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Electron Paramagnetic Resonance of Yb³⁺ in Scheelite Single Crystals*

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The electron paramagnetic resonance spectra of the ground state of trivalent ytterbium have been observed in eight single crystals with scheelite structure at 4.2 °K and X band frequencies. The crystals used were $CdMoO_4$, $CaWO_4$, $CaMoO_4$, $SrWO_4$, $SrMoO_4$, $PbWO_4$, $PbMoO_4$, and $BaWO_4$. The tetragonal spectra for Yb^{171}, Yb^{173}, and the even isotopes of ytterbium were best fitted with an axial spin Hamiltonian. The g factors were found to have a linear dependence on the crystal c-axis lattice constant. All ground-state wave functions were found to be $\Gamma_{5,6}$. The values of $\langle r^{-3} \rangle$ were calculated for Yb^{3+} in each of the crystals, and all were found to have the value $\langle r^{-3} \rangle = 12.5$ a.u. Inclusion of an orbital reduction factor correction changes this value to $\langle r^{-3} \rangle = 12.8$ a.u.

I. INTRODUCTION

Crystal-field theory has been very useful in describing the qualitative features of the optical spectra of rare-earth ions in solid insulators, but various attempts to account for the magnitude of the crystal-field parameters have been unsuccessful. A review of this situation has been given by Van Vleck.[1] Recently, attempts have been made to improve upon the crystal-field model by considering corrections due to overlap and exchange with ligand ions.[2,3] These calculations indicate that overlap and exchange can make important contributions to the crystal-field parameters, but further work will be necessary before it can be said that quantitative agreement with experiment exists. To provide a body of experimental data which may prove useful in obtaining a better understanding of the strong and weak points of the various theories, an investigation has been conducted at this laboratory of the electron paramagnetic resonance and optical spectra of trivalent ytterbium in a series of isomorphic crystals. The single crystals used for this study were the eight scheelites: cadmium molybdate, barium tungstate, and the molybdates and tungstates of calcium, strontium, and lead. The ytterbium ions appear to be located primarily in undistorted cation sites in these crystals and

have tetragonal point symmetry. A good theory should be capable of accounting for the variations observed in the Yb³⁺ spectra as the host crystal-lattice parameters change by approximately 12%.

In this paper, we wish to report on the EPR part of this investigation. The measurements were made at X band and 4.2 °K and fitted to an axial spin Hamiltonian. The g factors were used to calculate the ground-state wave functions for the Yb³⁺ ion in each of the crystals. From the values of the hyperfine parameters for the two isotopes Yb^{171} and Yb^{173}, calculations were made for $\langle r^{-3} \rangle$, the mean inverse cube radius of the Yb³⁺ $4f$ electrons.

II. THEORETICAL CONSIDERATIONS

The EPR spectra of rare-earth ions in various single crystal scheelites have been reported extensively. In particular, studies have been made previously of Yb³⁺ in calcium tungstate,[4,5] lead molybdate,[6] and barium molybdate.[7] In these and other crystals, it was found that the predominant spectra arose from the rare-earth ion in a site with tetragonal point symmetry. This fact, together with chemical arguments based on the valence and ionic size of the rare-earth ions,[8,9] indicates that the rare-earth impurity is located in an undistorted cation site whose point symmetry is S_4.

The ground configuration of Yb^{3+} $(4f^{13})$ has a single term ^2F, which is split approximately $10\,000$ cm^{-1} by the spin-orbit interaction. In a typical scheelite such as $CaWO_4$, it is found that the lowest multiplet $^2F_{7/2}$ is further split about 500 cm^{-1}.[10,11] Crystal-field theory predicts that a field of S_4 symmetry will decompose the eight-fold degenerate $^2F_{7/2}$ level into four Kramers doublets, two being $\Gamma_{5,6}$ and two being $\Gamma_{7,8}$. Taking account of a slight mixing of the $^2F_{5/2}$ states into the lower multiplet by the crystal field, the component states of the ground doublet will be either

$$|\Gamma_5\rangle = a|\tfrac{7}{2},\tfrac{5}{2}\rangle + b|\tfrac{7}{2}, -\tfrac{3}{2}\rangle + c|\tfrac{5}{2},\tfrac{5}{2}\rangle + d|\tfrac{5}{2}, -\tfrac{3}{2}\rangle \quad (1)$$

and

$$|\Gamma_6\rangle = -a^*|\tfrac{7}{2}, -\tfrac{5}{2}\rangle - b^*|\tfrac{7}{2},\tfrac{3}{2}\rangle$$
$$+ c^*|\tfrac{5}{2}, -\tfrac{5}{2}\rangle + d^*|\tfrac{5}{2},\tfrac{3}{2}\rangle \quad (2)$$

or

$$|\Gamma_7\rangle = e|\tfrac{7}{2},\tfrac{1}{2}\rangle + f|\tfrac{7}{2}, -\tfrac{7}{2}\rangle + g|\tfrac{5}{2},\tfrac{1}{2}\rangle + h|\tfrac{5}{2}, -\tfrac{7}{2}\rangle \quad (3)$$

and

$$|\Gamma_8\rangle = -e^*|\tfrac{7}{2}, -\tfrac{1}{2}\rangle - f^*|\tfrac{7}{2},\tfrac{7}{2}\rangle$$
$$+ g^*|\tfrac{5}{2}, -\tfrac{1}{2}\rangle + h^*|\tfrac{5}{2},\tfrac{7}{2}\rangle \quad (4)$$

in a $|4f^{13}LSJM_J\rangle$ basis with $(4f^{13}LS)$ suppressed.

