Spin-Resonance Properties of Scheelites. I. Vanadium in CaWO₄,*

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This paper is intended as the first of a series of investigations directed at obtaining information about charge compensation in CaWO₄. Vanadium, which lies immediately above niobium in the periodic table, is introduced as the microprobe. The EPR spectra produced by X irradiation and observed at 77° and 4.2°K indicate that vanadium can occupy a variety of sites. Arguments are given that two of these, referred to as Group A and Group C, are due to vanadiums in W and Ca sites, respectively.

I. INTRODUCTION

Following the discovery of laser action in CaWO₄ doped with a variety of paramagnetic impurities,¹ a beginning in the systematic study of these materials has been made in several laboratories. Among these are the programs carried out by the workers²,³ at the Bell Telephone Laboratory, where the unambiguous evidence for the importance of charge compensation in lowering laser threshold was obtained, and the results by Kedzie and his associates and others⁴–⁶ pointing to the possible multiple sites of the laser active centers.

The results presented in this and later papers resulted from our efforts to obtain further information on the questions raised in the above references. A preliminary study of CaWO₄:Nd doped with Na or Nb was carried out; but the ESR spectrum was found to be very complex, and dependent to a certain extent upon the Nd concentration, so that our attention was turned to vanadium, which we felt would provide less ambiguous results. The merits for using this dopant stem from: (1) The nuclear spin of the essentially 100% abundant isotope ⁵¹V of ½, which gives the readily recognizable paramagnetic resonance signature of eight HFS (hyperfine structure) lines; (2) the valence state can be readily changed by such radiations as x rays and gamma rays; (3) the ESR properties of vanadium are sensitive to the crystalline environment, as shown by the investigations carried out in our laboratories⁷–¹¹; and (4) of importance to the present specific problem is the fact that vanadium lies immediately above Nb in the group Vb column of the periodic table. For these reasons, it seemed to us that vanadium may be particularly suited for the diadoch of impurities in CaWO₄.

The results obtained thus far indicate that vanadium can occupy Ca and/or W sites, and that there are several crystal imperfection- and impurity-sensitive ESR spectra. To date, four types of spectra have been observed, of which one results from neutron irradiation.

In this paper, we shall present some of the experimental results and defer the theoretical interpretation to a later paper. A brief account of V in CaWO₄ was given earlier.¹²

II. EXPERIMENTAL PROCEDURE

The crystals were grown by the Czochralski technique in an apparatus similar to that described by Nassau and Broyer.¹³ Optical-grade calcium tungstate, rare-earth oxides of 99.9% purity, and reagent-grade vanadium pentoxide were used in the preparation of the melt. The melt was contained in an iridium crucible. The melt temperature was sensed by a jacketed platinum–platinum/rhodium thermocouple immersed in the melt and was stabilized to about ±2.5°C by the automatic adjustment of the rf generator power output. The use of a slightly conical alumina chimney above the crucible reduced markedly the temperature fluctuations on the melt surface and resulted in improved uniformity and

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optical quality of the crystals. The growth interface was still on the desirable conical shape. Pulling was performed in air with typical growth speeds of 0.25 to 0.30 in./h and turning rates ranging from 60–130 rpm.

The crystal axis determination and alignment were carried out by x rays. To produce the paramagnetic center, the samples were irradiated in the white beam of a tungsten-target x-ray tube operated at 50 kVp, 35 mA (about 6 × 10⁶ rad/min). In 15 min, the concentration of the V⁴⁺ ions reached almost its maximum value, i.e., about 6% of the total vanadium present.

This conversion ratio was determined using a CuSO₄ single crystal as an ESR intensity standard.

The V⁴⁺ ESR measurements were carried out at liquid-nitrogen (77°K) and liquid-helium (4.2°K) temperatures, using an X-band ESR spectrometer (similar to Varian V-4500), 5 kc/sec magnetic field modulation, in a 12-in. electromagnet on a rotating mount, with a TE₁₀₀ mode cylindrical cavity. The resonance frequency and the magnetic field were measured with a Beckman 7580 transfer oscillator (connected to a Universal 7380 EPUT and timer) and a Varian F-8 fluxmeter.

