

terms than this one; it is valid over a wider range of momentum transfers.

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Electron Paramagnetic Resonance of Manganese in TiO_2

HARRO G. ANDRESEN

U. S. Army Signal Research and Development Agency, Fort Monmouth, New Jersey

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The paramagnetic resonance spectrum of a manganese-doped single crystal of TiO_2 in its rutile structure was investigated at a frequency of 9.505 kMc/sec at room temperature. The following results were obtained: The manganese atoms replace the Ti^{4+} ions in the rutile and exist as tetravalent ions having a spin value of $S=3/2$ and strong admixtures of covalent bonds to their six oxygen neighbors. The parameters of the spin Hamiltonian were determined to be $g=1.990$, $|D|=12.1$ kMc/sec, and $|E|=0.388$ kMc/sec. Within the accuracy of this experiment the magnetic hyperfine structure was isotropic and could be described by $|A|=215$ Mc/sec.

INTRODUCTION

WITH only one exception, all previously investigated paramagnetic resonance data for manganese in various host crystals could be interpreted with the assumption that the manganese atoms exist in the crystals as Mn^{++} ions having a spin value of $S=5/2$. For all crystals the splitting of the $^6\text{S}_{5/2}$ ground level of the Mn^{++} ions due to the influence of the crystalline field was so small that the paramagnetic spectra consisted either of a single hyperfine structure pattern or of several strongly overlapped hyperfine structure patterns, each showing the characteristic six-line splitting resulting from the spin $I=5/2$ of the Mn^{55} nucleus.

Van Wieringen¹ and Matumura² systematically investigated the behavior of the g factors and the hyperfine structure parameters A for Mn^{++} in various host crystals. They showed that the parameter A decreases at a rate which is nearly proportional to the covalent character of the manganese bond to its crystal neighbors and that the g factor simultaneously increases slightly. Typical values for manganese atoms with strong ionic bonds (e.g., Mn-MgF_2) are $g=2.001$ and $|A|=271$ Mc/sec, whereas the resonances of manganese in ZnSe , which is an example of a Mn^{++} bond with strong covalent admixtures, can be described by $g=2.01$ and $|A|=180$ Mc/sec.

Mueller³ observed the paramagnetic resonance spectrum of a manganese-doped single crystal of SrTiO_3 and interpreted the spectrum using $g=1.994$ and $|A|=209$ Mc/sec. The combination of a relatively small

A factor and a g factor that is less than two does not fit into the scheme of the Mn^{++} resonances. Therefore, Mueller explained the spectrum by assuming that in SrTiO_3 the manganese atoms exist in a tetravalent state having a spin value of $S=3/2$.

The paramagnetic resonances of a manganese-doped TiO_2 single crystal in its rutile structure are, to a certain extent, similar to the resonances of manganese in SrTiO_3 , since, for both spectra, the g and A factors are nearly equal; thus Mueller's conclusions may also be extended to the resonances of manganese in rutile. In addition, however, manganese in rutile has a large fine-structure splitting, so that for most of the crystal orientations the hyperfine structure patterns are separated from each other. Therefore, the spin value, as well as the lattice position of the manganese impurity, can be determined in a more direct manner from the angular dependence of the resonances.

CRYSTAL STRUCTURE

The rutile form of TiO_2 is a tetragonal crystal belonging to the class D_{4h} .^{4,5} The unit cell (Fig. 1) consists of two nonequivalent Ti^{4+} ions. Each of these Ti^{4+} ions is surrounded by a slightly deformed oxygen octahedron, so that the local symmetry of a Ti^{4+} site is only orthorhombic. Nevertheless, there is overall tetragonal symmetry of the rutile crystal, because the surroundings of the two nonequivalent ions differ from one another only by a rotation of 90° around the c axis of the crystal. Thus the paramagnetic spectrum of an

¹ J. S. van Wieringen, Discussion Faraday Soc. **19**, 118 (1955).

² O. Matumura, J. Phys. Soc. Japan **14**, 108 (1959).

³ K. A. Mueller, Phys. Rev. Letters **2**, 153 (1959).

⁴ F. A. Grant, Revs. Modern Phys. **31**, 646 (1959).

