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F- and *X*-Band Spectroscopy on Fe^{3+} in Rutile

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The parameters in the spin Hamiltonian for Fe^{3+} in rutile (TiO_2) have been reevaluated using experimental data at 9.400 and 121.3 Gc/sec. With a Hamiltonian of the form

$$H=\beta \mathbf{H}\cdot g\cdot \mathbf{S}+D(S_z^2-35/12)+E(S_x^2-S_y^2)+(a/6)(S_x^4+S_y^4+S_z^4-707/16)$$
$$+(7/36)F[S_z^4-(95/14)S_z^2+81/16]+C[(7S_z^2-35/4)(S_x^2-S_y^2)+(S_x^2-S_y^2)(7S_z^2-35/4)],$$

with $g=2.000\pm0.005$, $D=20.38\pm0.01$ Gc/sec, $E=2.06\pm0.01$ Gc/sec, $F=0.68\pm0.02$ Gc/sec, $a=-0.84\pm0.04$ Gc/sec, and $C=0.00\pm0.01$ Gc/sec, the magnetic field strengths for ESR can be predicted within 1% or better for fields up to 12 kOe.

INTRODUCTION

The spin Hamiltonian and the associated parameters describing the energy-level structure of the ground state of Fe^{3+} in rutile were first published by Carter and Okaya.[1] Differences between the electron-spin-resonance spectrum calculated from this Hamiltonian and experimental data were already noted by Schollmeier[2] working at the *X* band, and were found to be intolerably large at high microwave frequencies like 120 Gc/sec (F band). For the present work the synthesis of the spin Hamiltonian for Fe^{3+} in rutile was reexamined and the parameters adjusted to obtain an improved representation of the spectrum at 9.4 and 121.3 Gc/sec.

The electronic configuration of the free Fe^{3+} ion is $3d^5\ {}^6S$ and therefore the ground state is a nondegenerate orbital singlet. For such cases the terms in the spin Hamiltonian are usually obtained from symmetry arguments. The unit cell of rutile contains two equivalent lattice sites of local orthorhombic (D_{2h}) symmetry[3,4] into which an Fe^{2+} ion can be substituted.

Neglecting nuclear interactions, the spin Hamiltonian may be broken down into a magnetic-field-dependent part and zero-field splitting terms. For reasonably low magnetic fields (say, up to 10 kOe), the dominant field-dependent term is $\beta\mathbf{H}\cdot g\cdot\mathbf{S}$,[5–7] where g is the spectroscopic splitting factor tensor, β is the Bohr magneton, $\mathbf{H}$ is the applied magnetic field, and $\mathbf{S}$ is the vector sum of the spin operators S_x, S_y, and S_z. The zero-field terms can be selected from tables of Stevens's angular momentum operator equivalents[5,8,9] by testing the tesseral harmonic expansion terms, which describe the crystalline electric field potential operators, for the symmetry properties of the paramagnetic site. For $S=\frac{5}{2}$, only terms involving the second and fourth powers of the spin operators are necessary.[5,8,10] Using the Hamiltonian coordinate system and parameters consistent with the literature,[1,2] the spin Hamiltonian for D_{2h} symmetry and $S=\frac{5}{2}$ is given by

$$H=\beta\mathbf{H}\cdot g\cdot\mathbf{S}+D(S_z^2-35/12)+E(S_x^2-S_y^2)$$
$$+(a/6)(S_x^4+S_y^4+S_z^4-707/16)+(7/36)$$
$$\times F[S_z^4-(95/14)S_z^2+81/16]+C[(7S_z^2-35/4)$$
$$\times(S_x^2-S_y^2)+(S_x^2-S_y^2)(7S_z^2-35/4)], \quad (1)$$

where g, D, E, a, F, and C, are parameters which must be evaluated experimentally. The last term in the above expression has so far not been included explicitly in the literature describing the spectrum of Fe^{3+} in rutile.

SPECTROSCOPIC MEASUREMENTS AND RESULTS

The spectrum of the strong transitions of Fe^{3+} in rutile was measured at 9.400±0.001 and 121.3±0.05 Gc/sec in the *ab* plane of the crystal as a function of the orientation and strength of the applied magnetic field using conventional electron-spin-resonance methods. Frequencies were measured with appropriately calibrated resonant wave meters while the magnetic field strength of the 12-in. magnet used was determined by NMR techniques to an accuracy of 1 part in 10^4. The homogeneity of the field over the region containing the

TABLE I. Spin-Hamiltonian parameters.

