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Electric-Field-Induced *g* Shifts for Loose Yb Ions in Three Scheelite Lattices

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The electric-field g shift of Yb^{3+} in the scheelite series $CaWO_4$, $SrWO_4$, and $BaWO_4$ has been measured. In $SrWO_4$, and especially in $BaWO_4$, the Yb ion is much smaller than the cation, and we find a substantial increase in the g shifts, which indicates less restraint to ionic motion. The lattice restoring forces for loose ions are investigated through the use of the Born-Mayer theory of ionic bonding. We find that the predicted ionic g shift is considerably larger than that observed. This may be due to substantial local distortion near a Yb impurity. Several other mechanisms for increasing the restoring forces on small ions are also considered.

I. INTRODUCTION

In recent years there have been a number of studies of the shifts in electron paramagnetic resonance frequencies which are produced by the application of external electric fields.[1-7] These shifts can be attributed to two sources: direct interaction of the applied field with the electron cloud (the electronic effect), and the displacement of the paramagnetic center relative to the host lattice (the ionic effect). Unfortunately it is hard to distinguish between these two mechanisms in practice, since both types of shift are described by third-rank tensors which are of the same form (i.e., they contain the same elements as the piezoelectric tensor for the relevant point symmetry[8]). There have been several theoretical descriptions of the electronic effect.[5,7,9] Quantitative calculations for the ionic case are fewer however, and are more difficult to make insofar as they involve additional assumptions relating to the mechanical restoring forces which act on ions in crystals.

In an effort to distinguish between the two effects we have studied the electric g shift of Yb^{3+} in the scheelite series $CaWO_4$, $SrWO_4$, and $BaWO_4$. The cation size increases by about 15% in going from Ca to Sr and increases again by about the same amount in going from Sr to Ba. In the same two steps the overall crystal dimensions change by 4 and 6%, respectively. As a result, the fit of the Yb^{3+} in the cation site becomes progressively looser and the crystal field weaker in going from $CaWO_4$ to $SrWO_4$ and $BaWO_4$. One might therefore expect the ionic displacement effect to increase and the electronic effect (which depends on the magnitude of the crystal field components) to undergo a concomitant reduction. As we shall see the first of these assumptions is borne out in theory and in experiment. The situation in regard to the electronic effect is less clear-cut than it appears at first sight. A careful calculation of the g shift in these scheelites shows that a scaled reduction of the crystal field causes an increase rather than a reduction in the electronic effect. However, this increase is a relatively small one, and the main conclusion that the increased shifts in the larger lattice are primarily due to ionic displacements still holds.

In analyzing these results, we have developed a formalism in which the ionic and electronic effects are treated in a very similar manner. While we get qualitative agreement with the loose-ion model, the predicted magnitudes are substantially too great for the larger lattices. The result is not surprising in view of the crudity of the kinematic model which we have adopted. Errors can arise from a number of causes, in particular from a modification of the restoring forces caused by local distortions of the lattice accompanying the substitution of small-sized impurities.

In Sec. II we discuss the results of the experiments. In Sec. III, the electronic g shift is calculated for the three scheelites.

Some of these results are used in Sec. IV, where we apply the Born-Mayer theory of ionic bonding in order to estimate the Yb^{3+} ionic displacements and hence infer the ionic g shifts. It will be seen in Sec. V that some interesting conclusions relative to the ionic motion and to the stability of impurities can be inferred from this model. The Appendix describes the equivalent even field operator technique and shows how it can be applied to the case of ionic motion.

One of the aims in performing these experiments has been to find a means for studying the physical motion

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[1] G. W. Ludwig and F. S. Ham, in *Proceedings of the International Conference on Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963). Many references to earlier papers are given here.

[2] E. B. Royce and N. Bloembergen, Phys. Rev. **131**, 1912 (1963).

[3] J. J. Krebs, Phys. Rev. **135**, A397 (1964).

[4] W. B. Mims, Phys. Rev. **140**, A531 (1965).

[5] A. Kiel and W. B. Mims, Phys. Rev. **153**, 378 (1967).

[6] J. J. Krebs, Phys. Rev. **155**, 246 (1967).

[7] F. I. B. Williams, Proc. Roy. Soc. (London) **71**, 111 (1967).

[8] C. S. Smith, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 229.

[9] A. Kiel, Phys. Rev. **148**, 247 (1966).

of individual ions in an applied electric field. Such a study might be expected to contribute to the understanding of ferroelectricity in much the same way as the study of dilute paramagnetic impurities has contributed to the understanding of bulk magnetic properties. Of special interest is the stability of small impurities in host lattices and conditions under which they might "switch" to off-center positions.

II. EXPERIMENTAL RESULTS

The electric g shifts of Yb^{3+} in the three crystals $CaWO_4$, $SrWO_4$, and $BaWO_4$ were determined by the electron spin echo method described in Ref. 4. The notation below follows Ref. 5. All experiments were performed at X band (9.4 GHz) and at 4.2°K. The properties of the crystal lattices, and the results of the experiments, are compiled in Table I. The symmetry of the g tensor and of the third-rank electric-effect tensor was, in all three cases, consistent with the assumption that the Yb^{3+} ion was situated at a normal cation lattice site without nearby charge compensation. The ionic radii were taken from Pauling.[10] From Table I we see that Yb (0.94 Å) fits comfortably in a Ca (0.99 Å) site. However, strontium (1.13 Å) and barium (1.35 Å) are substantially larger than Yb^{3+}, making Yb^{3+} a "loose" fit in $SrWO_4$ and $BaWO_4$. In the last two cases it may also be noted (Table I) that the lattice "expands" 50% more in the c direction than it does in the ab plane. All of these changes are, of course, small. It must be remembered, however, that the equilibrium conditions for a normal crystal correspond to a slight overlap of the electronic charge clouds, and that relatively small differences in the ionic radius of an impurity can have a large effect on the mechanical restoring forces which it experiences.

The $g_\perp$ of Yb^{3+} changes very little for the three host lattices (3.93, 3.88, 3.82), but $g_{\parallel}$ undergoes a very marked change. This may be readily explained in terms of the constitution of the Yb^{3+} ground doublet. In $CaWO_4$ we have a mixture of $|J,M\rangle$ states given by $\alpha|\frac{7}{2}, \pm\frac{5}{2}\rangle+\beta|\frac{7}{2}, \mp\frac{3}{2}\rangle$, with $\alpha=0.70$ and $\beta=0.71$. For $\alpha\simeq\beta$, $g_\perp$ is stationary and very large alterations in the crystal field are needed to make any significant difference in $g_\perp$. [The $g_\perp$ of Yb in almost any scheelite is approximately equal to $16\surd(3/7)$.] $g_{\parallel}$ is, on the other hand, comparatively sensitive to minor changes in the state constitution.