⁵ R. W. C. Wyckoff, *Crystal Structures Handbook* (Interscience Publishers, Inc., New York, 1958).

impurity substituting a Ti⁴⁺ ion should show a periodicity of 90° as the crystal is rotated around the *c* axis. It should be noted that if the magnetic field lies in the (010) or the (100) plane the two Ti⁴⁺ sites become magnetically equivalent.

EXPERIMENT

The crystal boules, which were grown by the Verneuil flame fusion method, were obtained from Linde Air Products, New York. In contrast to the Cr- or Fe-doped rutile boules, which consisted of fairly large single crystals, the Mn-doped boules were composed of many small single crystals of different orientations. After the largest single crystalline areas of the boules were isolated by systematic x-ray scanning, the samples were cut into cubes approximately $\frac{1}{8}$ in. on a side. With the aid of x-ray orientation, it was possible to cut the samples so that the faces of the cube were parallel to the (001), (100), or (010) planes, respectively, with an accuracy of better than $\pm 2^\circ$. The concentration of manganese was determined by spectrochemical analysis to be 0.01% by weight.

All measurements were performed at room temperature with a Varian EPR spectrometer at a frequency of 9.505 kMc/sec. The crystals, which were mounted in a rectangular cavity, were oriented in such a manner that the dc magnetic field could be rotated in either the (110), the (001), or the (100) planes. The rotational plane of the magnetic field could be specified with an accuracy of approximately $\pm 2^\circ$, whereas the orientation of the crystal in the rotational plane of the field could be determined to an accuracy of better than 0.5° by means of the symmetry properties of the paramagnetic spectrum. A NUMAR NMR gaussmeter was used

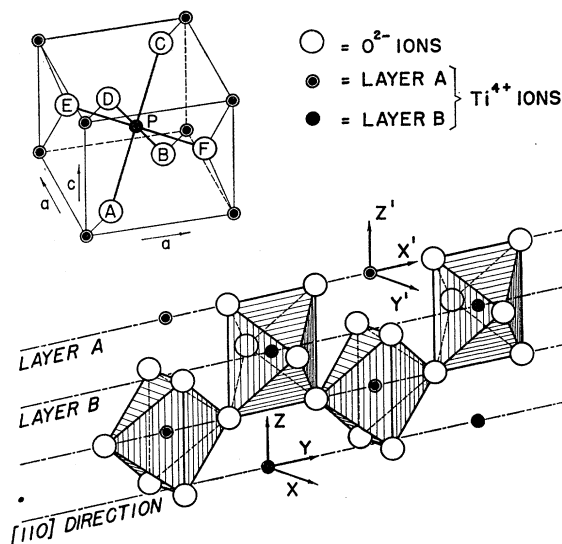


Fig. 1. Crystal structure of TiO₂ (rutile) and magnetic axes. $\angle APE = \angle BPE = 90^\circ$; $\angle DPC = \angle APB = 78^\circ$
 $EP = 1.99 \text{ \AA}$; $AP = BP = 1.89 \text{ \AA}$.

for precise measurements of the dc magnetic field; all field measurements could be correlated with the recorded paramagnetic spectrum with an accuracy of better than ± 3 gauss.

Figures 2 and 3 show the magnetic resonance field at the center of gravity of the hyperfine structure pattern as a function of the crystal orientation. Fe³⁺ resonances, which were also observed, have been omitted, since the manganese resonances could easily be distinguished from the former by the characteristic hyperfine structure.

