broad. With the limited amount of information about the crystalline-field parameters at this time, it might be presumptuous to push this point too much further. Nevertheless, for the specific case of V^{3+} in corundum crystals, γ apparently can be accounted for by the point-charge model. Even for τ the result from the empirical point-charge picture is not incompatible with the present optical and magnetic data.

ACKNOWLEDGMENTS

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Electron Paramagnetic Resonance of Cr^{3+} in SnO_2

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The paramagnetic resonance spectrum of the ground state of Cr^{3+} in SnO_2 (cassiterite) was studied at 23.5 and 34.4 kMc/sec. The derived constants of the spin Hamiltonian for the magnetic Z axis coinciding with the crystal c axis are: $|g|=1.975$, $D=+17.3$ kMc/sec, $|E|=8.44$ kMc/sec, and $|A|=42$ Mc/sec.

INTRODUCTION

THE resonance spectrum of the ground state of Cr^{3+} in SnO_2 has been studied to determine the constants of the spin Hamiltonian and to compare these results with those obtained for Cr^{3+} in TiO_2.[1] SnO_2 and the rutile form of TiO_2 belong to the same crystal class, each having tetragonal symmetry. The measured atomic parameters[2] of the two structures, as well as the constants of the spin Hamiltonian, are quite similar.

CRYSTAL STRUCTURE

SnO_2 is a member of the rutile class of crystal structures which are tetragonal and belongs to the D_{4h} point group.[3] The SnO_6 and TiO_6 octahedra differ only slightly from each other as noted below.[2] As in TiO_2, the unit cell consists of two nonequivalent Sn^{4+} sites which can be transformed into each other by a rotation of 90° about the c axis, [001] (Fig. 1). (See Ref. 8.) Even though the SnO_6 octahedra are slightly deformed thus giving local symmetry D_{2h}, i.e., orthorhombic, about an Sn^{4+} site, the resonance data give local symmetry of D_{4h} which is due to the particular way the two nonequivalent sites transform into each other. The two sites are magnetically equivalent when the dc magnetic field lies in the (100) or (010) planes.

	SnO_6 (Å)	TiO_6 (Å)
a	4.737	4.594
C	3.185	2.959
(A–B) site 1	2.052	1.944
(A–B) site 2	2.056	1.988

EXPERIMENT

The crystals used in the experiment were grown at Lincoln Laboratory under the direction of Dr. T. Reed. The growth habit of the Cr^{3+} doped crystals differed from those doped with other paramagnetic ions. The former had the c axis oriented perpendicular to the crystal-growth axis, whereas with other paramagnetic ions the two coincided. Data concerning the techniques for growing the crystals are described elsewhere.[4]

Nearly all resonance measurements were made at 77°K. A 100 kMc/sec phase-sensitive detection system was used and it, as well as the microwave system, are

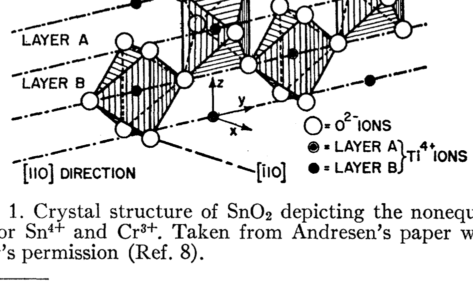

FIG. 1. Crystal structure of SnO_2 depicting the nonequivalent sites for Sn^{4+} and Cr^{3+}. Taken from Andresen's paper with the author's permission (Ref. 8).

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* Operated with support from the U. S. Army, Navy, and Air Force.

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

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[4] T. B. Reed, J. T. Roddy, and A. N. Mariano, J. Appl. Phys. 33, 1014 (1962).

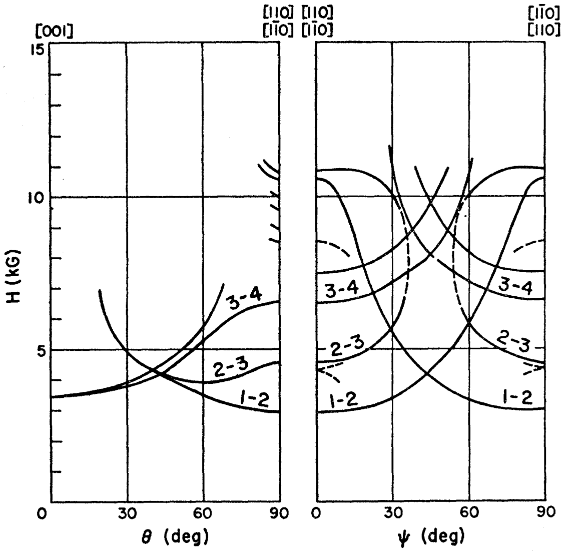

FIG. 2. Observed resonances of Cr^{3+} in SnO_2 at 23.5 kMc/sec.