TABLE I. g-shift parameters for Yb^{3+} in three scheelites. Ionic radii, lattice parameters, and electric-field-effect parameters for Yb^{3+} in $CaWO_4$, $SrWO_4$, and $BaWO_4$. $B_\perp$ and $B_{\parallel}$ give $\delta(g^2)$ per 10^9 V/cm of electric field applied ⊥ to, or ‖ to the c-axis. The variation of $\delta(g^2)$ with the orientation of E and H is given in Eqs. (1) to (3). The ionic radius of Yb^{3+} is taken to be 0.94 Å (see Ref. 10). The lattice constants are from J. D. H. Donney, American Crystalographic Association Monograph No. 5, 1963 (unpublished).

Property	$CaWO_4$	$SrWO_4$	$BaWO_4$
Cation radius (Å)	0.99	1.13	1.35
Lattice a_0(5.24 Å)	1.0	1.03	1.074
Lattice c_0/(11.38 Å)	1.0	1.046	1.11
Cation-to-O distance (Å)	2.45 Å	2.56 Å	2.73 Å
$B_\perp$	212	340	570
$B_{\parallel}$	81	500	1180
$\varphi_\perp$	106°	97°	97°
$\varphi_{\parallel}$	47°	4°	4°

The electric field shifts in Table I are expressed in terms[4] of $\delta(g^2)$. They were obtained with the E and H fields oriented as follows: (a) E along the c axis, H in the ab plane, (b) E along the a axis, H in the ac plane, (c) E along the a axis, H in the bc plane. It is shown in Ref. 4 that these measurements suffice to determine all the third-rank tensor parameters for an ion of S_4 symmetry, subject to some ambiguities regarding the sign of the effects. For E along the c axis and H in the ab plane we have

$$\delta(g^2)/E_c=(B_{31}^2+B_{36}^2)^{1/2}\sin(2\varphi-2\varphi_3)\,, \tag{1}$$

and for E along the a axis and H in an arbitrary direction we have

$$\delta(g^2)/E_a=(B_{14}^2+B_{15}^2)^{1/2}\sin 2\theta\sin(\varphi-\varphi_1)\,. \tag{2}$$

θ and φ are the polar coordinates of the magnetic-field relative to the abc axis system. The B are the third-rank tensor components written in the Voigt notation.[8] In the specific case of S_4 symmetry they are related to the electric effect terms $T_{ijk}E_iH_jS_k$ appearing in the

$$B_{31}=B_{311}=(2/\beta)g_\perp T_{311}\,,$$
$$B_{36}=B_{312}=(2/\beta)g_\perp T_{312}\,,$$
$$B_{14}=B_{123}=(1/\beta)(g_\perp+g_{\parallel})T_{123}\,,$$
$$B_{15}=B_{113}=(1/\beta)(g_\perp+g_{\parallel})T_{113}\,.$$

The angles φ_1 and φ_3 are defined by $\tan\phi_1=-B_{15}/B_{14}$ and $\tan 2\varphi_3=-B_{31}/B_{36}$. Since we shall, on numerous occasions, be comparing the effects of electric fields parallel to and perpendicular to the crystal c axis, it will be convenient for the purpose of the present article to adopt the notation

$$B_{\parallel}=(B_{31}^2+B_{36}^2)^{1/2}$$

and

$$B_\perp=(B_{14}^2+B_{15}^2)^{1/2}\,.$$

In accordance with this notation, we shall also designate the fields and characteristic angles by: $E_c=E_{\parallel}$, $E_{ab}=E_\perp$, $\varphi_{\parallel}=\varphi_3$, $\varphi_\perp=\varphi_1$. E_{ab} denotes an electric field applied in the ab plane at an angle of φ_E to the a axis. For this field we have

$$\delta(g)^2/E_\perp=B_\perp\sin 2\theta\sin(\varphi-\varphi_1+\varphi_E)\,. \tag{3}$$

Referring to the results of Table I, we see that there is a substantial increase in $B_\perp$ as we proceed along the sequence Ca, Sr, Ba, the over-all change between Ca and Ba being by a factor of 2.7. For the $E_{\parallel}$ cases, the

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[10] Linus Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, N. Y., 1960), 3rd ed.

increases in $B_{\parallel}$ are even more striking, particularly in going from $CaWO_4$ to $SrWO_4$, where the increase is by a factor greater than six. Other noteworthy features are the sudden change in $\varphi_{\parallel}$ in going from $CaWO_4$ to $SrWO_4$, and the approximately constant value in making the next step from $SrWO_4$ to $BaWO_4$.[11] We believe that these results indicate that in the $SrWO_4$ and $BaWO_4$ host lattices, the Yb^{3+} electric effect is predominantly ionic in character. The same is probably true of the $E_{\perp}$ effect in $CaWO_4$. The $E_{\parallel}$ effect for Yb^{3+} in $CaWO_4$ is, however, clearly out of line with the remaining body of data, both as regards the magnitude of the g shift and the characteristic azimuthal angle. For this particular case ($E_{\parallel}$ in $CaWO_4$) it is likely that the electronic g shift is comparable to the ionic effect.

III. ELECTRONIC g SHIFTS FOR THREE SCHEELITES

To substantiate the conclusions of the last section, we have calculated the electronic effect for the three lattices using the method described in Ref. 9. We shall see that the electronic effect is relatively small and that the $E_{\parallel}$ effect in $CaWO_4$ is the only case where this effect is at all comparable with the observed g shift.

Before presenting the calculations we must comment on the outcome of similar calculations in Ref. 9. There it was concluded that both the $E_{\parallel}$ and $E_{\perp}$ g-shifts for Yb^{3+} in $CaWO_4$ could be fully explained by the electronic effect. However, it now appears that the reported crystal-field parameters[12] and the oscillator strengths[13] used in this calculation were both in error, so that the theoretical values for the electronic effect were overestimated, particularly for $E_{\perp}$. We have therefore recomputed the electronic effect using the crystal-field values obtained by Jones[14] and the correct oscillator strengths. This computation is again based on the equivalent even-field formulation of the problem as described in Ref. 9, involving interaction via the odd crystal fields of the f^{13} ground manifold with the $f^{12}d$ and $f^{12}g$ manifolds (see Appendix).