For most of the crystal orientations the linewidth of

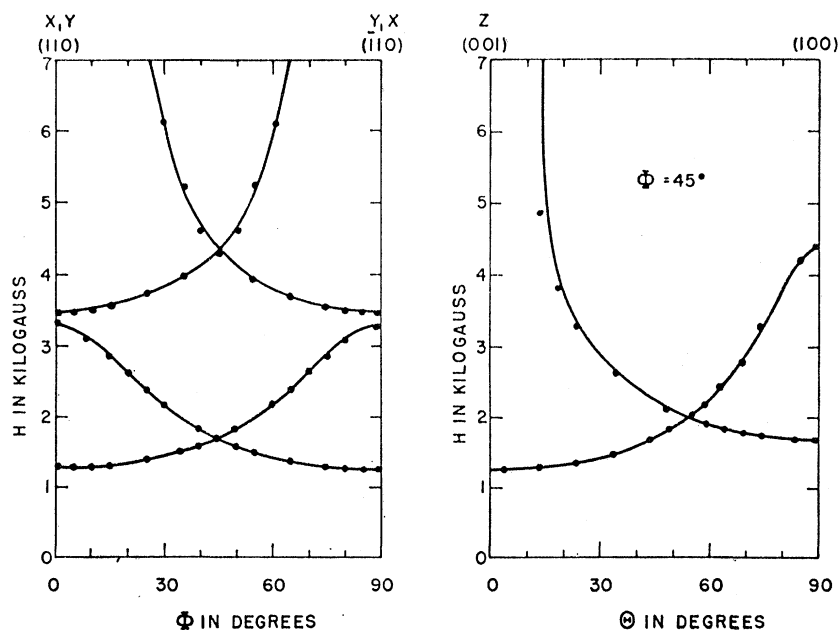


Fig. 2. The points shown in the figures are the observed resonances at 9.505 kMc/sec. The solid lines represent the theoretical resonance fields for the parameters stated in the text. θ is the angle between the *Z* axis and the magnetic field *H*; ϕ is the angle between the *X* axis and the projection of the magnetic field *H* in the *XY* plane.

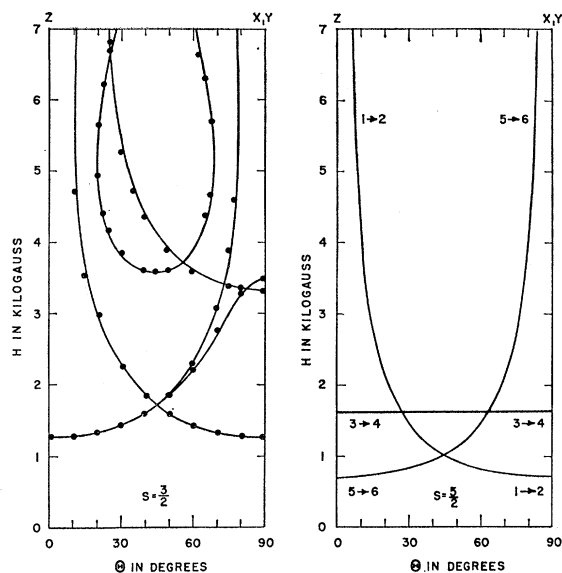


FIG. 3. The points shown in the figures are the observed resonances at 9.505 kMc/sec. The solid lines represent the theoretical resonance fields for the parameters stated in the text. In the figure for $S=5/2$ the value $E/D=0.333$ has been used instead of the E/D value stated in the text. θ is the angle between the Z axis and the magnetic field H .

the resonances varied between 2 and 8 gauss. The line-width data and the slope of the calculated curves of the energy levels versus magnetic field were used to obtain a typical value of $T_2=1.6 \times 10^{-8}$ sec for the relaxation time.

RESULTS

By observing a 90° period (Fig. 2) of the paramagnetic spectrum while turning the crystal around the c axis, one may conclude that the manganese atoms have actually replaced the Ti^{4+} ions in the rutile crystal.

The crystal field at the location of the manganese atom has orthorhombic symmetry, so that the spin Hamiltonian,⁶ which describes the lowest energy levels, should contain at least the following terms:

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2) + A\mathbf{S} \cdot \mathbf{I} \quad (1)$$

The axis of quantization Z was chosen parallel to the c axis of the crystal, because the E/D ratio for manganese assumes its smallest value in this direction. The magnetic axes X, Y, Z and X', Y', Z' of the two nonequivalent positions of the manganese atoms in the rutile lattice are shown in Fig. 1 in their relation to the directions of the crystal axes.