<table>
<tr><th>Parameter</th><th>Units</th><th>Carter and Okaya (1960)</th><th>Schollmeier (1966)</th><th>This work</th></tr>
<tr><td>g</td><td>···</td><td colspan="2">2.000±0.005</td><td>2.000±0.005</td></tr>
<tr><td>D</td><td>Gc/sec</td><td colspan="2">20.35±0.01</td><td>20.38 ±0.01</td></tr>
<tr><td>E</td><td>Gc/sec</td><td colspan="2">2.21±0.07</td><td>2.06 ±0.01</td></tr>
<tr><td>F</td><td>Gc/sec</td><td colspan="2">−0.5 ±0.3</td><td>0.68±0.02</td></tr>
<tr><td>a</td><td>Gc/sec</td><td>1.10±0.1</td><td>+1.10±0.1
(diag. elem.)
−1.10±0.1
(off-diag. elem.)</td><td>−0.84±0.04</td></tr>
<tr><td>C</td><td>Gc/sec</td><td>···</td><td>···</td><td>0.00 ±0.01</td></tr>
</table>

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TABLE II. Summary of experimental transition fields and corresponding deviations of calculated values for Fe^{3+} in rutile, $\phi=0°$.

Frequency (Gc/sec)	Transition	Angle θ (deg)	Experimental H (Oe)	Estimated possible error (Oe)	Deviations of calculated values from experimental values: Carter and Okaya (1960) (Oe)	Schollmeier (1966) (Oe)	This work (Oe)
9.400	$\frac{3}{2}\rightarrow-\frac{3}{2}$	0	1 191	± 5	+ 41	+ 3	− 3
	$\frac{1}{2}\rightarrow-\frac{1}{2}$	0	4 275	+ 5	+ 61	+ 75	+ 5
	$\frac{3}{2}\rightarrow-\frac{3}{2}$	45	1 551	± 5	+ 24	+ 35	− 3
	$\frac{1}{2}\rightarrow-\frac{1}{2}$	45	2 475	± 5	+161	−118	−12
	$\frac{1}{2}\rightarrow-\frac{1}{2}$	90	1 938	± 5	+ 24	− 9	−18
	$\frac{3}{2}\rightarrow-\frac{3}{2}$	90	2 638	± 5	+188	− 47	−15
121.30	$-\frac{5}{2}\rightarrow\frac{1}{2}$	0	400	± 5	+ 44	+ 46	− 1
	$-\frac{5}{2}\rightarrow-\frac{1}{2}$	0	562	± 5	+ 59	+ 64	+ 1
	$\frac{5}{2}\rightarrow-\frac{3}{2}$	0	3 719	± 5	+129	+140	+23
	$-\frac{5}{2}\rightarrow-\frac{1}{2}$	45	500	±15	+ 40	+ 44	− 5
	$\frac{5}{2}\rightarrow-\frac{3}{2}$	45	5 652	±15	+108	+151	+54
	$-\frac{5}{2}\rightarrow-\frac{1}{2}$	45	9 220	±40	−369	+ 56	+58
	$\frac{3}{2}\rightarrow-\frac{1}{2}$	45	11 025	±40	+513	+ 57	+48
	$\frac{3}{2}\rightarrow-\frac{1}{2}$	90	9 252	±10	+158	− 74	+51

sample and the NMR probe was better than 1 part in 10^4. All measurements were carried out on artificially grown rutile samples (courtesy of RCA, Camden, N.J.) containing 0.035–0.050% of Fe^{3+} as shown by spectrographic analysis. The crystal axes were determined within 1° by the Laue x-ray back-reflection method. The orientation in the magnetic field was checked again by observing the symmetry of the ESR spectrum.

The spin-Hamiltonian parameters listed in the last column of Table I were evaluated using experimental data for θ equal to 0°, 45°, and 90°, as is shown in Table II. The dependence of the magnetic field strengths required for various transitions on the individual spin-Hamiltonian parameters was studied numerically at these angles by diagonalizing the Hamiltonian matrix on an IBM 360 computer.

Weighting the experimental data according to the maximum expected experimental errors listed in Table II, the parameters were adjusted by iteration for minimum deviation between the calculated and the observed transition fields.

The possible uncertainty in the various parameters in the last column of Table I was determined by plotting the transition field deviations as a function of each parameter. The range over which the sum of the absolute values of errors for all transitions considered was constant within about 20% is given as the error associated with each parameter.

DISCUSSION OF RESULTS

Table II shows that the spin-Hamiltonian parameters presented here give a much improved description of the spectrum of Fe^{3+} in rutile. A more reliable evaluation of the parameters was made possible by the fact that some transitions at 121.3 Gc/sec are very sensitive to small changes in the Hamiltonian matrix. It is not felt that the data presented are peculiar to the particular crystal studied, as the same results were obtained, within the error, from measurements on a very dilute crystal obtained from a different source.

The estimated possible errors in Table II are ascribed to uncertainties in the determination of the resonance line center. At *X* band this error is expected not to exceed ±5 Oe, while at *F* band it could be as large as ±40 Oe, particularly for θ near 45°, where the transition fields are relatively independent of the magnetic field. By comparison, errors in the frequency and magnetic field strengths measurements are expected to be negligible.

For some transitions the deviations listed in the last column of Table II are still larger than the expected possible errors. This may indicate that the field-dependent term $\beta\mathbf{H}\cdot g\cdot\mathbf{S}$ is not sufficient to describe the splittings, and some of the terms involving higher powers of **H** may have to be included.[6,7] The calculation of the additional parameters would require measurements above 100 kOe, which was beyond the scope of this work.

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