The equivalent even field can be expanded in terms of the quantities $(2k+1/4\pi)^{1/2}a_k{}^qC_k{}^q(\theta,\varphi)$ where the $C_k{}^q$ are equal to $(4\pi/2k+1)^{1/2}$ times the normalized spherical harmonics $Y_k{}^q(\theta,\varphi)$ (see Appendix).

For Yb^{3+} in $CaWO_4$ we have

$$a_2{}^2=a_2{}^{-2}=-8.2\times10^{-8}\ \mathrm{cm}^{-1},$$
$$a_4{}^2=a_4{}^{-2}=-1.38\times10^{-8}\ \mathrm{cm}^{-1},$$
$$a_2{}^1=-a_2{}^{-1}=8.2\times10^{-8}\ \mathrm{cm}^{-1},$$
$$a_4{}^1=-a_4{}^{-1}=5.2\times10^{-7}\ \mathrm{cm}^{-1},$$
$$a_4{}^3=-a_4{}^{-3}=-7.0\times10^{-7}\ \mathrm{cm}^{-1}.$$

The corrected value for the odd field, $A_3{}^2=1500\ \mathrm{cm}^{-1}$ was used in deriving the above parameters and not the value $A_3{}^2=7500\ \mathrm{cm}^{-1}$ as used in Ref. 9. In obtaining these estimates we have written the equivalent even field in the real forms $a_2{}^2(C_2{}^2+C_2{}^{-2})$, etc. This procedure will give us the magnitudes of $B_{\parallel}$ and $B_{\perp}$ but not the characteristic angles $\varphi_{\parallel}$ and $\varphi_{\perp}$. It is equivalent to considering a D_{2d} symmetry rather than the lower S_4 symmetry in $CaWO_4$.

The crystal-field parameters for $SrWO_4$ and $BaWO_4$ have never been determined to our knowledge. Since crystals of suitable optical quality and Yb concentration were not available we were unable to attempt an empirical fit. We have, therefore, estimated the crystal-field parameters for these two scheelites by scaling the $CaWO_4$ values. In one estimate we simply assume that all the crystal fields are scaled according to the fractional change f of the lattice parameters [i.e., the kth order crystal-field component is reduced by $(k+1)f$]. In a second, and probably more realistic estimate, we change the higher-order crystal field parameters by the quantity $(k+1)f$, but allow the second-order term to undergo only small changes. This procedure (partial scaling) gives much better agreement between calculated and measured g values in $SrWO_4$ and $BaWO_4$. (Compare the fourth and fifth rows of Table II with the second and third rows.) Some justification for the partial scaling comes from the fact that $A_2{}^0$ is greatly reduced from its point-charge value by wave-function overlap. In going from $CaWO_4$ to the larger lattices, the decrease in electrostatic interaction is likely to be partially offset by a reduction in overlap. It is, of course, possible to question the accuracy of the values

TABLE II. Experimental and calculated g values. Experimental and calculated g values for Yb^{3+} in three scheelite lattices. The g values in $SrWO_4$ and $BaWO_4$ hosts shown in rows 2 and 3 were obtained by simple scaling of all crystal-field parameters $A_k{}^q$ for $CaWO_4$ by $1-(k+1)f$, where f is the relative change of lattice parameters. The g values in the fourth and fifth rows were obtained by scaling parameters for $k>2$ as above, but changing $A_2{}^0$ by a smaller amount (partial scaling).

	$g_{\perp}$		$g_{\parallel}$	
	Expt.	Calc.	Expt.	Calc.
$CaWO_4$	3.93	3.95	1.05	1.06
$SrWO_4$	3.88	3.94	0.58	0.83
$BaWO_4$	3.82	3.93	(0.3)	0.64
$SrWO_4$ (partial scaling)	3.88	3.93	0.58	0.67
$BaWO_4$ (partial scaling)	3.82	3.90	(0.3)	0.29

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[11] The crystal a, b, and c axes are determined by x-ray diffraction methods before cutting the samples. This determination is not sufficient to specify whether the angles φ should be taken in the positive or negative sense. It will be apparent from Eqs. (1) and (2) that $\varphi_{\parallel}$, $\varphi_{\perp}$ are indeterminate to within multiples of $\frac{1}{2}\pi$ and π, respectively. Where ambiguities exist, we have arbitrarily adopted those values of $\varphi_{\parallel}$ and $\varphi_{\perp}$ which afford the most consistent comparison.

[12] These were taken from U. Ranon and V. Volterra, Phys. Rev. **134**, A1483 (1964).

[13] These were given in R. Pappalardo and D. L. Wood, J. Mol. Spectroscopy 10, 81 (1963).

[14] G. R. Jones, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Wiley-Interscience, Inc., New York, 1967), p. 85.

TABLE III. Measured g shift and g shift calculated for pure electronic effect. Experimental values of the electric-field-effect parameters for Yb^{3+} in three scheelite lattices as compared with results calculated by assuming them to be due to electron cloud distortion without ionic motion. The parameters $B_\perp$, $B_{\parallel}$ give $\delta(g^2)$ per 10^9 V/cm of electric field applied $\perp$ to, or $\parallel$ to the c axis. The variation of $\delta(g^2)$ with the orientations of E and H is given in Eqs. (1) to (3). The second set of values for $SrWO_4$ and $BaWO_4$ were obtained by partial scaling as noted in Table II.

	$B_\perp$		$B_{\parallel}$	
	Expt.	Calc.	Expt.	Calc.
$CaWO_4$	212	5.8	81	44
$SrWO_4$	340	7.0	500	58
$BaWO_4$	570	10.6	1180	60
$SrWO_4$ (partial scaling)	340	9.0	500	60
$BaWO_4$ (partial scaling)	570	14.4	1180	86

we have adopted. They are, however, in reasonable accord with observed trends for the scheelites as reported in the literature.[15,16] Moreover, our principal objective now is to show that the calculated electronic effect in $SrWO_4$ and $BaWO_4$ is small in relation to the experimentally observed shifts, and that it remains small even when some of the more naive assumptions of crystal-field theory are modified. In a similar way one might argue that errors introduced by our procedure of deriving the $SrWO_4$ and $BaWO_4$ crystal fields from Jones's values for $CaWO_4$ are not likely to be large enough to have any significant influence on the gap between experimental and theoretical values.