The displacement of the center of each hyperfine structure complex, according to second-order contributions of the hyperfine structure interaction, is

⁶ B. Bleaney and K. W. H. Stevens in *Reports on Progress in Physics* (The Physical Society, London, 1953, Vol. 16, p. 107).

approximately 5 gauss at X-band frequencies.⁷ For most of the crystal orientations, this displacement lies well within the limits of experimental error, so that one may neglect hyperfine structure contributions of second order during the evaluation of the experimental results. Under this assumption each center of the hyperfine structure patterns can be described solely by the g, D , and E terms of the spin Hamiltonian.

Because of a large D parameter, the zero-field splittings of manganese in rutile are well above X-band frequencies and, therefore, cannot be used for the determination of the spin value in this experiment. With the exception of very few crystal orientations, all resonances that can be observed at 9.505 kMc/sec must be correlated with transitions between energy levels, which may be characterized by the quantum numbers $+m$ and $-m$, respectively, for the limit of a small E/D ratio and the magnetic field H parallel to the c axis. Since the hypothetical $+5/2 \rightarrow -5/2$ transition is highly forbidden for this orientation of the magnetic field, the number of resonances for $H \parallel c$ also cannot be used to establish the spin value unambiguously. At X-band frequencies the spin value of manganese in rutile can be derived most directly from the angular dependence of the resonances.

Peculiar to the manganese resonances is the almost perfect mirror symmetry of the spectrum in the ZY plane with respect to $\theta=45^\circ$ (Fig. 3). The nonsymmetrical curves of Fig. 3 refer to the other ion of the unit cell, and represent a θ variation in the ZX plane.⁸ The following consideration is concerned with the problem of establishing a relationship between the parameters of the spin Hamiltonian, which can explain the observed symmetrical behavior of the resonances. The result, as one would expect, will be shown to be independent of the spin value.

In order to establish the parameter relationship, it is useful to change the direction of the quantization axis Z from the c axis of the crystal to the direction of the magnetic field. The transformation may be carried out in one of two equivalent ways: Either the operators of the spin Hamiltonian may be transformed, or the matrix of the Hamiltonian may be transformed to $[D_s^{mm'}(\alpha, \beta, \gamma)]\mathcal{H}[D_s^{mm'}(\alpha, \beta, \gamma)]^\dagger$, where α, β , and γ are the three Euler angles, describing the rotation of the original coordinate system to the new one, and s is the dimensionality of \mathcal{H} .^{9,10} The first method is preferable in the present problem, because this transformation is independent of the spin value.

⁷ This estimate is only valid for transitions between energy levels that are not nearly parallel to each other in their functional relationship to the magnetic field.

⁸ For this identification of the rotational planes of the magnetic field, the sign of E/D has been arbitrarily chosen to be positive.

⁹ M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, and Chapman and Hall, Ltd. London, England, 1957).

¹⁰ A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).

TABLE I. Elements of rotational matrix and components of irreducible tensorial operator used in transforming the spin Hamiltonian.

m	$D_2^{2,m}(\alpha,\beta,0)$	$D_2^{0,m}(\alpha,\beta,0)$	$D_2^{-2,m}(\alpha,\beta,0)$	T_2^m
2	$+e^{-i2\alpha}(1+\cos\beta)^2/4$	$+(3/8)^{1/2}\sin^2\beta$	$+e^{i2\alpha}(1-\cos\beta)^2/4$	S_+^2
1	$-e^{-i2\alpha}\sin\beta(1+\cos\beta)/2$	$+(3/2)^{1/2}\sin\beta\cos\beta$	$+e^{i2\alpha}\sin\beta(1-\cos\beta)/2$	$-[S_+S_z+S_zS_+]$
0	$+e^{-i2\alpha}(3/8)^{1/2}\sin^2\beta$	$+\frac{1}{2}[3\cos^2\beta-1]$	$+e^{i2\alpha}(3/8)^{1/2}\sin^2\beta$	$(2/3)^{1/2}[3S_z^2-S^2]$
-1	$-e^{-i2\alpha}\sin\beta(1-\cos\beta)/2$	$-(3/2)^{1/2}\sin\beta\cos\beta$	$+e^{i2\alpha}\sin\beta(1+\cos\beta)/2$	$[S_-S_z+S_zS_-]$
-2	$+e^{-i2\alpha}(1-\cos\beta)^2/4$	$+(3/8)^{1/2}\sin^2\beta$	$+e^{i2\alpha}(1+\cos\beta)^2/4$	S_-^2