For the eight scheelites considered in this work, the first excited state is 100 cm^{-1} or more above the ground state[12] and is therefore not populated at $4.2\,°$K. Hence, at this temperature, the Yb^{3+} ions in scheelites will have an anisotropic g factor due to either a $\Gamma_{5,6}$ or a $\Gamma_{7,8}$ doublet. The g factor is designated $g_\parallel$ for the field along the crystal c axis and $g_\perp$ for the field perpendicular to the c axis. The effect of the J mixing by the crystal field is small and can be neglected for the purpose of determining whether the irreducible representation of the ground state is $\Gamma_{5,6}$ or $\Gamma_{7,8}$. It can be shown that for a pure $J=\tfrac{7}{2}$, $\Gamma_{5,6}$ ground state the g factors are related by the equation

$$4g_\perp^2 = -3g_\parallel^2 + 6\Lambda g_\parallel + 45\Lambda^2 . \quad (5)$$

For a pure $J=\tfrac{7}{2}$, $\Gamma_{7,8}$ ground state, the corresponding relationship is

$$4g_\perp^2 = g_\parallel^2 + 14\Lambda g_\parallel + 49\Lambda^2 , \quad (6)$$

where $\Lambda = \tfrac{8}{7}$ is the Lande factor for $J=\tfrac{7}{2}$.

The results of measurements of Yb^{3+} in $CaWO_4$[4,5] and $PbMoO_4$[6] indicate that the ground state in both of these crystals is $\Gamma_{5,6}$. The explicit expressions of $g_\parallel$ and $g_\perp$ in this case including the effect of J mixing are

$$g_\parallel = \Lambda(5|a|^2 - 3|b|^2) - \tfrac{1}{7}2\sqrt{6}(a^*c + ac^*)$$
$$- \tfrac{1}{7}2\sqrt{10}(b^*d + bd^*) + \Lambda'(5|c|^2 - 3|d|^2) \quad (7)$$

and

$$g_\perp = \left| 4\sqrt{3}\Lambda\, ab - \tfrac{1}{7}2\sqrt{30}\, ad \right.$$

$$\left. - \tfrac{1}{7}2\sqrt{2}\, bc - 2\sqrt{5}\Lambda'\, cd \right| , \quad (8)$$

where a, b, c, and d are the coefficients in Eqs. (1) and (2), and $\Lambda' = \tfrac{6}{7}$ is the Lande factor for $J=\tfrac{5}{2}$.

It has been pointed out that the experimental g factors are a few percent smaller than the values calculated using crystal-field theory.[13,14] A small degree of covalent bonding can cause such a decrease and may be taken into account by introducing an "orbital reduction factor" k, such that the Zeeman orbital operator L is replaced by kL.[15] Inoue has shown that the small reduction in the ground-state g factor observed for Tm^{2+} $(4f^{13})$ in CaF_2 may also result from the orbit-lattice interaction.[16] Relativistic corrections to the g factor have also been considered and are estimated to be less than 1%.[17]

Natural ytterbium has 69% even-mass isotopes with nuclear spin $I=0$, 14% Yb^{171} with $I=\tfrac{1}{2}$, and 16% Yb^{173} with $I=\tfrac{5}{2}$. Both odd isotopes give rise to nuclear hyperfine interactions with any unpaired electrons and a nuclear Zeeman interaction with the external magnetic field. The Yb^{173} isotope also has a nuclear electric quadrupole moment which interacts with the net electric field gradient at the nucleus. The contribution of these effects to the Hamiltonian for the system may be written as[18]

$$\mathcal{H} = \mathcal{H}_N + \mathcal{H}_Q + \mathcal{H}_Z .$$

$\mathcal{H}_N$ is the nuclear hyperfine interaction,

$$\mathcal{H}_N = 2\beta\beta_N \frac{\mu_N}{I} \sum_i \left(\frac{\vec{N}}{r_i^3} + \frac{8\pi}{3}\delta(r_i)\vec{s}_i \right) \cdot \vec{I} , \quad (9)$$

where

$$\vec{N}_i = \vec{I}_i - \vec{s}_i + 3\hat{r}_i(\hat{r}_i \cdot \vec{s}_i) \quad . \quad (10)$$

The second term in $\mathcal{H}_N$ is the Fermi contact term and is significant for trivalent rare-earth ions only if there is core polarization. Recent calculations[19] show that core polarization is essentially zero for free Yb^{3+} ions.

