

Paramagnetic Resonance Spectra of Cr^{3+} in ZnWO_4 *

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Paramagnetic resonance measurements have been carried out at millimeter and centimeter wavelengths on Cr^{3+} ions diluted in single crystals of ZnWO_4 grown from the melt. The spectrum is described by the spin Hamiltonian

$$H = D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + A\mathbf{I} \cdot \mathbf{S},$$

with $S = \frac{3}{2}$; $D = +25.47 \pm 0.01$ kMc/sec; $E = -2.42 \pm 0.03$ kMc/sec; $g_x = 1.958 \pm 0.002$; $g_y = 1.962 \pm 0.002$, and $g_z = 1.968 \pm 0.002$ at 293°K. The spin-orbit coupling constant found from these parameters is positive as expected. The magnetic hyperfine splitting factor $|A|$ for Cr^{63} ($I = \frac{3}{2}$) was found to be 0.052 ± 0.002 kMc/sec at 4.2°K and isotropic within the limits of error. The magnetic y axis is parallel to the monoclinic b axis and the magnetic z axis is rotated away from the crystal $+a$ axis toward the $+c$ axis by 4.2 ± 0.5 deg.

INTRODUCTION

ZINC tungstate is an interesting and convenient host structure for investigating the paramagnetic resonance spectra of transition-group ions for several reasons:

1. Large single crystals containing controlled amounts of $3d$ and $4f$ transition-group ions can be grown from the melt¹ by the Czochralski technique.
2. Zinc tungstate crystals are reasonably hard (approximately 5.5 on the Moh's scale²) and chemically stable. Also, they cleave readily in the (010) plane.³ This simplifies the alignment of the susceptibility axes, one of which must lie along the [010] direction.⁴
3. The two zinc sites in each unit cell are paramagnetically equivalent.
4. Absorption linewidths in the limit of low concentrations are quite small owing to the absence of significant abundances of ligand ions with nuclear magnetic moments. Such narrow absorption lines are convenient for investigating hyperfine structure with small splittings.
5. The low point symmetry of the substitution site gives the three susceptibility axes unique directions with respect to the crystallographic axes. Such information might be of interest in deriving the directional properties of orbital wave functions for different paramagnetic ions in the crystal. This paper gives the results for Cr^{3+} ($^4F_{3/2}$).

THE HOST CRYSTAL

Zinc tungstate belongs to an isostructural^{3,5} series of monoclinic tungstates which includes MgWO_4 and

NiWO_4 . Broch⁶ determined the most probable space group of MgWO_4 to be $C_{2h}^4(P2/c)$ with two formula units per unit cell. He also determined the unit cell dimensions of ZnWO_4 to be $a = 4.68$, $b = 5.73$, $c = 4.95$ Å, and $\beta = 90^\circ 30'$. Recent work by Keeling⁷ on NiWO_4 indicates that each metal ion is surrounded by six oxygen ions which form a distorted octahedron.

Zinc tungstate crystals doped with Cr^{3+} (0.001 to 0.1 mole % in the melt) were pulled from the melt by the Czochralski technique as described by Van Uitert and Preziosi.¹ The Cr^{3+} ion probably substitutes for Zn^{2+} rather than W^{6+} since in the former case there will be considerably less charge unbalance. Additional support for this conclusion was obtained by doing a point charge calculation using the susceptibility axes determined experimentally in the present work and assuming the oxygen positions given by Keeling for NiWO_4 . Chromium substitution in the zinc site yields D greater than E in magnitude and of opposite sign in agreement with experiment, whereas chromium substitution in the tungsten site gives E greater than D in magnitude and of the same sign in disagreement with experiment.

To insure charge compensation, lithium ions in molar concentrations about 1–10 times that of chromium were added to the melt. The Li^+ ions presumably substitute for Zn^{2+} ions to form $\text{Li}^+-\text{Cr}^{3+}$ compensated pairs. Samples prepared without added lithium ion in the melt exhibited a more complicated paramagnetic resonance spectrum for Cr^{3+} which appeared to be due to the presence of sites with slightly different rotation vs magnetic field characteristics. This more complicated spectrum may have its origin in local distortions around the substitution site caused by charge unbalance.