The transformation of the operators can be performed easily if the spin Hamiltonian is expressed in terms of components T_l^m of irreducible tensor operators. By definition, the components transform under a rotation of the coordinate system as follows⁹⁻¹¹:

$$T_l^{m'} = \sum_m D_l^{mm'}(\alpha,\beta,\gamma) T_l^m. \quad (2)$$

The symbols are as follows: l =rank of the tensor operator; $D_l^{mm'}(\alpha,\beta,\gamma)$ =rotational matrix of rank $2l+1$.¹²

Since the term $g\beta\mathbf{S}\cdot\mathbf{H}$ of the spin Hamiltonian (1) can be expressed as the scalar product of two tensor operators of rank 1, the form of this expression is invariant under a rotation of the coordinate system; the D and E terms of the spin Hamiltonian (1) can be expressed in terms of tensor components of rank 2, which are listed in Table I:

$$D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2) \\ = (1/6)^{1/2} D T_2^0 + \frac{1}{2} E (T_2^2 + T_2^{-2}). \quad (3)$$

For a rotation of the magnetic field in the (110) plane, transformation (2) is determined by the following three Euler angles: β is identical with the polar angle θ between magnetic field and c axis; α equals 0° or 90° , depending upon which of the two nonequivalent lattice sites is being considered; and γ is identically zero. By use of the explicit expressions given in Table I, the spin Hamiltonian (1) transforms to

$$\mathcal{H}(\theta) = [D(1 - 3/2 \sin^2\theta) \pm 3/2 E \sin^2\theta] \\ \times [S_z^2 - 1/3S(S+1)] - \frac{1}{2}(D \mp E) \sin\theta \cos\theta \\ \times [(S_+ + S_-)S_z + S_z(S_+ + S_-)] \\ + \frac{1}{4}[D \sin^2\theta \pm E(1 + \cos^2\theta)](S_+^2 + S_-^2). \quad (4)$$

In the sign combination of Eq. (4) and the following equation (5), the upper sign corresponds to $\alpha=0^\circ$, the lower sign to $\alpha=90^\circ$. For $\alpha=0^\circ$ and $3E=-D$, as well as for $\alpha=90^\circ$ and $3E=+D$, Eq. (4) changes to the simpler form

$$\mathcal{H}(\theta) = D \cos 2\theta [S_z^2 - 1/3S(S+1)] \\ \pm E \sin 2\theta [(S_+ + S_-)S_z + S_z(S_+ + S_-)] \\ \pm \frac{1}{2} E \cos 2\theta (S_+^2 + S_-^2). \quad (5)$$

¹¹ G. Racah, *Irreducible Tensorial Sets* (Academic Press, Inc., New York, 1959).

¹² It should be noted that $T_l^{m'}$ are tensor components in the rotated coordinate system; because $D_l^{mm'}(\alpha,\beta,\gamma)$ is a unitary matrix, the inverse transformation is given by

$$T_l^m = \sum_{m'} [D_l^{mm'}(\alpha,\beta,\gamma)]^* T_l^{m'}.$$

The matrix elements of this Hamiltonian satisfy the condition

$$[\mathcal{H}(\theta)]_{m,m'} = -[\mathcal{H}(90-\theta)]_{-m,-m'}. \quad (6)$$

As a consequence of Eq. (6) the energy levels of the Hamiltonian $\mathcal{H}(\theta)$ differ from those of the Hamiltonian $\mathcal{H}(90-\theta)$ only by a factor -1 , so that the transitions between two energy levels are exactly the same for both orientations of the magnetic field. A similar behavior is depicted by the calculated energy levels of manganese in rutile (Fig. 5), because the E/D ratio differs only slightly from $1/3$.