$\mathcal{H}_Q$ is the electric quadrupole term and is of the form[20]

$$\mathcal{H}_Q = P[I_z^2 - \tfrac{1}{3}I(I+1)] , \quad (11)$$

where only terms diagonal in I_z have been considered.

The nuclear Zeeman term $H_Z = -g_N\beta_N \vec{H}\cdot\vec{I}$ is too small to be of importance here and will be neglected.

The experimental results may also be discussed in terms of the spin Hamiltonian. The spin Hamiltonian appropriate to this investigation is

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta(H_x S_x + H_y S_y) + A I_z S_z$$
$$+ B(I_x S_x + I_y S_y) + P[I_z^2 - \tfrac{1}{3}I(I+1)] . \quad (12)$$

Here $S=\tfrac{1}{2}$ and $I=0$, $\tfrac{1}{2}$, and $\tfrac{5}{2}$ for Yb^{even}, Yb^{171}, and Yb^{173}, respectively. The quadrupole term is non-vanishing only for Yb^{173}.

III. SCHEELITE CRYSTALS

The scheelite crystals have tetragonal body-centered structure with space group C_{4h}^6 (*I4₁/a*). In a typical scheelite such as calcium tungstate, there are four molecular units per unit cell. The calcium ions are coordinated with eight oxygens, each of which is a member of a $(WO_4)^{2-}$ complex. Yb^{3+} ions substituted in undistorted calcium sites are all magnetically equivalent and have S_4 point symmetry. The lattice parameters for the scheelite crystals used in this study are given in Table I.

The crystals were grown at this laboratory by the Czochralski method as described by Nassau and Broyer.[8] Most of the crystals were clear and free from optical imperfections. However, some crystals showed evidence of strains when viewed with polarized light, and the sample of BaWO$_4$ used for measuring $g_{\parallel}$ had cracks. The cadmium molybdate and some of the calcium molybdate crystals were bluish green, the lead tungstate and lead molybdate crystals had a yellowish cast, and all other crystals were colorless. A suitable sample of barium molybdate could not be obtained since these crystals developed severe cracks on cooling to room temperature and were highly discolored.[24] Similar results with this material have been reported previously.[25]

The ytterbium impurity was added to the melt used for growth as Yb$_2$O$_3$. To achieve charge compensation for the excess positive charge on the Yb^{3+} ion, the results obtained by Nassau and Loiacono for CaWO$_4$[9] were assumed to hold roughly for all the scheelites, and sodium was added to the melt in the ratio of four sodium to one ytterbium. Most samples were prepared with 0.05 at.% ytterbium in the melt. For BaWO$_4$, however, it was necessary to use a sample prepared with 4 at.% in the melt, since the resonance signal along the c axis was extremely weak due to a large linewidth.

All crystals were annealed in oxygen at temperatures between 1000 and 1300 °C for 24 h. Sections of the crystals approximately 0.05×0.25

TABLE I. Lattice parameters of scheelite crystals.

Crystal	c (Å)	a (Å)	Ref.
CdMoO$_4$	11.194	5.1554	21
CaWO$_4$	11.376(3)	5.243(2)	22
CaMoO$_4$	11.43	5.226	21
SrWO$_4$	11.951	5.4168	21
SrMoO$_4$	12.020	5.3944	21
PbWO$_4$	12.046	5.4616	21
PbMoO$_4$	12.1065(39)	5.4312(16)	23
BaWO$_4$	12.720	5.6134	21
BaMoO$_4$	12.821	5.5802	21

×0.30 in. were used for most of the measurements. Because of the weak signal in BaWO$_4$ larger sections of this crystal were used.

IV. EXPERIMENTAL CONSIDERATIONS

The paramagnetic resonance spectrometer used for this investigation was an X band superheterodyne instrument using derivative detection and similar to that described by Feher.[26] All measurements were made in the absorption mode with the signal klystron locked to the microwave sample cavity resonant frequency. The cavity was a rectangular cavity resonant in the TE$_{102}$ mode, and was adjusted to near critical coupling by an externally controllable vane tuner. A small sample of diphenyl picryl hydrazyl was used to check the alignment of the spectrometer before and after each measurement. The microwave frequency was measured to 0.1 MHz with a commercial transfer oscillator and electronic counter. Microwave frequencies at about 9 GHz were used for all crystals except BaWO$_4$. The low value of $g_{\parallel}$ for this crystal and the limited available magnetic field required reducing the spectrometer frequency to about 7.7 GHz.

The measurements were made at the 4.2 °K with either a Varian 12-in. electromagnet which had a maximum field of 12 kG or a Varian 22-in. magnet which had a maximum field of 22 kG in the air gap used. The latter magnet was only necessary for the $g_{\parallel}$ measurement of Yb^{3+} in BaWO$_4$. The magnetic field was measured with a NMR gaussmeter and electronic counter. Both magnets were rotatable in a horizontal plane.

