

Paramagnetic Resonance of Yb^{3+} in CaWO_4 †

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Paramagnetic resonance of Yb^{3+} has been observed in single crystals of CaWO_4 at 20°K and 3 cm. A tetragonal as well as two rhombic spectra were found. The tetragonal spectrum is fitted to an axial spin Hamiltonian with $g_{\parallel}=1.058\pm 0.002$, $g_{\perp}=3.920\pm 0.005$, $|^{173}A|= (77\pm 1)10^{-4}$ cm⁻¹, $|^{173}B|= (285\pm 1)10^{-4}$ cm⁻¹, $|^{173}P| < 2.10^{-3}$ cm⁻¹, $|^{171}A|= (279\pm 3)10^{-4}$ cm⁻¹, $|^{171}B|= (1034\pm 3)10^{-4}$ cm⁻¹. The rhombic spectra have the y and z axes in the $\{110\}$ planes. One has the z axis at $6^\circ\pm 1^\circ$ to the crystallographic c axis and $g_x=3.012\pm 0.005$, $g_y=4.788\pm 0.005$, $g_z=0.975\pm 0.003$. The other has the z axis at $7^\circ\pm 1^\circ$ to the c axis and $g_x=4.155\pm 0.005$, $g_y=3.704\pm 0.005$, $g_z=1.155\pm 0.003$. The spectra arise from Yb^{3+} ions at Ca^{2+} sites and the rhombic symmetry is caused by charge compensation at next-nearest-neighbor Ca^{2+} sites. The possibility of W^{6+} substitution is discussed.

I. INTRODUCTION

CRYSTALS of the CaWO_4 structure (sheelite), doped with rare-earth ions have been used extensively in the past few years as solid-state lasers. This fact stimulated the optical as well as paramagnetic resonance studies of these crystals.^{1,2}

Paramagnetic resonance in CaWO_4 has been reported on the trivalent ions gadolinium,³ terbium,⁴ and neodymium.^{5,6} In all these cases the symmetry of the crystalline field at the sites of the paramagnetic ions was found to be tetragonal. Recently, orthorhombic spectra of Fe^{3+} and Nd^{3+} have been reported.⁶ These spectra were attributed to substitutional sites of W^{6+} ions in the WO_4^{2-} complex.

The purpose of this paper is to report on the investigation of Yb^{3+} in CaWO_4 . A tetragonal as well as two rhombic spectra have been found and the results cast some doubt on the attribution of rhombic spectra to the W^{6+} sites.

II. THE STRUCTURE OF CaWO_4

CaWO_4 (sheelite) is a tetragonal body-centered crystal which belongs to the C_{4h} point group. The point symmetry at the sites of the Ca^{2+} ions is S_4 . The structure is shown in Fig. 1. The distorted oxygen tetrahedra which surround the W^{6+} ions, are represented schematically.

III. THEORY

The ion Yb^{3+} has $4f^{13}$ electrons and the ground term of the free ion is $^2F_{7/2}$. In the rare earths, the interaction

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¹ L. F. Johnson, *J. Appl. Phys.* **34**, 897 (1963).

² L. F. Johnson and R. A. Thomas, *Phys. Rev.* **131**, 2038 (1963).

³ C. F. Hempstead and K. D. Bowers, *Phys. Rev.* **118**, 131 (1960).

⁴ P. A. Forrester and C. F. Hempstead, *Phys. Rev.* **126**, 923 (1962).

⁵ U. Ranon, *Phys. Letters* **8**, 154 (1964).

⁶ R. W. Kedzie and K. Kestigian, *Appl. Phys. Letters* **3**, 86 (1963).

with the crystal field is usually much weaker than the spin-orbit coupling and therefore J is a good quantum number. In crystal fields of lower than cubic symmetry the J manifold of the ground state of the free Yb^{3+} ion, splits into four Kramers doublets. Paramagnetic resonance is observable at liquid-hydrogen temperature where only the lowest Kramers doublet is populated.

