and¹¹ $\kappa=0.26$ for $\text{TiO}_2:\text{Co}^{2+}$ and $\text{TiO}_2:\text{Cu}^{2+}$, respectively.

A comparison of the hfs of Mn^{3+} with that of Mn^{2+} and Mn^{4+} in TiO_2 gives the following results: In Mn^{2+} , the hfs constant A is isotropic and equal to $(-)77\times 10^{-4}\text{ cm}^{-1}$. In Mn^{4+} , the value of A is $(-)72\times 10^{-4}\text{ cm}^{-1}$. For Mn^{2+} and Mn^{4+} , $A=-\kappa P$. This implies that κ doesn't change much for the two different valence states if one assumes equal values for $\langle r^{-3}\rangle$. For Mn^{3+} , the value of κP is $73\times 10^{-4}\text{ cm}^{-1}$ using $P=140\times 10^{-4}\text{ cm}^{-1}$ and $\kappa=0.52$. The other possibility for Mn^{3+} , ruled out earlier, is $38\times 10^{-4}\text{ cm}^{-1}$, which is not in agreement with the value for the other valence states. This comparison agrees with the previous result that the correct values of P and κ for Mn^{3+} are $140\times 10^{-4}\text{ cm}^{-1}$ and 0.52 , respectively.

Note added in proof. If one converts the $\kappa\langle r^{-3}\rangle$ values into magnetic fields at the nucleus, one obtains: 200 kg (Mn^{4+}), 210 kg (Mn^{3+}), and 220 kg (Mn^{2+}). This is in agreement with S. Geschwind's findings (private communication) that the core polarization fields vary but little in the $3d^n$ containing oxides.

CONCLUSIONS

The observed EPR spectrum of Mn^{3+} in TiO_2 is in reasonable agreement with crystal-field theory. The g values, close to 2.00, the constant D , and the hyperfine splitting, are all explainable with theory. No attempt has been made to explain the very large a term derived from the experiments. The electrostatic field is not sufficiently strong to cause spin quenching. The value of $\langle r^{-3}\rangle$ is 30% below that for the free ion, indicating the presence of rather strong covalent bonding. A similar amount of reduction is suggested by the work¹⁶ on Cu^{2+} and Cu^{3+} in Al_2O_3 .

¹⁴ R. E. Watson, Solid State and Molecular Theory Group, MIT Technical Report, 1959 (unpublished).

¹⁵ E. Yamaka and R. G. Barnes, Phys. Rev. 126, 1568 (1962).

¹⁶ W. E. Blumberg, T. Eisinger, and S. Geschwind, Phys. Rev. 130, 900 (1963).

The technical importance of $3d^4$ systems and possibly $3d^6$ systems for masers operating at frequencies of several hundred kMc/sec, coupled with the observation of rather narrow lines and fairly long relaxation times, makes the study of Mn^{3+} , Cr^{2+} , and Fe^{2+} ions of interest.

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Low-Field de Haas-van Alphen Effect in Indium

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De Haas-van Alphen data for indium, up to fields of 18 kG, have been obtained using an automatic torsion balance. The resulting extremal areas agree qualitatively with the third zone surface predicted by the free-electron model. A detailed comparison shows, however, that the experimental areas are considerably smaller than those given by the single orthogonalized plane-wave theory and that the arms are close to being cylindrical over a considerable part of their length. For certain ranges of field orientation, the amplitude of the oscillatory susceptibility is much lower than would be expected. An explanation of this effect is considered.

I. INTRODUCTION

THE free-electron model¹ gives surprisingly accurate predictions concerning the Fermi surface of indium, at least insofar as the second-zone surface is concerned. Less information concerning the third-zone surface is available and it is of interest to know whether this also conforms to a single orthogonalized plane wave (OPW) model. Low-field de Haas-van Alphen (dHvA) data would be very helpful in settling this question. Unfortunately, however, there is considerable disagreement among the existing data.²⁻⁴ Since the data are incomplete and are thought to be subject to errors in crystal orientation, the present series of measurements was undertaken to rectify these deficiencies. Very complete data up to 18 kG have been obtained for [100], [001], [110], [011], and [111] crystal suspensions using an automatic torsion balance. The measurements show that the free-electron model gives a correct *qualitative* description of the third-zone surface, although the extremal areas differ considerably from those obtained experimentally. In addition, the arms of the third-zone surface are almost cylindrical along a considerable part of their length. As noted by previous observers,² the amplitude of the oscillatory susceptibility is very small for $H \sim [001]$. A possible explanation of this effect is considered.

¹ Walter A. Harrison, Phys. Rev. **118**, 1190 (1960).

² D. Shoenberg, Phil. Trans. Roy. Soc. (London) **A245**, 1 (1952).

³ B. I. Verkin, B. J. Lazarev, and N. S. Rudenko, Zh. Eksperim. i Teor. Fiz. **20**, 93 (1950).

⁴ B. I. Verkin, B. J. Lazarev, and N. S. Rudenko, Zh. Eksperim. i Teor. Fiz. **20**, 995 (1950).

II. EXPERIMENTAL METHOD

Measurements of the de Haas-van Alphen effect were made using an automatic torsion balance similar to that described by Croft, *et al.*⁵ Fields up to 18 kG were produced in a Harvey-Wells type-L128 electromagnet and type HS-1050 regulated power supply. A Rawson type-820 rotating coil gaussmeter, calibrated *in situ* by means of the Li^7 resonance line, was used to measure the field at the sample. Data were recorded automatically by scanning the field over an appropriate interval and

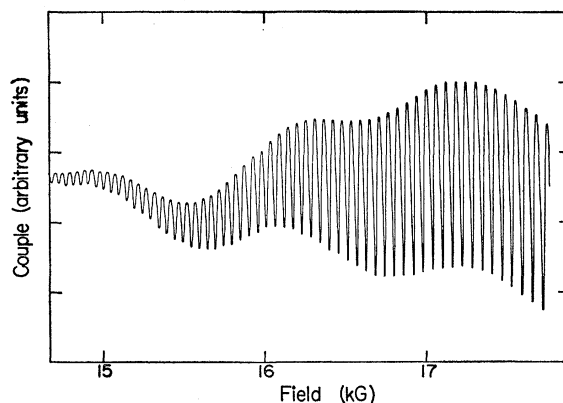


FIG. 1. Typical recorder trace of feedback current versus magnetic field with [001] axis of suspension. The field is inclined at 24° to [100]; the temperature is approximately 1.2°K.

⁵ G. T. Croft, J. F. Donahoe, and W. F. Love, Rev. Sci. Instr. **26**, 360 (1955).