To obtain further alignment of the crystal with respect to the external field, the sample was mounted in the cavity so that it could be rotated in a vertical plane during the course of the measurement.[27] The samples were cut from boules which had been x-ray oriented or whose approximate orientation was known from the growth habit of the crystal. The sample was placed in the cavity with the c axis approximately in a vertical plane. By successively rotating the crystal and the magnet, while noting the field required for resonance, orientation of the crystal c axis along or perpendicular to the external field could be made very accurately.

V. SPIN HAMILTONIAN PARAMETERS

All crystals examined in this study showed a predominant tetragonal spectrum for Yb^{3+} which could be fitted to the spin Hamiltonian given in Eq. (12). Most crystals also showed additional weak extra lines in the region of the tetragonal spectrum. These weak lines have been reported

previously for Yb^{3+} in $CaWO_4$[4,28] and have been attributed to Yb^{3+} ions perturbed by nearby charge defects. There was no evidence of other paramagnetic impurities in these crystals. The relative intensities of the lines in the tetragonal spectrum were in the proportion expected for naturally abundant ytterbium. In some cases, when the lines due to the various isotopes of ytterbium overlapped, crystals were used which contained ytterbium enriched with Yb^{171} or Yb^{173}.

The values of $g_{\parallel}$ and $g_{\perp}$ for the Yb^{3+} in each of the crystals were determined from the resonance due to the $I = 0$ isotopes and are listed in Table II. Also listed are the corresponding peak-to-trough derivative linewidths $\Delta H_{\parallel}$ and $\Delta H_{\perp}$. It is seen that except for $CdMoO_4$, the linewidths are larger for the field along the c axis than perpendicular to the c axis. As discussed above, the extremely broad linewidth for Yb^{3+} in $BaWO_4$ necessitated the use of a crystal grown with a higher concentration of ytterbium than in other samples. The measurement of $g_{\perp}$ in this material was made with a sample grown with about 0.05 at.% ytterbium, however. The line shape of the derivative resonance in $BaWO_4$ was very asymmetric, having a high low-field peak and a weak high-field peak. The extremely small value of $g_{\parallel}$ in this crystal appears to be in the lowest directly measured g factor for a paramagnetic material.

Also listed in Table II are the values for the spin Hamiltonian parameters reported previously for Yb^{3+} in scheelite crystals. The estimated value of $g_{\parallel}$ for $BaMoO_4$ reported by Antipin et al.[7] should be treated cautiously we believe, since we have found that it is very difficult to know the orientation of the crystal accurately enough to estimate the value of $g_{\parallel}$ when the g factor is highly anisotropic.

For Yb^{171}, $I = \frac{1}{2}$. The 4×4 spin Hamiltonian matrix can easily be diagonalized to obtain the following expressions for the hyperfine parameters:

$$|A(\text{cm}^{-1})| = \frac{2(\nu/c)|H_2 - H_1|}{|4H_0 - H_1 - H_2|}, \tag{13}$$

where ν is the microwave frequency, c is the speed of light, and H_0, H_1, and H_2 are, respectively, the c-axis fields for resonance of the $I = 0$ line, and the two $I = \frac{1}{2}$ lines; and

$$|B(\text{cm}^{-1})| = \frac{1}{2}|(\gamma_2^2 + \alpha^2)^{1/2} - (\gamma_1^2 - \alpha^2)^{1/2}$$
$$+ (\gamma_2^2 + \delta^2)^{1/2} - (\gamma_1^2 + \delta^2)^{1/2}|, \tag{14}$$

where $\alpha = \frac{1}{2}(A - B)$, $\delta = \frac{1}{2}(A + B)$, and $\gamma_i = (\nu/c)$ $\times (H_i/H_0)$. Here H_0, H_1, and H_2 are the fields for resonance of the $I = 0$ line and the two $I = \frac{1}{2}$ lines when the external magnetic field is perpendicular to the c axis. The values of the hyperfine parameters A^{171} and B^{171} are listed in Table II; the corresponding errors are due primarily to the linewidths. Because of the breadth of the resonance line along the c axis for Yb^{3+} in $BaWO_4$, no value of A could be measured. The estimated values of A for $BaWO_4$ listed in Table II were obtained using the Elliott-Stevens relation,[29] $A = g_{\parallel}B/g_{\perp}$, which holds for a pure $J = \frac{7}{2}$ ground state and is approximately true here.