### III. CRYSTAL STRUCTURE AND SITE SYMMETRY

The crystal structure of calcium tungstate (scheelite) is characterized by space group $C\alpha₄$, or the tetragonal $I\ 4_1/a$, with four molecules in the unit cell. The tetragonal body-centered unit cell has the dimensions

\[ a = b = 5.243 \pm 0.002 \ \text{Å}, \quad c = 11.376 \pm 0.003 \ \text{Å}. \]

The site symmetry at both Ca and W is $S₄$. The structure of CaWO₄ may be viewed as composed of WO₄⁻ anions ionically bonded to the Ca⁺⁺ cations. The metal sites are found on planes separated by $c/4$ and perpendicular to the $c$ axis; the metal ions on the planes at $c/4$ and $3c/4$ are related to those on the $ab$ and $c/2$ planes by glides. The nearest metal ions lie in planes separated by $c/4$, and the direction joining the two ions, Ca–Ca, W–W, and W–Ca, makes an angle of 42°40' with the $c$ axis.

Each tungsten ion in CaWO₄ is bonded to four oxygens, forming a slightly distorted (squashed) tetrahedron with the W–O distance of 1.78 Å [Fig. 1(a)]. The diagonal plane of this tetrahedron makes an angle of about 31°54' with the $a$ axis [Fig. 1(b)]. The calcium atoms, on the other hand, are surrounded each by eight oxygens, which form two distorted tetrahedra with Ca–O distances of 2.44 and 2.48 Å [Figs. 2(a) and 2(b)], respectively.

### IV. CHEMICAL ANALYSIS

It was found that all samples contained Mn⁴⁺, producing ESR spectrum comparable in intensity to the vanadium spectra. In one sample, Nd³⁺ was observed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V/Ca (at. %)</th>
<th>RE/Ca (at. %)</th>
<th>V/Ca (at. %)</th>
<th>RE/Ca (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaWO₄:V</td>
<td>0.5</td>
<td>0</td>
<td>0.05</td>
<td>0</td>
</tr>
<tr>
<td>CaWO₄:V, Tb</td>
<td>1</td>
<td>1</td>
<td>0.13</td>
<td>0.3</td>
</tr>
<tr>
<td>CaWO₄:V, Nd</td>
<td>1</td>
<td>1</td>
<td>0.13</td>
<td>0.2</td>
</tr>
</tbody>
</table>
SPIN RESONANCE OF SCHEELITES.

![Graph](https://via.placeholder.com/150)

**Fig. 3.** X-band spectrum of X-irradiated CaWO₄:V(0.5%) at T=77°K, for an arbitrary direction of the magnetic field. Group-C lines are identified by C₁, C₂, C₃, and C₄. These lines do not occur for properly RE compensated samples.

although this rare earth was not intentionally added. Its presence is due probably to Nd adhering to the iridium crucible, or evaporating off the walls of the crystal growing equipment, thus showing the extreme sensitivity of the equipment to paramagnetic ions. The vanadium concentrations in these samples were determined for us using arc discharge by the Physics Instrumentation Laboratory, Department of Industrial Health, University of Michigan. The results are tabulated in Table I. The last column in Table I shows the rare-earth concentrations estimated from their coefficients in calcium tungstate. These values give \( k' = 0.08 \) for Cr³⁺, the value given by Nassau and Broyer.¹³ The rare-earth concentrations in the samples, shown in the last column, were computed from the known distribution coefficients for Nd³⁺ and Tb³⁺.

**V. VANADIUM ESR SPECTRA**

The ESR spectra observed prior to X irradiation were those of the Mn²⁺ impurity and additives other than vanadium, such as Nd³⁺ and Tb³⁺. After irradiation, new groups of lines were detected at 77° and 4.2°K. The additional spectra, which show hyperfine structure of eight lines, are assigned to \( ^{51}V \) \((I = \frac{1}{2})\). The possibility that the observed resonances may be due to unintended cobalt \( ^{59}Co \) \((I = \frac{3}{2})\) impurity was ruled out, because a sample doped with this element failed to show the additional lines.

The complexity of the ESR spectra produced by x rays is shown in Figs. 3 and 4. Three groups designated...
as Groups A, B, and C have been identified. Of these, Group A is the sharpest and most intense, as shown in Figs. 3 and 4. Figure 3 also shows the structure stemming from the Group-C lines. For an arbitrary direction of the magnetic field, this group breaks up into four sets (labeled C₁, C₂, C₃, and C₄) of eight lines, spanning a total of about 1100 G. The relative intensities of Group A to Group C is about 100: 70. The much weaker Group-B lines are shown in Fig. 4. This group consists of two sets of eight components when the magnetic field is along one of the twofold axes, but it collapses into one set along the c axis. The relative intensity of Group A to B is about 100: 20.