The location of the crystallographic and susceptibility axes was found from a crystal which was cleaved in the (010) plane. A back reflection Laue x-ray photograph with the incident beam along the b axis was used to locate the a and c axes. The identification of the crystal-

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¹ L. G. Van Uitert and S. Preziosi, *J. Appl. Phys.* (to be published).

² L. G. Van Uitert and R. R. Soden, *J. Appl. Phys.* **31**, 328 (1960).

³ F. Palache, H. Berman, and C. Frondel, *Dana's System of Mineralogy* (John Wiley & Sons, Inc., New York, 1951), 7th ed., Vol. II, p. 1070.

⁴ B. Bleaney and K. W. H. Stevens, *Repts. Progr. Phys.* **16**, 108 (1953).

⁵ F. Machatschki, *Z. Krist.* **67**, 163 (1928).

⁶ E. K. Broch, *Z. physik. Chem.* **1B**, 409 (1928), *E. K. Broch, Skrifter Norske Videnskaps-Akad Oslo. I. Mat. Naturv.* **K1**, **K7**, 8 (1929).

⁷ R. O. Keeling, *Acta Cryst.* **10**, 209 (1957).

lographic axes was verified by direct measurement of the lattice constants using an x-ray goniometer with $\text{Cu-K}\alpha$ radiation in second-order Bragg reflection. The values obtained for the unit cell parameters a , b , c , and β were in good agreement with the early work of Broch.⁶ Also, the odd reflections along the c^* axis ($00l$ with l odd) were found to be absent as expected for the $P2/c$ space group.⁸ Keeling⁷ obtained a similar result for NiWO_4 . The principal susceptibility axes for Cr^{3+} in ZnWO_4 were found to be oriented with y along the b axis, x and z in the (010) plane, and z rotated 4.2 ± 0.5 deg from the $+a$ towards the $+c$ axis.

EXPERIMENTAL APPARATUS

The millimeter-wave spectrometer consisted of a backward-wave oscillator, a tunable transmission cavity and a crystal detector. The absorption line was displayed on an oscilloscope using 60-cps modulation to sweep both the magnetic field and oscilloscope simultaneously. Frequencies were measured by zero-beating the backward-wave oscillator against a stabilized X-band klystron and measuring the klystron frequency with a transfer oscillator and an electronic frequency counter. The X-band measurements were made on a bridge-type superheterodyne spectrometer which used a single sideband generator to derive the signal frequency from the local oscillator frequency. Magnetic fields were measured by superimposing on a dual-trace oscilloscope the proton or lithium resonance absorption from a nuclear magnetic resonance fluxmeter and the paramagnetic resonance absorption.

RESULTS AND DISCUSSION

The observed paramagnetic spectra were fitted to the spin Hamiltonian for Cr^{3+} ion in a monoclinic crystalline field which is given by⁹

$$H = \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + D(S_z^2 - \frac{1}{3}S(S+1)) + E(S_x^2 - S_y^2) + A\mathbf{I} \cdot \mathbf{S},$$

where β is the Bohr magneton and $S = \frac{3}{2}$. Initial measurements were made along the z axis at low magnetic fields (below 1000 gauss). The energy levels for H parallel to the z axis are given by⁹

$$W(\pm\frac{3}{2}) = \pm(g_z\beta H/2) + (D^2 + 3E^2 \pm 2g_z\beta DH + g_z^2\beta^2 H^2)^{1/2},$$

$$W(\pm(\frac{1}{2})) = \mp(g_z\beta H/2) - (D^2 + 3E^2 \mp 2g_z\beta DH + g_z^2\beta^2 H^2)^{1/2},$$

where "pseudo" low field quantum numbers are used to label the energy levels.