For Yb^{173} with $I = \frac{5}{2}$, the problem is greatly overdetermined, and values of the parameters A, B, and P may be found which best fitted the spectra. A best-fitted set of spin Hamiltonian parameters was calculated by computer using an iterative procedure which included diagonalization of the 12×12 spin Hamiltonian matrix. The results for A^{173} and B^{173} obtained with the quadrupole term omitted from the spin Hamiltonian are listed in Table II. It is estimated that the percentage error in a hyperfine parameter for Yb^{173} is 2 to 3 times the percentage error in the corresponding Yb^{171} parameter. It was found that the inclusion of the quadrupole term with $P < 7 \times 10^{-4}$ cm^{-1} resulted in only a slight change in the values of A and B and no improvement in the agreement between calculated and observed spectra. For

TABLE II. Spin Hamiltonian parameters and linewidths for Yb^{3+}.

Crystal	$g_{\parallel}$	$g_{\perp}$	$\Delta H_{\parallel}$ (G)	$\Delta H_{\perp}$ (G)	A^{171} (10^{-4} cm^{-1})	B^{171} (10^{-4} cm^{-1})	A^{173} (10^{-4} cm^{-1})	B^{173} (10^{-4} cm^{-1})
$CdMoO_4$	1.2393(1)	3.917(1)	1.1	1.2	310.0(3)	1027(1)	85.5	283.4
$CaWO_4$	1.0530(1)	3.916(1)	5.0	2.6	263.2(5)	1028(1)	72.4	283.8
	1.058(2) [a]	3.920(5) [a]	···	···	279(3) [a]	1034(3) [a]	77(1) [a]	285(1) [a]
	1.054(1) [b]	3.914(1) [b]	···	···	270(1) [b]	···	72(1) [b]	285(3) [b]
$CaMoO_4$	0.9901(2)	3.912(1)	10.2	2.6	248(1)	1028(1)	68.9	283.7
$SrWO_4$	0.5966(3)	3.882(2)	56.2	7.0	141(3)	1023(3)	41.4	282.7
$SrMoO_4$	0.6131(2)	3.881(1)	15.1	3.7	149(1)	1023(1)	41.8	283.9
$PbWO_4$	0.6513(1)	3.886(1)	9.0	2.8	160(1)	1024(1)	44.4	283.1
$PbMoO_4$	0.6622(1)	3.883(1)	18.9	3.8	163(1)	1023(1)	45.3	283.1
	0.663(4) [c]	3.86(2) [c]	100 [c]	10 [c]	177(7) [c]	1027(17) [c]	47.1(30) [c]	278.5(70) [c]
$BaWO_4$	0.234(15)	3.822(3)	1500	11.3	62(Est)	1014(4)	17(Est)	280.5
$BaMoO_4$	0.43(4)(Est) [d]	3.91(1) [d]	···	···	···	1038(7) [d]	···	287(3) [d]

[a]Reference 4.   [b]Reference 5.   [c]Reference 6.   [d]Reference 7.

$P > 7 \times 10^{-4}$ cm^{-1} the agreement was poorer. Ranon and Volterra[4] have reported $P < 20 \times 10^{-4}$ cm^{-1} for Yb^{3+} in CaWO$_4$.

The values for A^{173} and B^{173} listed in Table II resulted in spectra which agreed with the observed perpendicular spectra to within an average of about one-sixth of a linewidth. For the field parallel to the c axis, except for CdMoO$_4$, the fit was within an average of about a third of a linewidth. For CdMoO$_4$ the rms fit was equal to the linewidth, but the linewidth was much narrower than in other crystals. Best-fitted parameters were also calculated using Bleaney's third-order perturbation formula.[30] There was no significant difference between the parameters calculated by either method.

VI. DISCUSSION OF RESULTS

The values obtained for the ground-state g factors for Yb^{3+} in scheelites may be used to determine the S_4 irreducible representation of this state. For this purpose one may neglect J mixing and use the relationships between $g_\parallel$ and $g_\perp$ given in Eqs. (5) and (6) for the $\Gamma_{5,6}$ and $\Gamma_{7,8}$ ground states. These equations are plotted in Fig. 1 for the region of interest. Since the curves are symmetric about the $g_\parallel$ axis, only the positive axis of $g_\perp$ need be shown. The experimental values $g_\parallel$ and $g_\perp$ for each crystal are also indicated in the figure. Only the magnitude of $g_\parallel$ is measured, so both positive and negative values of $g_\parallel$ have been plotted for each crystal. From the proximity of an experimental $(g_\perp, g_\parallel)$ point to one of these curves, the ground state of Yb^{3+} in a crystal may be identified as either a $\Gamma_{5,6}$ or a $\Gamma_{7,8}$. From the figure it can be seen that reasonable agreement between theory and experiment is obtained if we say for all crystals except BaWO$_4$ that $g_\perp$ is positive, and the ground state transforms as a $\Gamma_{5,6}$. The sign of $g_\perp$ is indeterminate.