The angular variation of the spectra shows that each group arises from non-equivalent paramagnetic sites with an effective spin of $S = \frac{1}{2}$. In the remainder of this section, each group is discussed in detail.

### A. Group-A Spectrum

This is the strongest and the sharpest of the three groups (see Figs. 3 and 4), and has been seen at 77°K after irradiation in all samples containing vanadium. The spectrum at liquid-nitrogen temperature is characterized by an isotropic $g$ value ($g = 2.0245 \pm 0.0005$) and a slightly anisotropic $A$ tensor, which $A_{||} = (17.9 \pm 0.2) \times 10^{-4}$ cm$^{-1}$ along the c axis, and $A_{\perp} = (19.0 \pm 0.2) \times 10^{-4}$ cm$^{-1}$ in the ab plane.

At 4.2°K, for an arbitrary direction of the magnetic field, each HFS component splits into four lines, as shown in the lower trace of Fig. 5. However, if the magnetic field is in the ab plane, there are two sets, and along the c axis the four sets collapse into one. The $g$ and the $A$ values along the three crystal axes are:

$$
\begin{array}{ccc}
g & a & b & c \\
2.033 & 2.017 & 2.024 \\
A \ (10^{-4} \text{ cm}^{-1}) & 19.8 & 18.4 & 17.9 \\
\end{array}
$$

The angular dependence of the $g$ value in a plane containing the c axis and making 30° with the a axis is shown in Fig. 6. The maximum $g$ and $A$ values are found to be $g_{\text{max}} = (19.9 \pm 0.2) \times 10^{-4}$ cm$^{-1}$ for $\theta = 60° \pm 3$. 

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![Fig. 6. Angular variation of the Group-A g-value at 4.2°K.](image)

$H$ varies in a plane containing the c axis and making $\phi = 30°$ with the ac plane. $\theta$ is measured from the c axis.

![Fig. 7. Angular variation of the linewidth of the Group-A spectra in the ab plane at 77°K.](image)

A. Group-A Spectrum

![Fig. 8. ESR spectra of X-irradiated CaWO₄:V (0.5%) at 77°K for $H \parallel c$, a axis, respectively.](image)

B. H PARALLEL TO c-AXIS
Thus the direction of the one principal axis of the $g$ tensor is, within experimental error, along the W–O bond. [see Fig. 1(a) and 1(b)].

The splitting into four sets and the anisotropy of Group A can be attributed to the Jahn–Teller distortion of the central metal ion (V) towards one of the four oxygens. Then two of the $g$ tensor principal axes are expected to be in the vertical diagonal minor planes \(\phi = 31^\circ 54'\) and \(-58^\circ 6'\); see Fig. 1(b)], and the third $y$ axis normal to this plane and hence in the $ab$ plane. Measurements show that the maximum and minimum in the $g$ value do indeed occur near $30^\circ$ and $-60^\circ$ from the $a$ axis in the $ab$ plane.

Figure 7 shows the angular dependence of the line-width at 77°K. Note that the variation is more marked with samples containing the rare earths Nd and Tb, in addition to vanadium.

### B. Group-B Spectrum

Upon careful examination of Fig. 4, it will be noted that there are groups of eight lines, whose intensities are about 0.9 of the Group-A lines. These have been designated as Group B. The origin of this group is uncertain, since it has been detected only in two samples examined so far, containing Nd and Tb, respectively. The $g$ tensor has axial symmetry with $g_{1} = 2.068 \pm 0.001$ and $g_{4} = 2.004$. The special axis lies in the $ab$ plane at $10^\circ$ from the $a$ axis. There is some evidence for a small anisotropy in the $A$ value. The measured values varied from about 8.9–9.3 G; this variation, however, is not outside the limits of error.