In Table III we compare the experimental values of $B_{\parallel}$ and $B_\perp$ with theoretical values of the electronic effect calculated by means of the above equivalent even-field values. The second and third rows show the $SrWO_4$ and $BaWO_4$ results which are obtained using a simple scaling of all the crystal-field components. Rows 4 and 5 of Table II give alternative values calculated using the partial scaling procedure. It is important to note that only for $B_{\parallel}$ in $CaWO_4$ is the electronic effect substantially close to the observed shift (see Table III). This result is in general agreement with the observations presented in Sec. II.

It is, perhaps, surprising to find that the calculated electronic effect *increases* despite the fact that scaling leads to smaller odd fields (Table III). The reasons for this may be seen from the following considerations. The equivalent even-field parameters a_k^q are roughly proportional to $V_{\text{odd}}[E(f)-E(d)]$, where V_{odd} is the magnitude of the odd crystal field and $E(f)-E(d)$ is the energy separation between f and d manifolds (see the Appendix). The g shifts are, on the other hand, proportional to $a_k^q\chi_{ji}/(E_j-E_i)$, where E_j-E_i is the separation between the lowest doublet and an excited doublet of the $^2F_{7/2}$ ground manifold, and where χ_{ji} depends on the exact state compositions of the doublets concerned. Scaling to larger lattice spacings has a negligible effect on $E(f)-E(d)$ and will, clearly, reduce V_{odd}, thus reducing a_k^q and suggesting that there should be a reduction of the electronic effect. Scaling, however, may also reduce the doublet separation E_j-E_i and change the χ_{ji} which are primarily determined by the *even* crystal field. Roughly speaking, we may say that the electronic g shift varies with the ratio between odd and even crystal-field terms, rather than with the magnitude of the odd terms alone, for host lattices of a given symmetry type.

Before leaving this topic we may note that a reduction in the doublet separation, and changes in the state composition arising from the scaling down of even-crystal-field components, may play an important part in determining the magnitude of ionic g shifts. An ionic displacement introduces additional even-field components (see Sec. IV B and the Appendix) which the change the composition of states in the ground manifold. If the new even-field parameters are described by b_k^q, the ionic g shift is proportional to $b_k^q\chi_{ji}/(E_j-E_i)$. As in the electronic case, scaling to larger lattices may increase χ and/or reduce E_j-E_i sufficiently to lead to a net increase in the g shift. Thus we might expect the increase in the ionic effect observed for the larger lattices to be due in part to changes in χ_{ji} and E_j-E_i and not to originate solely in the greater freedom of movement of the Yb ion. In computing the ionic g shifts in Sec. IV B we take this effect into account.

IV. RESTORING FORCES AND IONIC EFFECT

A. Reduction of Restoring Forces for "Loose-Fitting" Impurity Ions

In Sec. II we presented experimental evidence suggesting that the movement of impurity ions in response to an applied electric field is dramatically enhanced when these ions become smaller than the ions for which they are substituted. We shall now try to estimate the changes in restoring forces for these "loose ions." To do this we shall adopt the Born model of repulsive forces, following the treatment outlined in the review by Tosi.[17]

According to this model the repulsive potential in crystals may be written in the form[18]

$$W(\text{rep})\simeq N\beta_{+-}b_+b_-e^{-r/\rho}. \tag{4}$$

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[15] M. L. Meilman, M. I. Samoilovich, L. I. Potkin, and N. I. Sergeeva, Fiz. Tverd. Tela **8**, 2336 (1966) [English transl.: Soviet Phys.—Solid State **8**, 1864 (1967)]; I. N. Kurkin, *ibid.* **8**, 585 (1966).

[16] The existing body of work on rare earths in scheelites (e.g., Ref. 15) indicates that scaling the fourth- and higher-order terms with lattice parameters is reasonable. The data also seems to indicate that the second-order crystal-field terms do not change very much with lattice size.

[17] Mario Tosi, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1965), p. 1.

[18] We have simplified the expression given in Ref. 16, Eq. (5.12), by leaving out the energy of repulsion between next-nearest-neighbor ions (i.e., the repulsion between Ca^{2+} and Ca^{2+}, Yb^{3+} and Ca^{3+}, etc.). Since we may expect that significant errors will in any case result from our attempt to impose an alkali halide type of treatment on a more complicated lattice, there seems little point in retaining these terms. Other effects, such as reorientation of the $(WO_4)^{2-}$ ions, may be responsible for larger changes in the magnitude and direction of the repulsive forces when small ions are substituted in a scheelite lattice.

N is the number of nearest neighbor ions (negatively charged oxygen atoms belonging to the WO_4^{2-} molecular ion in our case) and ρ is the "hardness" parameter ($\sim$0.32 Å) which is approximately constant for all salts of a given series. β_{+-} is a constant of the order of unity depending on the charge distributions and is given by

$$\beta_{+-}=1+(v_+/n_+)+(v_-/n_-)\,, \tag{5}$$

where v_+, v_- are the ionic valences of positive and negative ions and n_+, n_- are their respective numbers of valence electrons. The parameters b_+, b_- denote the strength of the repulsive interaction and are proportional to $e^{r+/\rho}$ and $e^{r-/\rho}$, where r_+, r_- are the radii of the positive and negative ions. The interionic distance $r=r_++r_-+\Delta$, where Δ is a small quantity (from -0.11 to 0.08 Å) depending on the coordination number. The total potential, including the electrostatic attraction may be written as

$$U=Ae^{-r/\rho}-\alpha q_+q_-/r\,, \tag{6}$$

where α is the Madelung constant, q_+, q_- are the ionic charges, and $A=N\beta_{+-}b_+b_-$.

To obtain the equilibrium ionic distance r_0 in a normal unsubstituted material we set $dU/dr=0$. Thus we have

$$(r_0/\rho)^2e^{-0/\rho}=\alpha' q_+q_-/\rho A\,, \tag{7}$$

where α' is a constant analogous to and of the same order of magnitude as the Madelung constant α. In practice $r_0/\rho\gg 1$ and we can solve (7) approximately, giving

$$r_0/\rho=2\ln(\eta^{1/2}\ln\eta)\,, \tag{8}$$

where

$$\eta=\alpha' q_+q_-/\rho A\,.$$

The logarithmic form of (8) suggests that the substitution of a trivalent ion for a divalent ion of the same size would not of itself have any significant tendency to change the local lattice spacings. (This might also be inferred from the short-range nature of the repulsive forces.) Inclusion of the next-nearest-neighbor (Ca^{2+},Ca^{2+}) forces, discarded in Eq. (4), would further reinforce this conclusion, since these forces tend to increase lattice rigidity and to render the environment less susceptible to distortion caused by changes of ionic charge.