described in an unpublished report,[5] with the exception that the 100 kMc/sec modulation and phase detection system described in the report was replaced by one designed and manufactured by Triconix, Inc. The cavity design techniques[5] permitted accurate orientation of the crystals since adjustments could be made *in situ*. Also, crystals could be transferred from a cavity at one frequency to that of another without requiring removal of the crystal from its mount. The resonance data were taken directly from a scope presentation on which, on a shared time basis, was superimposed the nuclear magnetic resonance (NMR).

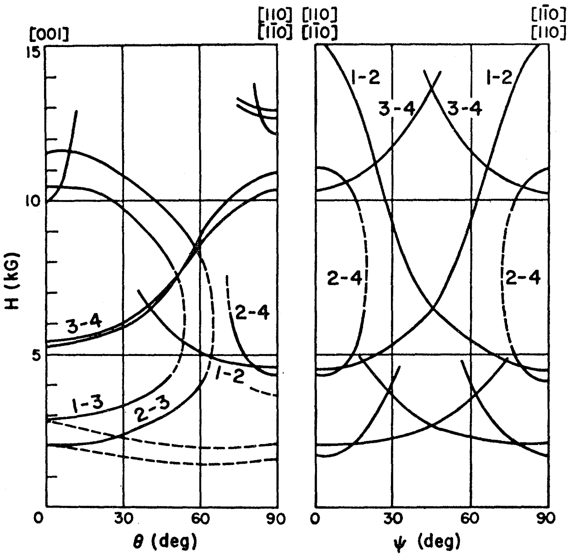

FIG. 3. Observed resonances of Cr^{3+} in SnO_2 at 34.4 kMc/sec.

Thus, accurate measurements of the magnetic field could be made directly and this technique also afforded a check on the microwave frequency in conjunction with the observed hydrazyl resonance.

The resonance data obtained at 23.5 and 34.4 kMc/sec as a function of magnetic field and orientation are given in Figs. 2 and 3. Figure 4 depicts the measurement of the zero-field splitting. An additional check was made at 60.6 kMc/sec with H parallel to C.

Spectrochemical analysis indicated the Cr^{3+} impurity replaced approximately 0.05% of the Sn ions and that Cu, V, and Al were also present and their concentrations were more than one order of magnitude less than that of Cr^{3+}. The vanadium resonance was recognized, but some other existing lines were not identified.

RESULTS

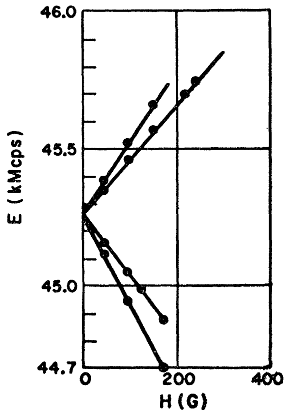

FIG. 4. Extrapolation of resonance data to zero magnetic field.

The ground state of Cr^{3+} is a spin quadruplet $^4F_{3/2}$ which in an orthorhombic environment is described by the following spin Hamiltonian[6]:

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

The constants $|g|$, D, $|E|$, and $|A|$ were machine-computed from the resonance data at 23.5 and 34.4 kMc/sec with the results

$$\begin{aligned}|g|&=1.975\pm0.005,\\ D&=17.3\pm0.1\text{ kMc/sec},\\ |E|&=8.34\pm0.1\text{ kMc/sec},\\ |A|&=42\text{ Mc/sec}.\end{aligned}$$

These data are given according to the magnetic z axis coinciding with the c axis. There is a convention, however, that the z axis be the one for which the ratio E/D is a minimum. By using the technique outlined in Bowers and Owen,[7] this can be easily achieved giving

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[5] W. H. From, and E. D. Mills, Lincoln Laboratory, MIT, Report 82G-1, 1962 (unpublished).