Since it is known, from the symmetrical behavior of the resonances in the ZY plane, that the E/D ratio is very close to $1/3$ independently of the spin value, the comparison of the angular dependence of the resonances for different spin values can easily be performed. The right side of Fig. 3 depicts the θ dependency of the resonances in the ZY plane for $S=5/2$ and for the parameters $E/D=1/3$, $D=12.1$ kMc/sec, and $g=1.990$. Only the transitions $1 \rightarrow 2$, $3 \rightarrow 4$, and $5 \rightarrow 6$ are shown, because these transitions are comparatively independent of a variation of the parameter D at large D values. The numbers of the energy levels refer to the order of ascending energy. The $5 \rightarrow 6$ transition starts for $\theta=0^\circ$ at field strengths below 1000 gauss, and its intensity is more than ten times weaker than the strong transitions for $S=5/2$. The comparison of these results with the measured and theoretical curves for $S=3/2$ in Fig. 3 proves that the electronic configuration of manganese in rutile must be described by $S=3/2$, because the curve whose symmetry behavior is equivalent to the $5 \rightarrow 6$ transition for $S=5/2$ starts above 1000 gauss with strong intensity. The spin value of $S=3/2$ indicates that the manganese atoms in rutile exist in a tetravalent state.

For $H\parallel Z$ the solutions of the secular determinant of the spin Hamiltonian (1) can be written explicitly:

$$W_{4,1} = \pm \frac{1}{2} g\beta H \pm [(g\beta H + D)^2 + 3E^2]^{1/2}, \quad (7)$$

$$W_{3,2} = -\frac{1}{2} g\beta H \pm [(g\beta H - D)^2 + 3E^2]^{1/2}.$$

The form of the transformed spin Hamiltonian (4) shows that these equations may be extended to $H\parallel X$ and $H\parallel Y$ if one changes D and E in Eq. (7) to the corresponding terms of the spin Hamiltonian (4). In order that the eigenvalues of the spin Hamiltonian (1) could be calculated for an arbitrary orientation of the magnetic field, the secular determinant was developed in the form:

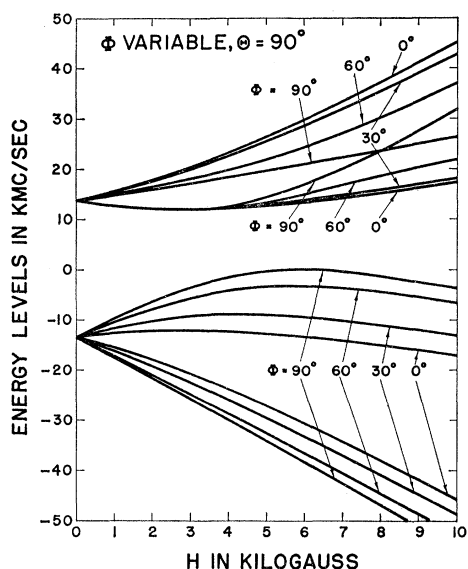


FIG. 4. Energy levels of manganese in rutile for various magnetic field orientations in the XY plane.

$$0 = W^4 - W^2 \left[\frac{5}{2} (g\beta H)^2 + 2D^2 + 6E^2 \right] + W (g\beta H)^2 (2D - 6D \cos^2 \theta - 6E \sin^2 \theta \cos 2\phi) + (D^2 + 3E^2)^2 + \frac{9}{16} (g\beta H)^4 + \frac{1}{2} (g\beta H)^2 (D^2 - 6D^2 \cos^2 \theta + 9E^2 \cos 2\theta + 12DE \sin^2 \theta \cos 2\phi). \quad (8)$$

The symbols are as follows: W = energy, θ = angle between Z axis and magnetic field, and ϕ = angle between X axis and the projection of the magnetic field in the XY plane. The linear term of Eq. (8) vanishes for

$$E/D = \frac{1}{3} (1 - 3 \cos^2 \theta) / \sin^2 \theta \cos 2\phi. \quad (9)$$