At this stage we make a broader and much less easily justified assumption. That is, that the environment of a loose ion remains the same as the environment of the unsubstituted positive ions in the normal scheelite, in spite of the very considerable changes in the repulsive energy term due to the size mismatch. Making this assumption we find, from Eq. (6), that the restoring force on a positive ion displaced by an amount δ from its equilibrium position in the unsubstituted lattice is given by

$$F=\left[\left(\frac{N\beta_{+-}b_+b_-}{\rho^2}\right)e^{-r_0/\rho}-\frac{2\alpha' q_+q_-}{r_0^3}\right]\delta\,. \tag{9}$$

The same equation, with the same values for N, ρ, b_-, α', q_-, and r_0 is assumed to give the restoring force for a loose substituted ion, the differences occurring in β_{+-}, q_+, and in the repulsive-interaction constant b_+. The change in β_{+-} is relatively trivial.[19] For Ca^{2+} in $CaWO_4$, Sr^{2+} in $SrWO_4$, etc., β_{+-} is 2.33; for Yb^{3+} in $CaWO_4$, etc., it is $\sim$3. The major change occurs in the constant b_+ which is proportional to $e^{r+/\rho}$. Writing $\bar{F}=(N\beta_{+-}b_+b_-/\rho)e^{-r_0/\rho}$ (where all parameters refer to an unsubstituted lattice) we deduce from (7) that $\bar{F}$ is also given by

$$\bar{F}=\alpha' q_+q_-/r_0^2\,.$$

The force constant $k=F/\delta$ in Eq. (9) can therefore be written as the sum of repulsive and attractive portions k(rep) and k(attr) in the form

$$k=k(\text{rep})-k(\text{attr})=\bar{F}/\rho-2\bar{F}/r_0\,. \tag{10}$$

Equation (10) refers to the cation in a normal lattice. For the substituted cation we have

$$\begin{aligned}k'(\text{rep})&=(\beta_{+-}'/\beta_{+-})\exp[(r_+'-r_+)/\rho]k(\text{rep})\\&=1.3[\exp(\Delta r/\rho)]k(\text{rep})\end{aligned}$$

and

$$k'(\text{attr})=(q_+'/q_+)k(\text{attr})=1.5k(\text{attr})\,,$$

giving

$$k'=(\bar{F}/\rho)(1.3e^{\Delta r/\rho}-3\rho/r_0)\,. \tag{11}$$

Primed quantities refer to the substituted cation; r_0 is the equilibrium ionic distance in the normal scheelite, and Δr is the ionic size mismatch $r_+'-r_+$.

Taking the ionic radii in Table I and setting $\rho=0.32$ Å we could, in principle, use Eq. (11) to calculate the required force constants. We are here primarily interested in making comparisons, however. Referred to k (Ca in $CaWO_4$) as unity, we have the following values for $k_{\text{ratio}}=k'$ (substituted ion)/k(Ca in $CaWO_4$):

$$\begin{aligned}k_{\text{ratio}}(\text{Yb-CaWO}_4)&=1.03\,,\\k_{\text{ratio}}(\text{Yb-SrWO}_4)&=0.52\,,\\k_{\text{ratio}}(\text{Yb-BaWO}_4)&=0.12\,.\end{aligned} \tag{12}$$

We see that the restoring force for Yb in $SrWO_4$ is about twice as small as the restoring force for Yb in $CaWO_4$. In $BaWO_4$ the restoring force is about a factor of 8 smaller than in $CaWO_4$. An absolute value for the reference standard (Ca in $CaWO_4$) might be obtained from first principles by calculating α' and substituting the appropriate quantities in Eq. (10). Values which follow more directly from physical measurements can be derived by setting $k=M\omega^2$, where M is the mass of the cation and ω is the optical-mode frequency. For Ca in $CaWO_4$, $\omega=2.6\times10^{13}$ rad/sec[20] and $M=6.5\times10^{-23}$ g. Hence $k(\text{Ca-CaWO}_4)=4\times10^4$ dyn/cm and the restoring force constants for Yb

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[19] It has been assumed that the quantities v_- and n_- in Eq. (5) are 2 and 6, respectively. It would perhaps be equally reasonable to treat $(WO_4)^{2-}$ as an ion and thus to arrive at values of 2 and 4. Fortunately, this does not make a great deal of difference to the results.

[20] S. P. S. Porto and J. F. Scott, Phys. Rev. **157**, 716 (1967).

follow from (12). These values will undergo some modification if, as suggested in Tosi's paper,[17] we allow the hardness parameter ρ to increase slightly through the scheelite series. For example, if $\rho(\mathrm{Ca})=0.32$, $\rho(\mathrm{Sr})=0.34$ and $\rho(\mathrm{Ba})=0.36$ the three values of k_{ratio} become 1.03, 0.55, and 0.18. Small changes in the Born-Mayer parameters do not have a large effect on restoring forces in the first two lattices but they are of great importance in $\mathrm{BaWO_4}$, where $k(\mathrm{rep})$ and $k(\mathrm{attr})$ are more nearly balanced.

It should be emphasized that the entire analysis given above assumes that the restoring force will be the same for all directions of ionic displacement. This assumption has been made in order to present the argument in the simplest possible form. It is not, however, the result which one would anticipate on more general grounds. Indeed, it is not even a plausible approximation for the case under consideration. An ion subjected to a small displacement, $u_j(j=1$ to 3), from its equilibrium position experiences a restoring force with components $P_i=\partial V/\partial x_i$ where V is the mechanical potential energy in the displaced position. By expanding V as a Taylor series $V=V_0+u_j(\partial V/\partial x_j)+\ldots$, it is easy to show that (to the first order in u_j) $P_i=u_j(\partial^2V/\partial x_i\partial x_j)^{u}{}_{j=0}$. The force constant k is therefore a second rank tensor, $k_{ij}=\partial^2V/\partial x_i\partial x_j$, and as such must display the symmetry properties appropriate to the point group of the site occupied by the undisplaced ion. In the S_4 case, k_{ij} is characterized by two values $k_{\parallel}$ and $k_{\perp}$ (in analogy to the g tensor). We should therefore expect to find two different force constants for the cation in the scheelite series corresponding to "hard" and "easy" directions of motion.