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

[7] K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 321.

the results

$$|g| = 1.975,$$
$$D = -21.31 \text{ kMc/sec},$$
$$|E| = 4.43 \text{ kMc/sec},$$
$$|A| = 42 \text{ Mc/sec}.$$

The author believes, in this case, that such a convention would be confusing since the arrangement used in the text is the more natural one. The magnetic axes are

z axis is parallel to c, [001] direction,
x axis is parallel to the [110] direction,
y axis is parallel to the [1$\bar{1}$0] direction.

By the use of standard techniques,[8] the operators in the above Hamiltonian can be transformed to a more useful form for arbitrary orientation of the applied magnetic field with respect to the crystal axes. This was done in order to easily calculate the E/D ratio as well as the zero-field splitting. The transformed 4×4 secular determinant leads to the fourth-degree equation

$$\begin{aligned} W^4 - W^2[\tfrac{5}{2}(g\beta H)^2 + 2D^2 + 6E^2] + W(g\beta H)^2 \\ \times[2D - 6D\cos^2\theta - 6E\sin^2\theta\cos 2\phi] \\ + \tfrac{9}{16}(g\beta H)^4 + \tfrac{1}{2}(g\beta H)^2[D^2 - 6D^2\cos^2\theta \\ + 9E^2\cos 2\theta + 12DE\sin^2\theta\cos 2\phi] \\ + (D^2+3E^2)^2 = 0. \end{aligned}$$

$H \equiv$ applied dc magnetic field;
$\theta \equiv$ angle between the z axis and H;
$\phi \equiv$ angle between the x axis and the projection of H in the xy plane.

The zero-field splitting is obtained by setting $H=0$ and the result is

$$W_{3,4} - W_{1,2} = 2(D^2+3E^2)^{1/2}.$$

By setting the coefficient of W to zero, one obtains symmetric energy levels, i.e., $W_1 - W_2 = W_3 - W_4$, where the ordering is according to increasing energy. The orientations under which this condition is prescribed lead to the determination of the ratio of E to D, i.e.,

$$\frac{E}{D} = \frac{1-3\cos^2\theta}{3\sin^2\theta\cos 2\phi}.$$

For $\theta = 90°$, experimental checks were made at 23.5 and 34.7 kMc/sec for the angle ϕ at which the transition $W_1 - W_2$ crossed that of $W_3 - W_4$. The angle ϕ was determined to be 23.4°±0.3° and this served as a check of the computed values of E and D. The sign of D was determined from measurements at 4.2 and 1.6°K.

TABLE I. Comparison of results.

	Cr^{3+} in SnO_2	Cr^{3+} in TiO_2
Dielectric constant[a]	23–24	86–170
Zero-field splittings (kMc/sec)	45.3±0.1	43.3
Relaxation time (sec)	$\sim 10^{-2}$	5×10^{-2}
Constants of spin Hamiltonians		
$\|g\|$	1.975	1.97
D (kMc/sec)	17.3	16.5
$\|E\|$ (kMc/sec)	8.4	8.1
$\|A\|$ (Mc/sec)	42	45

[a] *Handbook of Physics and Chemistry* (The Chemical Rubber Publishing Company, Cleveland, Ohio, 1960–61), 42nd ed.

CW relaxation-time measurements[9] were made at 4.2°K and 23.03 kMc/sec on the W_{1-2} and W_{3-4} transitions. Saturation occurred at 0.75 and 0.92 mW, respectively, for these transitions. The resultant calculations using the respective linewidths of 11 and 17 G gave approximate values of T_1 of 10^{-2} sec.

COMPARISON OF Cr^{3+} IN SnO_2 AND TiO_2

The energy levels of Cr^{3+} in SnO_2 show remarkable similarity to those of Cr^{3+} in TiO_2. The relaxation time of Cr^{3+} in SnO_2 may be slightly shorter than that of Cr^{3+} in TiO_2; however, the CW measurement gives only an order-of-magnitude measurement. A comparison of results for the two crystals is given in Table I.

The difference in the hyperfine structure constants $|A|$ could be due to stronger covalent bonding in the SnO_2 complex than in the TiO_2 complex.[7] With increasing covalent bonding one would also expect, in this case, an increase in the g factor which is noted but is not significant.

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[8] H. G. Andresen, Phys. Rev. **120**, 1606 (1960).

[9] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).