For BaWO$_4$, the fit is inconclusive. If $g_\parallel$ is positive, the ground state is $\Gamma_{5,6}$, but if $g_\parallel$ is negative, it is possible that the ground state be a $\Gamma_{5,6}$ or a $\Gamma_{7,8}$, since the point fits either assignment equally well. However, an argument can be made from the optical data which support the choice of $\Gamma_{5,6}$ for the ground state.[12] The polarization of the absorption transition from the ground state to the highest crystal-field level of the $^2F_{5/2}$ manifold does not change throughout the scheelite series, as would occur if either the initial or final states changed group character. Since the optical data preclude any change of character for the upper state, and the polarization of the line does not change, we conclude that the ground state of Yb^{3+} in BaWO$_4$ is $\Gamma_{5,6}$ as in the other crystals.
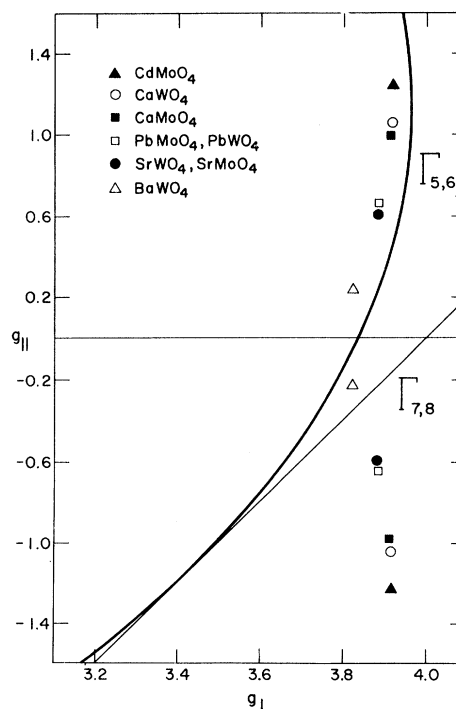

FIG. 1. Calculated curves for $g_\parallel$ versus $g_\perp$ for possible Yb^{3+} ground states together with experimental values of $g_\parallel$ and $g_\perp$. Since only $|g_\parallel|$ is measured, both positive and negative values of the experimental values are plotted.

The deviations of the experimental $(g_\perp, g_\parallel)$ points from the theoretical curve for a $\Gamma_{5,6}$ ground state assuming a pure $J = \frac{7}{2}$ state are small but definite and outside experimental error. This indicates that mixing by the crystal field of the $J = \frac{5}{2}$ state into the ground state cannot be neglected for calculation of the g factors, although the $J = \frac{5}{2}$ states are separated about 10 000 cm^{-1} from the ground state. The calculation of $g_\parallel$ is especially sensitive to the effect of J mixing. This may be seen from the expression for $g_\parallel$ given in Eq. (7) and from consideration of the fact that for most of the scheelites the wave-function coefficients a and b are approximately equal. For a given set of crystal-field parameters, when the effect of J mixing is included in the calculation of $g_\parallel$ for Yb^{3+} in CaWO$_4$, $g_\parallel$ increases by about 7% from its pure $J = \frac{7}{2}$ value, whereas $g_\perp$ increases by about 1%.[12]

However, even when J mixing is considered in the determination of the best-fitted set of crystal-field parameters from the optical and EPR spectra, a small discrepancy still exists between the observed g factors and the calculated values.[12] The discrepancy can be eliminated if one assumes that the measured g factors are reduced by about 2% from the values calculated on the basis of

crystal-field theory. As indicated above, such a reduction can come about due to covalency[15] or an orbit-lattice interaction.[16] If an orbital reduction factor $k < 1$ is used where L is replaced by kL,[15] the calculated g factors are reduced by the factor $\frac{1}{4}(3k+1)$. The value of k is found to be 0.979 for Yb^{3+} in all of the scheelites investigated except for $PbMoO_4$ and $BaWO_4$ where $k = 0.978$.

It has been pointed out that the ground-state g factors for Nd^{3+} in scheelites have a near linear dependence on the c-axis lattice constant[31] and the unit-cell volume.[32] In Figs. 2 and 3, we see that there is also an approximately linear dependence of the g factors on c for Yb^{3+} in the scheelites. The sole exception is the value of $g_\perp$ for Yb^{3+} in $BaMoO_4$ reported in Ref. 7. The reason for the near linear dependence of the g factors on the lattice parameter is not clear at this time and must be regarded as an empirical fact. The wave-function coefficients in Eqs. (7) and (8) may be evaluated explicitly in terms of the crystal-field parameters which in turn may be expressed as sums over the ion coordinates of the lattices. The result is a complicated polynomial involving the lattice parameters with no apparent linear dependence on the c-axis lattice constant.