B. Ionic Motion and g Shifts

The displacement u of the $\mathrm{Yb^{3+}}$ ion in an electric field may be deduced from the results obtained in Sec. III A. Let us assume an effective dielectric constant of unity in calculating the actual field seen by the cation (see Ref. 21). Then, taking the restoring constant $k(\mathrm{Ca\text{-}CaWO_4})=4\times10^4$ dyn/cm, we have $u(\mathrm{Ca\text{-}CaWO_4})=0.8\times10^{-16}$ cm/V.[21] From the fact that $\mathrm{Yb^{3+}}$ has 1.5 times the charge of $\mathrm{Ca^{2+}}$, and from the result $k_{\mathrm{ratio}}(\mathrm{Yb\text{-}CaWO_4})=1.03$, we infer that $\Delta r(\mathrm{Yb\text{-}CaWO_4})=1.2\times10^{-16}$ cm/V. Likewise $u(\mathrm{Yb\text{-}SrWO_4})=2.4\times10^{-16}$ cm/V and $u(\mathrm{Yb\text{-}BaWO_4})=9.6\times10^{-16}$ cm/V. If we use the modified values of the hardness parameter ρ as indicated near the end of Sec. IV A, we obtain $u(\mathrm{Yb\text{-}SrWO_4})=2.3\times10^{-16}$ cm/V and $u(\mathrm{Yb\text{-}BaWO_4})=6.0\times10^{-16}$ cm/V. It will of course be apparent that once an impurity ion approaches the condition of critical stability in the host lattice, as is the case with Yb in $\mathrm{BaWO_4}$, small changes in the repulsive part of the force constant will have a disproportionately large effect on the total force constant, and hence, on u.

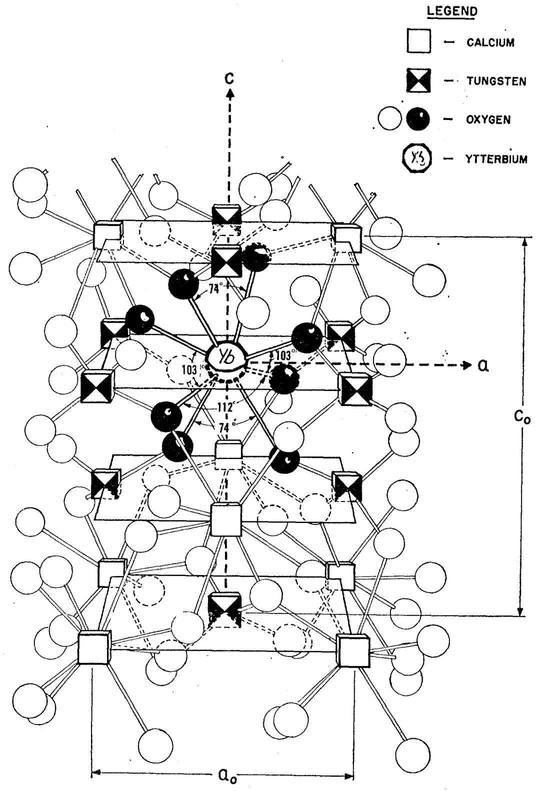

FIG. 1. The $\mathrm{CaWO_4}$ lattice with a Yb impurity at a Ca site.

Figure 1 shows the position of the undisplaced $\mathrm{Yb^{3+}}$ ion in a scheelite lattice. The nearest neighbors consists of eight oxygens [belonging to different $(\mathrm{WO_4})^{2-}$ ions] which, taken alone, give D_{2d} point symmetry at the $\mathrm{Yb^{3+}}$ ions with two fold axes at 8° to the a and b crystal axes. The more remote W and Ca atoms likewise give D_{2d} point symmetry but with twofold axes at 45° to the a and b axes.

When the $\mathrm{Yb^{3+}}$ ion is displaced by the applied electric field it ceases to be at a site of S_4 symmetry and new terms appear in the crystal field. The effect of a displacement of the Yb ion on the local crystal field is discussed in some detail in the second part of the Appendix. It is shown there that the new even-field terms introduced by a displacement[22] u_μ is given by

$$V_K{}^Q(\theta,\varphi)=(u_\mu/R)\eta(K,Q)F_{K+1}{}^{Q-\mu}C_K{}^Q(\theta,\varphi)\qquad(13)$$

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[21] As a check of the calculated force constant for Ca in $\mathrm{CaWO_4}$, one can calculate the polarization resulting from the movement obtained in the text and compare this with the ionic polarization based on the dielectric constant. We had for a 1-V/cm field, $u=0.8\times10^{-16}$ cm/V for $\mathrm{Ca^{2+}}$. For a field of 1 esu per cm, the polarization of 1 cm³ (1.26×10^{22} $\mathrm{Ca^{2+}}$ ions) is $P=0.8\times10^{-16}\times300\times1.26\times10^{22}\times9.6\times10^{-10}\simeq0.29$. This polarization is due to ionic motion of $\mathrm{Ca^{2+}}$ ions with $\mathrm{WO_4{}^{2-}}$ ions stationary. Now if the mean dielectric constant is 9 and the refractive index is 1.94, the ionic part of the dielectric constant ~5. From $P=[(\epsilon-1)/4\pi]E$ we have $P=4/4\pi\simeq0.32$. This is very close to the value 0.29 above, indicating that our force constant, $k=4\times10^4$ dyn/cm cannot be far wrong.

[22] u_μ stands for the components r_0, $r\pm$ of a spherical vector. $r_0=z$, $r\pm=\mp(\psi\pm iy)/\sqrt{2}$. See Ref. 23, Chap. 5.

with

$$\eta(K,Q)=(-)^{+KQ}[(2K+3)(2K+1)(K+1)]^{1/2}\times\begin{pmatrix}K & 1 & K+1\\ Q & \mu & Q-\mu\end{pmatrix}$$

and

$$F_{K+1}{}^{Q-\mu}=\sum_j \frac{r^{k-1}}{R_j{}^{k+1}} Z_j e^2 C_k{}^q(\theta_j,\varphi_j)\,.$$

Note that K,Q now replaces $k-1$, $q+\mu$ in Eqs. (A4) through (A6) in the Appendix. The $3j$ symbol in η is defined in Ref. 23. We will restrict ourselves to the terms $V_2{}^1$, $V_2{}^2$ in the Yb^{3+} electric effect so that only the $F_3{}^2$ term enters [Eq. (A6)]. As discussed in the Appendix [after Eq. (A6)], the most reasonable procedure to follow is to set $F_3{}^2=(\alpha/\bar{R})A_2{}^0$, where α is the proportionality constant between the sums

$$\sum_j \tfrac{1}{2}[C_3{}^2(\theta_j,\varphi_j)+C_3{}^{-2}(\theta_j,\varphi_j)]/R_j{}^3 \quad\text{and}\quad \sum_j C_2{}^0(\theta_j)/R_j{}^3\,,$$