IV. RESULTS

Two crystals of CaWO_4 , doped with Yb^{3+} , were investigated by paramagnetic resonance at 3 cm and 20°K. They were obtained from Isomet Corporation and Semi-Elements Inc. The concentration of Yb^{3+} in the former was nominally 0.01% and higher in the latter. An intense tetragonal spectrum was observed in the two crystals and the hyperfine structure of the

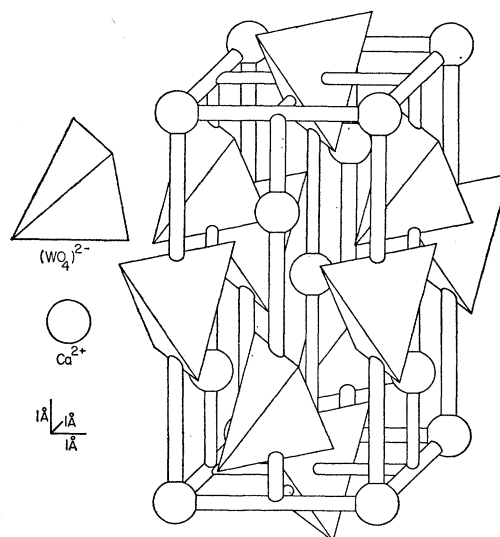


Fig. 1. Unit cell of CaWO_4 . For clarity the oxygen tetrahedra are presented schematically.

isotopes Yb 171 ($I=\frac{1}{2}$) and Yb 173 ($I=\frac{5}{2}$) was clearly resolved. Two spectra of rhombic symmetry which were much weaker, were also shown by each of the two crystals.

The Tetragonal Spectrum

The tetragonal spectrum fits the spin Hamiltonian,

$$\mathcal{H}C = g_{11}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + AS_z I_z + B(S_x I_x + S_y I_y) + P(I_z^2 - 1/3I(I+1)), \quad (1)$$

where the z axis is parallel to the crystallographic c axis and the parameters are

$$\begin{aligned} g_{11} &= 1.058 \pm 0.002, \\ |^{173}A| &= (77 \pm 1)10^{-4} \text{ cm}^{-1}, \\ |^{173}B| &= (285 \pm 1)10^{-4} \text{ cm}^{-1}, \\ |^{173}P| &< 2.1 \cdot 10^{-3} \text{ cm}^{-1}, \\ g_{\perp} &= 3.920 \pm 0.005, \\ |^{171}A| &= (279 \pm 3)10^{-4} \text{ cm}^{-1}, \\ |^{171}B| &= (1034 \pm 3)10^{-4} \text{ cm}^{-1}. \end{aligned}$$

These results give $|g_{11}A/g_{\perp}B|=1$ within the experimental error, and therefore the admixture of $J=\frac{5}{2}$ into the ground state is negligible.⁷ Accordingly, the Kramers doublet can be described by an eigenfunction within the $J=\frac{7}{2}$ manifold. In a tetragonal field this eigenfunction may be of the form $a|\pm\frac{7}{2}\rangle + b|\mp\frac{5}{2}\rangle$ or $c|\pm\frac{5}{2}\rangle + d|\mp\frac{3}{2}\rangle$. Only the latter expression is compatible with the measured g factors, giving $g_{11}=1.052$ and $g_{\perp}=3.957$ when $c=0.700$ and $d=0.714$.

The gradient of the electric field at the nucleus is determined by four contributions: (i) that of the $4f$ electrons, (ii) the shielding effect of the inner core on these electrons, (iii) the gradient of the crystal field, and (iv) the shielding of the latter by the inner core. The first two are proportional to the matrix elements of the operator $(J_z^2 - \frac{1}{3}J(J+1))$, while the other two have usually been neglected. The contribution of the quadrupole moment in paramagnetic resonance is then given by the last term in (1) where⁷ $P = -9e^2Q/4I(2I+1) \times \langle r^{-3} \rangle \langle J || \alpha || J \rangle \langle \Psi | J_z^2 - \frac{1}{3}J(J+1) | \Psi \rangle$. In the case of Yb³⁺ in CaF₂ it was found that⁸ $\langle \Psi | J_z^2 - \frac{1}{3}J(J+1) | \Psi \rangle = -3.9$ and $P = (86 \pm 4)10^{-4} \text{ cm}^{-1}$. In the present case, the eigenfunction gives for the matrix element the value of -1.16 , with the result that $P = 25.10^{-4} \text{ cm}^{-1}$. This value is higher than the upper limit for P obtained from our experimental results. We have no satisfactory explanation for this discrepancy. Possibly the contributions (iii) and (iv) to the gradient of the electric field are not negligible.