The transition frequency versus magnetic field data along the z axis at low fields for the $-(\frac{1}{2}) \rightarrow -(\frac{3}{2})$ and $+(\frac{1}{2}) \rightarrow +(\frac{3}{2})$ absorption lines were fitted to

TABLE I. Spin Hamiltonian parameters for Cr^{3+} ion in ZnWO_4 .^a

$g_x = 1.958 \pm 0.002$ (290°K)
$g_y = 1.962 \pm 0.002$ (290°K)
$g_z = 1.968 \pm 0.002$ (290°K)
$D = +25.47 \pm 0.01$ kMc/sec (290°K)
$E = -2.42 \pm 0.03$ kMc/sec (290°K)
$ A $ for $\text{Cr}^{53} = 0.052 \pm 0.002$ kMc/sec (42°K)

^a y axis along monoclinic b axis; z axis in (010) plane rotated 4.2 ± 0.5 from $+a$ toward $+c$ axis.

straight lines. The intercept at zero field gave a zero-field splitting [equal to $2(D^2 + 3E^2)^{1/2}$] of 51.625 ± 0.040 kMc/sec. Also, the slope of the transition frequency versus magnetic field plots for these resonances is given very nearly at low fields by $\pm g_z\beta/h$ from which an initial value of g_z was determined. The final values of g_x , g_y , and D listed in Table I were obtained from measurements on several transitions in the intermediate field region (10 to 20 kG) where greater accuracy can be obtained.

Expressions for the energy levels with the magnetic field parallel to the x and y axes are obtained by making the customary substitutions for D , E , and g_z given in Bowers and Owen.⁹ By using the value of D determined above, $g_x = 2$, $g_y = 2$ and the value of E calculated from the zero field splittings, sufficiently accurate calculated spectra were obtained for assigning transitions at intermediate fields along the x and y axes. Precise measurements on several of these transitions gave the final values of g_x , g_y and E given in Table I.

The positive sign for D was determined from a comparison of the intensity ratio for the two Kramers doublets at 4.2 and 1.5°K. The negative sign of E was chosen so that the y axis would lie along the monoclinic b axis in conformity with the usual convention.^{10,11} Measurements of the hyperfine structure constant of Cr^{53} were done on a low concentration sample at 4.2°K using the X-band spectrometer mentioned above. The value of A was found to be isotropic to within the experimental error. The calculated spectra (using the parameters listed in Table I) were found to agree with measured spectra to within ± 30 Mc/sec.

As various workers have suggested the signs of D and E can also be deduced from the g values in the spin Hamiltonian.¹²⁻¹⁴ From the derivation of the spin Hamiltonian,^{15,16} it can be shown that

$$2D = \lambda[g_z - \frac{1}{2}(g_x + g_y)],$$

and

$$4E = \lambda[g_x - g_y],$$

¹⁰ M. Peters, Phys. Rev. **113**, 801 (1959).

¹¹ M. Peter, L. G. Van Uitert, and J. B. Mock, in *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), p. 435.

¹² J. E. Geusic, thesis, Ohio State University, 1958 (unpublished), p. 60.

¹³ S. Geschwind and J. P. Remeika, J. Appl. Phys. **33**, 370 (1962).

¹⁴ G. Emch and R. Lacroix, Helv. Phys. Acta **33**, 1021 (1960).

¹⁵ M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

¹⁶ A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

⁸ *International Tables for X-Ray Crystallography* (The Kynoch Press, Birmingham, England, 1952), Vol. I, p. 97.

⁹ K. D. Bowers and J. Owen, Repts. Progr. Phys. **18**, 304 (1955).

where λ is the spin-orbit coupling constant (positive for less than half-filled shells). In deriving these relations, it is assumed that the lowest orbital level is non-degenerate, that there is no mixing of this level with higher orbital states and that spin-spin interactions within the ion can be neglected. From the g values given in Table I, these relations predict D positive and E negative in agreement with experiment. However, the magnitude of λ calculated from the equation for $2D$ is significantly larger than the free-ion value¹⁷ of $+92 \text{ cm}^{-1}$ in apparent disagreement with the decrease in λ usually

¹⁷ D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. IX, p. 428.

found^{18,18,19} in the crystal. This anomaly may indicate that the effect of configurational mixing or spin-spin interactions should be taken into account in the derivation of the equations for D and E given above.