$\bar{R}$ is an average distance between the Yb ion and its neighbors, and $A_2{}^0$ is the empirical value for the second degree crystal-field parameter. According to Ref. 14 $A_2{}^0=750$ cm^{-1}. Rough calculation of the sums give a value of α of about 0.6. (The correct value of α depends on the choice of the average distance $\bar{R}$.) We take $\bar{R}$ to be the unit cell size 10.38 Å. The displacement is $u_\mu=ZeE_\mu/k$, where E_μ is in the laboratory applied field, Z is now equal to 3, and $k=4\times10^4$ dyn/cm. Therefore in a field of 1 V/cm, $u_\mu=1.2\times10^{-16}$ cm. It is easy to show that $\eta(2,2)=\eta(2,1)=\sqrt{5}$. Finally writing $V_K{}^Q$ as $(2K+1/4\pi)b_K{}^Q C_K{}^Q(\theta,\varphi)$ we have the result $b_2{}^2=+b_2{}^1=1.3\times10^{-6}$ cm^{-1} per V/cm. These values give $B_\parallel=660\times10^{-9}$ per V/cm and $B_\perp=130\times10^{-9}$ per V/cm. The calculation value of $B_\perp$ is reasonably close to the measured value for Yb^{3+} in $CaWO_4$ (212×10^{-9}). However $B_\parallel$ is now much larger than the measured value in $CaWO_4$ (81×10^{-9}).

To calculate the ionic g shifts in the loose ions cases, $SrWO_4$ and $BaWO_4$, we use the changes in force constants calculated in the first part of Sec. IV for determining u_μ. The new even field parameters are as follows:

$$CaWO_4\text{:}\quad b_2{}^2=b_2{}^1=1.3\times10^{-6}\ \text{cm}^{-1},$$

$$SrWO_4\text{:}\quad b_2{}^2=b_2{}^1=2.5\times10^{-6}\ \text{cm}^{-1},$$

$$BaWO_4\text{:}\quad b_2{}^2=b_2{}^1=7.5\times10^{-6}\ \text{cm}^{-1}.$$

The g-shift parameters based on these values are given in Table IV. In computing $B_\parallel$ and $B_\perp$ we have taken into account the alteration in the energy levels and wave functions introduced by the partial scaling (see end of Sec. III).

TABLE IV. Calculated ionic g-shift parameters. ρ is taken as 0.32 for Ca, 0.34 for Sr, and 0.36 for Ba. We used the partially scaled crystal field for Sr and Ba (see Sec. III and Table I) and included the crystal-field effect discussed at the end of Sec. III. r is the ratio of the g shift in Sr or $BaWO_4$ to the shift in $CaWO_4$. B gives $\delta(g^2)$ per 10^9 V/cm.

	E parallel				E perpendicular			
	Expt.		Calc.		Expt.		Calc.	
	$B_\parallel$	$r_\parallel$	$B_\parallel$	$r_\parallel$	$B_\perp$	$r_\perp$	$B_\perp$	$r_\perp$
$CaWO_4$	81		800		212		130	
$SrWO_4$	500	6.2	2000	2.5	340	1.6	390	3
$BaWO_4$	1180	14.5	9600	12.0	570	2.7	1950	15

V. DISCUSSION

In Sec. III we pointed out that, except for the $E_\parallel$ effect in Yb-$CaWO_4$, it is unlikely that the electronic effect contributes significantly to the observed g-shift parameters. It remains, therefore, to compare these parameters with the results of the ionic effect calculations of the last section. This should provide some reasonable basis for judging the validity of the simple model we have assumed. The comparison can be made under the following headings: (i) absolute and relative magnitudes of $B_\parallel$ and $B_\perp$, (ii) increases in $B_\parallel$ and $B_\perp$ as we ascend the series of scheelite host lattices, and (iii) the characteristic angles $\varphi_\parallel$ and $\varphi_\perp$.

(i) The experimental magnitudes are smaller than the calculated values shown in Table IV. It is difficult to gauge the significance of the differences of the absolute values between calculated and observed parameters because of the uncertainty introduced by the factor $\alpha A_2{}^0$ in the theory of the ionic effect. (However, without this adjustment, which reconciles point charge calculations with actual observations of crystal fields, the calculated values would have been still greater.) If, as we believe, our estimate of α is substantially correct, the overestimates of $B_\parallel$, $B_\perp$ must be due to an underestimate of the ionic force constant k. Before proceeding along this line we observe (Table IV) that while the perpendicular effect in $CaWO_4$ is fairly well accounted for, the measured parallel effect is much too small. In $SrWO_4$, the agreement for both parallel and perpendicular effects improve substantially although the calculated $B_\parallel$ is still a factor of 4 too large. In $BaWO_4$ the situation worsens, with the calculated values of $B_\parallel$ and $B_\perp$ too large by factors of 8.5 and 3.5. These results imply deviations of the force constant for small ions from the predictions of the simple Born-Mayer model as regards to magnitude and the assumed isotropy.

A possible flaw in our model arises from the assumption that the crystal environment will not change when a small, loose-fitting ion is substituted in the lattice. In fact, one would expect some accommodation of the immediate surroundings of the small ion to occur, leading to larger restoring forces and smaller ionic motion. (It should be noted, however, that any such

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[23] A. R. Edmonds, *Angular Momentum In Quantum Mechanics* (Princeton University Press, Princeton, N. J., 1957), p. 45.

accommodation does not change the S_4 point symmetry and does not in any way involve "switching" of the Yb ion to an off-center position. Any such change in the point symmetry would be relatively easy to detect in electric-effect experiments.) The comparison of the relative magnitudes of $B_{\parallel}$ and $B_{\perp}$ showed that the discrepancy between theoretical and experimental values is greatest for $B_{\parallel}$. We already pointed out (end of Sec. IV A) that the force constant k should be replaced by a second rank tensor with two independent terms $k_{\parallel}$ and $k_{\perp}$ for displacements perpendicular or parallel to the c axis. The results suggest that $k_{\parallel}$ is greater than $k_{\perp}$, i.e., the c axis is a relatively hard direction for ionic motion. This impression may be at least qualitatively confirmed by a consideration of the ionic radii and the distance to the oxygens surrounding Yb^{3+}. If, for instance, we draw a plane through the oxygen atoms shown subtending the 74° angle in Fig. 1 and the Yb ion at the vertex, the circle's representing the O^{2-} cross sections in $CaWO_4$ are nearly touch [Fig. 2(a)]. A similar drawing [Fig. 2(b)] for the oxygen atoms above and below the plane (which subtend the 103° angle in Fig. 1) suggests that there is more space for movement in this direction.