⁷ R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) A218, 553 (1953).

⁸ W. Low and U. Rosenberger, Compt. Rend. 254, 1771 (1962).

The Rhombic Spectra

The rhombic spectra can be fitted to the spin Hamiltonian

$$\mathcal{H}C = \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I},$$

where g and A are tensors with principal values g_x, g_y, g_z , and A_x, A_y, A_z , respectively.

Each of the rhombic spectra shows the existence of four inequivalent sites. For both spectra, one of the orthorhombic axes is perpendicular to the c direction, and we call it the y axis. Two sites of each spectrum have y along the $[110]$ direction whereas the other two have it along the $[\bar{1}\bar{1}0]$ direction. The other two axes lie then in the (110) and $(\bar{1}\bar{1}0)$ planes, respectively. The sites of the more intense of the two rhombic spectra, which we shall call spectrum one, have the z axis at an angle of $6^\circ \pm 1^\circ$ to c , while the sites which belong to the weaker spectrum (number two), have the z axis at an angle of $7^\circ \pm 1^\circ$ to c .

Two orientations of z with respect to c are possible in each of the (110) and $(\bar{1}\bar{1}0)$ planes, giving rise to four inequivalent sites which are interchangeable in pairs by a rotation of 90° about the c axis.

Spectrum number one has the parameters $g_x=3.012 \pm 0.005$, $g_y=4.788 \pm 0.005$, and $g_z=0.975 \pm 0.003$.

Spectrum number two has the parameters $g_x=4.155 \pm 0.005$, $g_y=3.704 \pm 0.005$ and $g_z=1.155 \pm 0.003$. The intensity of the even isotope lines in spectrum number one, was approximately 5% of that in the tetragonal spectrum, and the intensity in spectrum number two was about 2% of that of the tetragonal lines. On account of the four inequivalent sites for each rhombic spectrum it is found that about 16% of the Yb³⁺ ions occupy rhombic sites which correspond to spectrum one, and about 6% occupy sites corresponding to spectrum two.

The relative abundance of the two odd isotopes, 171 and 173, of ytterbium is 14% and 17%, respectively and therefore the hyperfine lines of the rhombic spectra were masked by the hyperfine lines of the tetragonal spectrum in such a way that only a few of the former were observable. Therefore the parameters of A could not be evaluated.

From the results of the tetragonal spectrum we assume that in the rhombic sites also, the admixture of $J=\frac{5}{2}$ is negligible. Since now the symmetry is rhombic, the eigenfunctions are of the form $a|\pm\frac{7}{2}\rangle + b|\mp\frac{5}{2}\rangle + c|\mp\frac{5}{2}\rangle + d|\pm\frac{3}{2}\rangle$. The three g values g_x, g_y, g_z and the normalization of the function give four quadratic equations in the four coefficients (a, b, c, d). In this case therefore the existence of a solution of the four equations does not imply that the admixture of $J=\frac{5}{2}$ is negligible, as opposed to the tetragonal case where there are three equations in two unknowns.

From the g values it can be seen that the deviation of the rhombic field from the tetragonal is not large. Therefore, we have looked for a function which is close to

that in the tetragonal case, obtaining for spectrum 1, $0.160|\pm\frac{7}{2}\rangle - 0.262|\mp\frac{1}{2}\rangle + 0.678|\mp\frac{5}{2}\rangle + 0.680|\pm\frac{3}{2}\rangle$ and for spectrum number 2,

$$-0.093|\pm\frac{7}{2}\rangle + 0.099|\mp\frac{1}{2}\rangle + 0.708|\mp\frac{5}{2}\rangle + 0.693|\pm\frac{3}{2}\rangle.$$

V. DISCUSSION

The tetragonal spectrum is usually interpreted as being due to ions at substitutional sites of Ca^{2+} . Kedzie and Kestigian⁶ explained their rhombic spectra of Fe^{3+} and Nd^{3+} as being due to ions which occupy tungsten sites in the WO_4^{2-} complex. The distortion from tetragonal symmetry is explained by them in these cases by assuming a deformation of one of the oxygen bonds along the bond direction in the substituted WO_4 complex, giving rise to four inequivalent sites.