In this case the solutions of Eq. (8), which can be ob-

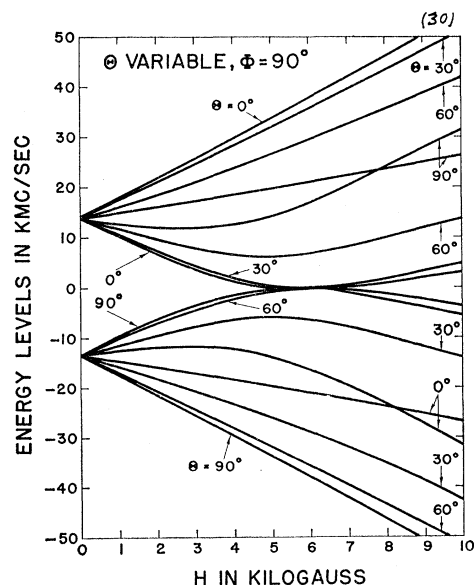


FIG. 5. Energy levels of manganese in rutile for various magnetic field orientations in the ZY plane.

tained explicitly, indicate that the difference between energy levels 1 and 2 is equal to the difference between levels 3 and 4. Thus the E/D ratio can be determined independently of the other parameters of the spin Hamiltonian, provided there is a superposition of the two transitions $1 \rightarrow 2$ and $3 \rightarrow 4$. These superpositions were actually observed for two different crystal orientations at $\theta = 71^\circ$, $\phi = 18.5^\circ$ and $\theta = 82^\circ$, $\phi = 3^\circ$. The E/D ratios, which were calculated by means of Eq. (9), agreed within the limits of error with the value found by a more accurate method described below. The more precise E/D ratio was derived from the difference between the magnetic fields $H_1 = 3295$ gauss and $H_2 = 3475$ gauss, attributed to the transitions $1 \rightarrow 2$ and $3 \rightarrow 4$ at $\theta = 90^\circ$ and $\phi = 0^\circ$. By changing D and E in Eq. (7) to the corresponding terms of the spin Hamiltonian (4) for $H \parallel X$, expanding, where possible, the square roots

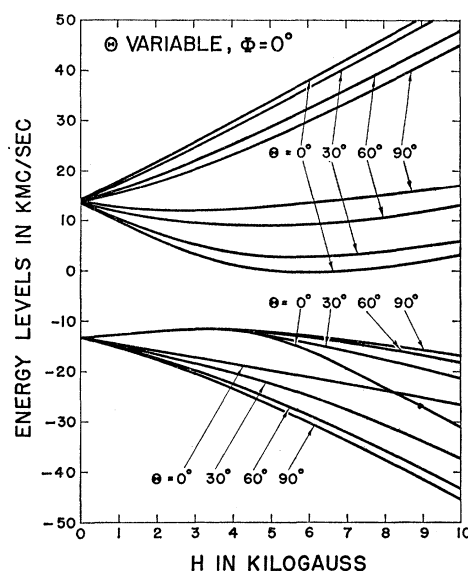


FIG. 6. Energy levels of manganese in rutile for various magnetic field orientations in the ZX plane.

to first order,¹³ and utilizing the fact that both transitions were measured at the same frequency, one may obtain the equation

$$H_2 - H_1 = (3E/D - 1)D \{ H_1 [(g\beta H_1)^2 + \frac{3}{4}(E+D)^2]^{-\frac{1}{2}} + H_2 [(g\beta H_2)^2 + \frac{3}{4}(E+D)^2]^{-\frac{1}{2}} \}. \quad (10)$$

This relationship is very useful for an accurate determination of the ratio E/D , provided the E/D ratio differs only slightly from the value $1/3$. The g factor could be determined most accurately from the $3 \rightarrow 4$ transition at 1247 gauss and $\theta = 0^\circ$. The parameter D was determined by fitting the solutions of Eq. (8) to the resonances that show a minimum at $\theta = 45^\circ$ in the ZY plane (Fig. 3). These resonances are related to the $2 \rightarrow 3$ transition and are, therefore, sensitive to any

¹³ The expansion of the roots is based on the assumption $|(3E-D)[\frac{1}{4}(3E-D) \pm g\beta H]| \ll (g\beta H)^2 + \frac{3}{4}(E+D)^2$.

variation of the parameter D . The results are

$$g = 1.990 \pm 0.003, \quad |E/D| = 0.321 \pm 0.001, \\ |D| = 12.1 \pm 0.1 \text{ kMc/sec.}$$

Using these values, Eq. (8) was solved numerically on a Burroughs 220 digital computer; the resulting energy levels are shown in Figs. 4, 5, and 6 for different crystal orientations as a function of the magnetic field. The centers of all observed hyperfine structure patterns (Figs. 2 and 3) agree with an accuracy of better than 1% with those predicted by Eq. (8).