As in the case for Nd^{3+} in scheelites,[31] the smooth behavior of the g factors with varying lattice constant strongly suggests that the Yb^{3+}
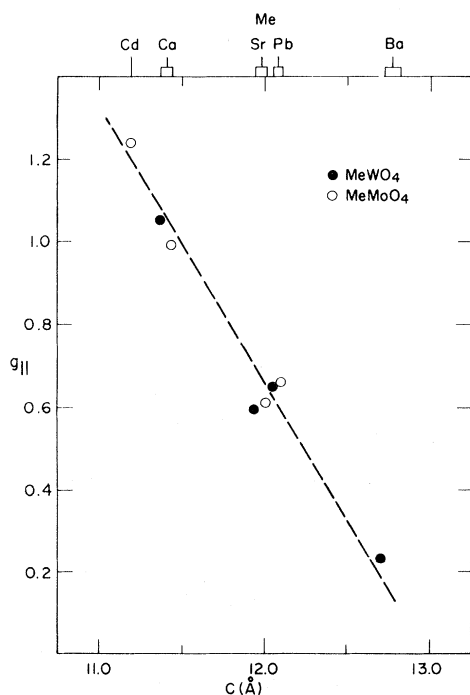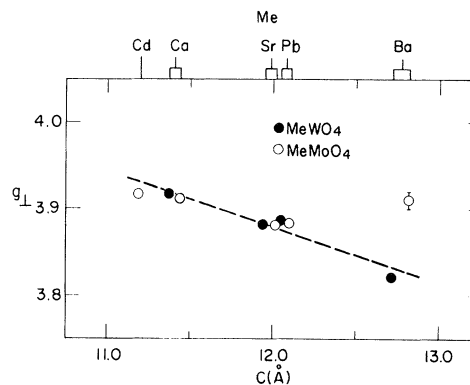

FIG. 3. Experimental values of $g_\perp$ for Yb^{3+} in scheelites plotted versus crystal c-axis lattice constant. The value of $g_\perp$ for Yb^{3+} in $BaMoO_4$ is taken from Ref. 7.

ions are located in the same type of site in the scheelite crystals we have investigated. Considerations of valence, ionic size,[8,9] and the tetragonal symmetry of the resonance indicate that the Yb^{3+} ions are located in the calcium site in $CaWO_4$. We therefore conclude that the Yb^{3+} are located in the cation site in the scheelites reported here.

The measured hyperfine parameters A and B of the spin Hamiltonian may be used to calculate the value of $\langle r^{-3} \rangle$, the expectation value of the inverse cube of the $4f$ electron radial coordinate. Neglecting the Fermi contact term in the Hamiltonian of Eq. (9), it can be shown that[29]

$$A = 4\beta\beta_N(\mu_N/I)\langle r^{-3} \rangle \langle + |N_z| + \rangle \tag{15}$$

and $$B = 4\beta\beta_N(\mu_N/I)\langle r^{-3} \rangle \langle + |N_x| - \rangle, \tag{16}$$

where $|+\rangle$ and $|-\rangle$ are the Kramers conjugate states of Eqs. (1) and (2) and the operator $\vec{N}$ is given in Eq. (10). The magnetic moments for Yb^{171} and Yb^{173} have been measured[33] and are $\mu^{171} = 0.49188\beta_N$ and $\mu^{173} = -0.67755\beta_N$. We have used the complete ground-state eigenvectors determined from the optical spectra and g factors[12] to compute the matrix elements $\langle + |N_z| + \rangle$ and $\langle + |N_x| - \rangle$. The values of $\langle r^{-3} \rangle$ can be computed from the measured A and B parameters for both ytterbium isotopes. The quantities $\langle r^{-3} \rangle_{||}$ are the values calculated from A, and $\langle r^{-3} \rangle_\perp$ are the values calculated from B. We find that just as the calculated values of $g_{||}$ were much more sensitive to the degree of J mixing than $g_\perp$, the matrix elements $\langle + |N_z| + \rangle$ were similarly more sensitive than $\langle + |N_x| - \rangle$. Consequently, the values of $\langle r^{-3} \rangle_{||}$ show considerably more variation from scheelite to scheelite than $\langle r^{-3} \rangle_\perp$. In Table III we list the average values of $\langle r^{-3} \rangle$ for Yb^{171} and Yb^{173} in the eight scheelites investigated here together with the rms deviations.

FIG. 2. Experimental values of $g_{||}$ for Yb^{3+} in scheelites plotted versus crystal c-axis lattice constant.

TABLE III. Average values of $\langle r^{-3} \rangle$ calculated for two odd isotopes of ytterbium with and without orbital reduction factor k for Yb^{3+} in eight scheelites. $\langle r^{-3} \rangle_\parallel$ and $\langle r^{-3} \rangle_\perp$ are calculated from the spin Hamiltonian parameters A and B, respectively.

| | $k = 1$ | | $k < 1$ | |
Isotope	$\langle r^{-3} \rangle_\parallel$	$\langle r^{-3} \rangle_\perp$	$\langle r^{-3} \rangle_\parallel$	$\langle r^{-3} \rangle_\perp$
Yb^{171}	12.5(2)	12.50(2)	12.6(2)	12.80(3)
Yb^{173}	12.7(2)	12.54(3)	12.8(2)	12.85(3)

It is of some interest to see the effect of assuming an orbital reduction factor k such that L is replaced by kL in the operator $\vec{N}$. The results are listed in Table III under the columns for $k < 1$. As discussed above, the values of k were determined for each crystal from the discrepancy between the calculated and measured g factors.[12]

The ratio of $\langle r^{-3} \rangle$ obtained from measurements on the two isotopes Yb^{171} and Yb^{173} is equal to unity within the accuracy of the measurement. A ratio different from unity would indicate a hyperfine structure anomaly, that is, an isotopic dependence of the hyperfine interaction such as would arise from a nonvanishing Fermi contact term. We therefore conclude that the neglect of core polarization effects is justified for Yb^{3+} in the scheelite crystals studied here.