We disagree with this interpretation of the rhombic spectra for the following reasons.

(1) It seems unlikely that trivalent ions, such as the rare-earth ions should substitute for the hexavalent tungsten, which is part of a covalent complex. Furthermore, the ionic radii of the rare-earth ions are much larger than the radius of W^{6+} .

(2) The W-O bonds in the WO_4^{2-} complex are not situated in any crystallographic plane.⁹ A deformation of such a bond, therefore, cannot cause a rhombic distortion with axes lying in the (110) plane, whereas our investigations, as also those of Kedzie and Kestigian, show that such rhombic distortion does actually occur.

(3) There seems to be no reason why the deformation of the complex—which is situated in a tetragonal environment—will be such as to prefer one single direction (namely, a bond direction) which does not coincide with the tetragonal axis.

(4) In our case, *two* rhombic spectra are observed. Even if we assume the W^{6+} substitution, only one of these spectra could be explained. Furthermore, the crystal field at the tungsten sites will be completely different from the tetragonal field, while our results show only a small deformation of the tetragonal field at both rhombic sites. This is evident from the fact that the g values of the rhombic spectra do not differ considerably from those of the tetragonal spectra and that the trace of the g tensor is almost the same in the three cases.

Therefore we assign the rhombic spectra of Yb^{3+}

⁹ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers Inc., New York 1957), Vol. 2, Chap. 8.

to ions at Ca^{2+} sites where the deformation of the tetragonal field is caused by charge compensation. It is well known that in crystals like CaF_2 , where also trivalent ions substitute Ca^{2+} , different charge compensations are possible and these give rise to different local symmetries of the crystal field.

In CaWO_4 two forms of charge compensation suggest themselves. These are: (i) Ca^{2+} vacancies, and (ii) substitutional Ca^{2+} sites occupied by monovalent cations when the crystals are grown with such ions.

The nearest-neighbor Ca^{2+} sites lie in the (100) and (010) planes while the orthorhombic axes lie in the (110) planes. The latter is consistent with charge compensation at next-nearest-neighbor Ca^{2+} sites. Cases where charge compensation is affected at more distant sites rather than at nearest-neighbor sites, were observed in CaF_2 ¹⁰ as well as in SrF_2 and BaF_2 .¹¹

Hempstead and Bowers³ and Kedzie and Kestigian⁶ found that Mn^{2+} (which does not require charge compensation) is situated exclusively in a tetragonal field. The latter authors found that the isoelectronic Fe^{3+} (which does require charge compensation) shows only an orthorhombic spectrum.

The fact that the spectra of Mn^{2+} and Fe^{3+} are completely different is not, in our opinion, a conclusive indication that Fe^{3+} does not occupy Ca^{2+} sites, as suggested by Kedzie and Kestigian. As these authors pointed out, the spectrum of Fe^{3+} can only be explained by assuming a strong axial field where the Stark splitting* is larger than the Zeeman splitting. The following consideration shows that this may occur at the Ca^{2+} sites; it is well known that the Stark splitting in Fe^{3+} is at least one order of magnitude larger than in Mn^{2+} . The splitting³ between the closest doublets of Mn^{2+} at the Ca^{2+} sites is 0.0275 cm^{-1} . Thus the splitting in Fe^{3+} should be of the order of the Zeeman splitting, or larger.

In view of the present results and the uncertainty in the assignment of the rhombic sites, it seems worthwhile that further investigations be undertaken of other rare-earth ions in CaWO_4 as well as in other crystals having the sheelite structure.

ACKNOWLEDGMENTS

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¹⁰ E. Mahlab, W. Low, V. Volterra, and A. Yariv, *Phys. Rev.* **131**, 920 (1963).

¹¹ U. Ranon and A. Yaniv, *Phys. Letters* **9**, 17 (1964).