The hyperfine structure pattern consists of at least six lines, resulting from the spin value $I = 5/2$ of the Mn⁵⁵ nucleus. At some crystal orientations five additional lines, occurring about halfway between the six main lines, were observed. These lines may be attributed to "forbidden" transitions $|\Delta M| = 1$, $|\Delta m| = 1$. Along the three magnetic axes X , Y , and Z , the over-all splitting between the outer lines of the hyperfine structure pattern was determined to be 390, 379, and 390 gauss, respectively. Because of the apparent anisotropy, the hyperfine structure interaction should be described by a term $A_x S_x I_x + A_y S_y I_y + A_z S_z I_z$. Along the three magnetic axes, the over-all splitting, in the first approximation, is independent of the parameters D , E , and the magnetic field H , and is given by the terms $(5A_x/g\beta)$, $(5A_y/g\beta)$, and $5A_z/g\beta$, respectively. However, since the resulting parameters $|A_x| = 218$ Mc/sec, $|A_y| = 211$ Mc/sec, and $|A_z| = 218$ Mc/sec indicate only a small deviation from isotropy, one may describe, within the accuracy of this experiment, the hyperfine structure interaction by an isotropic term $A\mathbf{S} \cdot \mathbf{I}$ with $|A| = 215$ Mc/sec. It seems worthwhile, however, to analyze the hyperfine structure more precisely, especially since the "forbidden" transitions are comparatively sensitive to a nuclear quadrupole interaction.

DISCUSSION

The Mn⁴⁺ ion has the same electronic configuration as the Cr³⁺ ion. Comparing the paramagnetic data of both ions¹⁴ when they replace the Ti⁴⁺ ions in the rutile crystal, one observes two essential differences: Sub-

stituting Mn⁴⁺ instead of Cr³⁺ for a Ti⁴⁺ ion in the rutile crystal results in a slightly different distortion of the surrounding oxygen octahedron, since the smallest E/D ratio of Cr³⁺ is correlated with the Z axis parallel to the $[110]$ direction, whereas the E/D ratio of Mn⁴⁺ is smallest for $Z \parallel c$. The g factor of Mn⁴⁺ (1.99) is considerably larger than the g factor of Cr³⁺ (1.97); it is nearly the same as that of Cr^{III}($3d^3$) in the $[\text{Cr}(\text{CN})_6]^{3+}$ complex,¹⁵ where strong covalent bonding is present. Therefore, one may assume that manganese in rutile also has strong admixtures of covalent bonds, so that the notation Mn^{IV}($3d^3$) instead of Mn⁴⁺ is more appropriate. This is confirmed by the comparatively small hyperfine structure parameter $|A| = 215$ Mc/sec,^{1,2} since one can show that Mn⁴⁺ should have at least a hyperfine structure parameter of 365 Mc/sec or larger, assuming that the bonds of Mn⁴⁺ and Cr³⁺ in rutile are exactly equivalent. This estimate can easily be made if one takes into consideration the well-known hyperfine structure splitting of (Cr⁵³)³⁺ in rutile,¹⁴ the different spins and magnetic moments of the Mn⁵⁵ and Cr⁵³ nuclei, and the contraction of the electron orbits of Mn⁴⁺ due to the higher effective charge. Manganese in rutile is another example which proves that a tetravalent atom has stronger covalent bonds than a trivalent atom with the same electronic configuration and in the same lattice position.¹⁶ This fact also increases the possibility that the Ti bond in rutile is not completely ionic, but has additional admixtures of covalent bonds.¹⁷

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¹⁵ J. M. Baker, B. Bleaney, and K. D. Bowers, Proc. Phys. Soc. (London) **B69**, 1205 (1956).

¹⁶ J. Owen, Proc. Roy. Soc. (London) **A227**, 183 (1955).

¹⁷ W. H. Baur, Acta Cryst. **9**, 515 (1956).

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