The above results are in good agreement with recent electron-nuclear double resonance measurements of Yb^{3+} in CaF$_2$[34] where a value of $\langle r^{-3} \rangle = 12.7$ a.u. and a hyperfine anomaly much less than 1% were reported. These measurements are also in good agreement with calculated values of $\langle r^{-3} \rangle$ by Lindgren[35] who found $\langle r^{-3} \rangle = 12.18$ a.u. and by Freeman and Watson[36] who obtained $\langle r^{-3} \rangle = 13.89$ a.u.

The constant value obtained for $\langle r^{-3} \rangle$ for Yb^{3+} in scheelites indicates that there is no change in the radial wave function in the region of the nucleus, although the ion is substituting for cations with varying atomic radii.

VII. CONCLUSIONS

The EPR spectra of the ground state of Yb^{3+} have been obtained in eight scheelite single crystals. The ion was found to be located in a site with tetragonal symmetry, and it is surmised that it is in an undistorted cation site. Both g factors were found to have an approximately linear dependence on the c-axis lattice constant. The value of $g_\parallel$ for BaWO$_4$ was measured to be 0.234 and is believed to be the lowest g factor ever actually measured for a paramagnetic ion. All of the ground-state wave functions are determined to be $\Gamma_{5,6}$.

The spin Hamiltonian hyperfine parameters were determined for Yb^{171} and Yb^{173} in the eight scheelites studied. The values of $\langle r^{-3} \rangle$ were calculated from these parameters and found to have a constant value of 12.5 a.u. in all crystals. Inclusion of an orbital reduction factor raises this value to 12.8 a.u. No hyperfine anomaly was found, indicating that neglect of core polarization in these crystals is justified. It was found that the coefficient P of the quadrupole term was less than 7×10^{-4} cm^{-1}.

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Unusual Electron Paramagnetic Resonance Hyperfine Spectra of Yb³⁺ in Scheelites*

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The tetragonal X band electron paramagnetic resonance spectrum of Yb³⁺ shows an unusual hyperfine spectrum in the scheelite crystals $SrWO_4$, $SrMoO_4$, $PbWO_4$, and $PbMoO_4$. For these crystals, the principal $2I+1$ hyperfine absorption lines of the parallel spectrum do not go continuously into the $2I+1$ lines of the perpendicular spectrum as the angle of the magnetic field is varied from the crystal c axis. At some angles, more than the usual $2I+1$ transitions are observed. This unusual behavior is completely explained by the axial spin Hamiltonian $\mathcal{H}$ $=g_\parallel \beta H_z S_z + g_\perp \beta(H_x S_x + H_y S_y) + A I_z S_z + B(I_x S_x + I_y S_y)$ and the relatively large ratio of B/A for Yb³⁺ in these crystals.

I. INTRODUCTION

The EPR spectrum of trivalent ytterbium in crystalline sites with tetragonal symmetry can be described by the spin Hamiltonian

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta(H_x S_x + H_y S_y)$$

$$+ A I_z S_z + B(I_x S_x + I_y S_y) , \qquad (1)$$

where $S = \frac{1}{2}$, $I = 0$ for even-mass isotopes of ytterbium, and $I = \frac{1}{2}$ and $\frac{5}{2}$ for Yb¹⁷¹ and Yb¹⁷³, respectively. The parameters of this Hamiltonian have been measured for Yb³⁺ at X band and 4.2 °K in a series of eight single crystals having the scheelite structure.[1] These measurements have included those for Yb³⁺ in tetragonal sites of cadmium molybdate, and of the tungstates and molybdates of calcium, strontium, and lead. In this paper, we

report on an unusual behavior of the hyperfine spectra observed in some of these crystals. For an ion with $S = \frac{1}{2}$, $2I+1$ absorption lines are usually observed. The isotopes Yb¹⁷¹ and Yb¹⁷³ exhibit this behavior in all scheelite crystals when the magnetic field is parallel or perpendicular to the crystal c axis. However, in some crystals, corresponding hyperfine absorption lines do not move continuously into one another as the magnetic field varies from the c axis to a perpendicular direction. Furthermore, four rather than two absorption lines are observed along some directions for Yb¹⁷¹. We have found that these spectra can be explained by the spin Hamiltonian of Eq. (1) with no additional terms, and are due to the large anisotropy of the hyperfine parameters observed for some of these crystals.