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¹⁸ J. Owen, Proc. Roy. Soc. (London) A227, 183 (1955).

¹⁹ M. Tinkham, Proc. Roy. Soc. (London) A236, 549 (1956).

Paramagnetic Resonance and Charge Compensation of Tetravalent Uranium (U^{4+}) in Calcium, Strontium, and Barium Fluorides

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A new electron spin paramagnetic resonance spectrum in CaF_2 doped with uranium is attributed to U^{4+} . The spectrum possesses axial symmetry about the $\langle 111 \rangle$ directions and is describable by a spin Hamiltonian with $g_L = 0 \pm 0.15$ and $g_{11} = 3.238 \pm 0.005$ at $4.2^\circ K$. The trigonal symmetry is due to the presence of charge compensating O^{2-} ions along the $\langle 111 \rangle$ directions. The spectrum is absent in crystals grown under reducing conditions. Similar results were also observed in SrF_2 and BaF_2 .

I. INTRODUCTION

PARAMAGNETIC resonance studies of uranium have been limited mostly to the trivalent ion.¹⁻³ Ghosh, Gordy, and Hill⁴ have reported a resonance in UF_4 ; unfortunately, the powder form of the sample and the high concentration made the interpretation difficult. Paramagnetic resonance on solid solutions of $ThO_2:U^{4+}$ has been observed by Llewellyn⁵ with $g \approx 2.7$. In this paper we report on a paramagnetic resonance spectrum observed in single crystals of CaF_2 doped with $\sim 0.1\%$ of uranium. After accounting for the resonance lines arising from U^{3+} ions in sites of fourfold symmetry¹ and lines due to U^{3+} ions in sites lacking axial symmetry, we are left with a set of lines possessing a threefold symmetry about the $\langle 111 \rangle$ cube diagonals. This spectrum is assigned to U^{4+} ions substituting for Ca^{++} ions. The extra positive charge ($+2e$) is believed to be com-

pensated by two O^{2-} ions replacing two F^- ions along any of the $\langle 111 \rangle$ directions, thus giving rise to the observed trigonal spectrum. The assignment of this spectrum to U^{4+} ion ($5f^2$) rather than U^{3+} ions ($5f^3$) is based on certain features of the paramagnetic resonance which can be explained if we assume a low-lying non-Kramer's doublet arising from an even number of electrons. This assignment is strengthened further by the dependence of the U^{4+} spectrum on the crystal growing conditions. The bulk of the investigation was devoted to CaF_2 host crystals. The presence of U^{4+} was detected also in SrF_2 and BaF_2 .

II. EXPERIMENTAL RESULTS

The ground state of tetravalent uranium is 3H_4 . The presence of compensating charges along the $\langle 111 \rangle$ directions, which is described in Sec. V, causes the local symmetry of the U^{4+} ion, which substitutes for a Ca^{++} ion, to be of the trigonal, C_{3v} , type. The ninefold degeneracy is split into

$$2A_1 + A_2 + 3E_1,$$

i.e., into three doublets and three singlets with one of the doublets lying lowest. The observed paramagnetic

¹ B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Phys. Soc. (London) A69, 858 (1956).

² G. Vincow and W. Low, Phys. Rev. 122, 1390 (1961).

³ C. A. Hutchinson, Jr., P. M. Llewellyn, E. Wong, and B. P. Dorain, Phys. Rev. 102, 292 (1956).

⁴ S. N. Ghosh, W. Gordy, and D. G. Hill, Phys. Rev. 96, 36 (1954).

⁵ P. M. Llewellyn, thesis, Oxford, 1956 (unpublished).