### C. Group-C Spectrum

This group, with intensity of about 60%–70% of Group A, was observed only in samples containing vanadium only or partly compensated with rare earths such as Nd (V, 1.0%; Nd, 0.1%). The lines do not show splittings at 4.2°K, so that all measurements were conducted at 77°K. In general, there are four sets of lines that reduce to two sets in the $ab$ plane and collapse into one set along the $c$ axis. The $g$ values, in contrast to those of Groups A and B, are less than 2. The hyperfine structure varies between 36 and 176 G, as shown in Fig. 8. The four nonequivalent sites with the principal axes are shown in Table II. In the table, $\theta$ and $\phi$ are the polar angles of each principal axis.

*In units of $10^{-4}$ cm$^{-1}$.

### Table III. Average values of $V^{\text{IV}}$ $g$ and $A$ tensors in several crystals.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Host crystal</th>
<th>$g$</th>
<th>$A^*$</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^{\text{IV}}$</td>
<td>TiO$_2$</td>
<td>1.928</td>
<td>72</td>
<td>b</td>
</tr>
<tr>
<td>$V^{\text{IV}}$</td>
<td>SnO$_2$</td>
<td>1.928</td>
<td>69.7</td>
<td>c</td>
</tr>
<tr>
<td>$V^{\text{IV}}$</td>
<td>GeO$_2$</td>
<td>1.935</td>
<td>69.5</td>
<td>d</td>
</tr>
<tr>
<td>$V^{\text{IV}}$</td>
<td>Al$_2$O$_3$</td>
<td>1.97</td>
<td>132</td>
<td>e</td>
</tr>
<tr>
<td>$V^{\text{IV}}$</td>
<td>Tutton salt</td>
<td>1.9648</td>
<td>108.8</td>
<td>f</td>
</tr>
<tr>
<td>$V^{\text{IV}}$</td>
<td>CaWO$_4$</td>
<td>1.952</td>
<td>88</td>
<td>This work</td>
</tr>
</tbody>
</table>

*See Ref. 9.
not coincide. The angular dependences of $g$ and $A$ in the $ab$ plane are given in Figs. 9 and 10, respectively.

D. Group-N Spectrum

This group is observed in CaWO$_4$:V sample following reactor-fast neutron irradiation of about $10^{16}$ $nvt$. At 77°K, the spectrum consists of four sets of eight lines, in addition to Groups A and C. The relative intensity is about 2% of Group C. In the $ab$ plane, the $g$ value varies between 1.93 and 1.96, and the $A$ value, from 70–100 G. For Group C, as will be recalled, $g$ varies from about 1.926–1.986 and $A$ from about 36–134 G.

We tentatively propose that this spectrum is due to a vanadium in a Ca site associated with an oxygen vacancy. Further detailed measurements, however, are needed.

VI. DISCUSSION

A conspicuous result revealed by the present investigation is the striking difference between the Group A and C spectra. For Group C, the $\Delta g$ is negative, and the HFS is large, i.e., $\Delta g_{zz} = -0.012$, $\Delta g_{yy} = -0.037$, $\Delta g_{xx} = -0.101$, and $\langle A \rangle = 88 \times 10^{-4}$ cm$^{-1}$, as obtained from Tables II and III. For Group A, on the other hand, $\Delta g$ is positive, and $\langle A \rangle$ is about $18.7 \times 10^{-4}$ cm$^{-1}$, which is less than a fourth of that of Group C.

We interpret these results as evidence that Group A and C are to be assigned to vanadiums in the strongly covalent W site and the predominantly ionic Ca site, respectively. For, according to the covalent theory, $\Delta g$ can be positive, if the contributions to the $g$ value stemming from the promotion of electrons in the lower paired state to the spin unpaired ground state is taken into account.$^{14}$ On the other hand, $\Delta g$ for a single-electron system is always negative if only the excited electron states are taken into account, as is the case for strongly ionic bonding. Additional evidence supporting the site assignments is the relative magnitudes of the hyperfine structure. As has been pointed out by several investigators, the HFS is expected to decrease with increasing degree of covalency.$^{15}$

The results for vanadium described above prompted the re-examination of CaWO$_4$ crystals containing Nb, and some of the initial results were reported in a recent note.$^{16}$ Also in this laboratory, a study of paramagnetic centers produced by fast neutron irradiation has been carried out, and one center has been identified as a paramagnetic tungsten associated with an oxygen vacancy.$^{17}$ Thus, it appears that CaWO$_4$ is particularly useful for the study of the properties of impurities and defects in solids.

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$^{15}$ See, for example, R. S. Title, Phys. Rev. 131, 623 (1963); other references are given in the paper.