Another factor which possibly can enhance the anisotropy (as well as the magnitude) of the restoring force is the difference in electronic structure of an alkaline earth as compared to a Yb ion. The former always have noble gas structures in the divalent state so that the charge cloud has perfect spherical symmetry. Yb^{3+} has an unfilled $4f$ shell nominally within the filled $5p$ shell. Configuration interaction between the f and p electrons will cause lobes in the electronic charge cloud of the Yb. This could make it relatively more difficult (or easy) for the Yb to move in certain directions than a spherical ion of the same *average* radius. This effect would clearly be more pronounced in smaller $CaWO_4$ lattice.

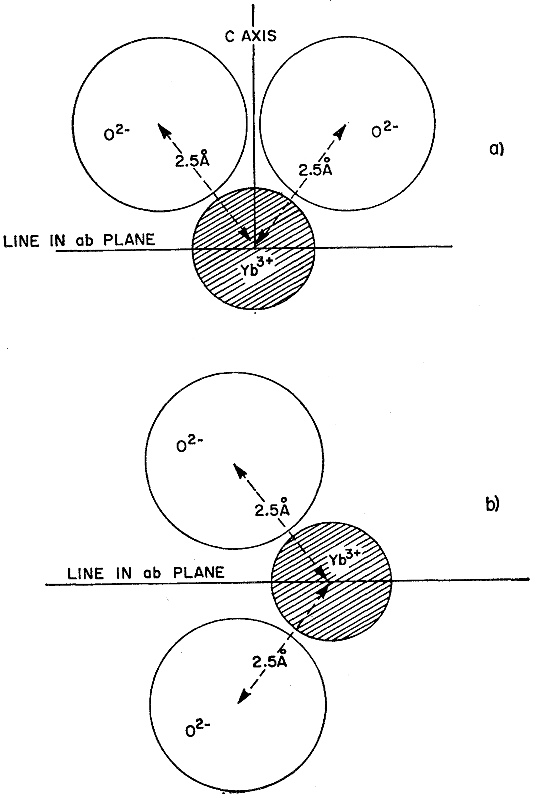

FIG. 2. Geometrical relation between Yb^{3+} and adjacent O^{2-} in undistorted $CaWO_4$. [Ionic radii (Pauling, Ref. 10) are 0.94 Å and 1.4 Å for Yb^{3+} and O^{2-}, respectively.] (a) Yb^{3+} and O^{2-} ions shown subtending the 74° angle in Fig. 1. (b) Yb^{3+} and O^{2-} ions shown subtending the 103° angle in Fig. 1.

If the c axis is indeed a relatively hard direction of motion this could help explain why the $E_{\parallel}$ effect in Yb-$CaWO_4$ stands alone and seems not to be completely dominated by ionic motion. In $SrWO_4$, the lattice is somewhat larger and, even including any local accommodation, the Yb should find motion along the c axis much easier. Even so, it is difficult to see why there should be as much as the observed sixfold increase in $B_{\parallel}$ in going from $CaWO_4$ to $SrWO_4$.

(ii) With the above exception, the increase in $B_{\parallel}$ and $B_{\perp}$ in the scheelite series can be roughly correlated with increasing ionic looseness. If, however, the observed electric shifts are to be taken as a measure of looseness, we must conclude that the Yb ion in $BaWO_4$ is not as loose as the simple Born-Mayer model predicts. This could mean that the local accommodation of the lattice is greater for this lattice than for the other scheelites. Indeed, simple calculations based on the Born-Mayer model (Sec. IV A) show that if the local oxygens move enough to take up $\frac{1}{3}$ of the 0.4 Å size mismatch in $BaWO_4$ (an oxygen movement of 0.14 Å), the force constant for Yb in $BaWO_4$ will increase from 0.7×10^4 dyn/cm to 1.4×10^4 dyn/cm. This will lead to $\frac{1}{2}$ the g-shift parameter predicted for the Yb:$BaWO_4$ case in Table IV. In the case of $SrWO_4$, the same relative oxygen movement ($\frac{1}{3}$ of 0.19 Å$\cong$0.06 Å) leads to a reduction of $B_{\parallel}$, $B_{\perp}$ (we are assuming uniform change in the force constant only out of necessity) of about 20%. The force constant is of course exceedingly sensitive to small changes in ionic separation when we approach critical stability as in $BaWO_4$.

A different type of omission in the theory may also explain some of these discrepancies. We have ignored dynamic effects entirely and relied on a kinematic approach. There is good reason, however, to expect the zero-point vibrations to assert themselves, particularly in a loose lattice. For instance, the rms fluctuation in position, $\langle x^2\rangle^{1/2}$ of the Yb ion (assuming a fixed environment) is proportional to $k^{-1/4}$. In $CaWO_4$ this zero point fluctuation of Yb proves to be $\sim$0.06 Å while in $BaWO_4$ we get $\langle x^2\rangle^{1/2}\approx0.1$ Å. This apparent increase in the size of the ion would increase the stiffness parameters k by $\sim$35% in $CaWO_4$ and by over 100% in $BaWO_4$. [These estimates involve the use of Eq. (11).]

According to our calculations, a trivalent ion of radius less than about 0.8 Å would be mechanically unstable in a static, undistorted cation site in $BaWO_4$. (By unstable we mean that the restoring force has become negative.) While the zero-point vibrations and local lattice accommodation will reduce the critical radius below 0.8 Å, we might reasonably expect that a number of ions in the first transition series (3*d*), both divalent and trivalent, would be sufficiently small to be unstable in $BaWO_4$. Small ions of this type would presumably find a different equilibrium position, possibly by switching to off-center positions about the cation site.[24]

(iii) The angles $\varphi_{\parallel}$ and $\varphi_{\perp}$ depend on the relative values of the new crystal field terms, $V_2^2(\theta,\varphi)$, $V_2^1(\theta,\varphi)$ introduced by the ionic displacement. It is somewhat difficult to draw any obvious physical inferrences from these angles for a symmetry as low as S_4. The results in Table I do, however, show a remarkable similarity (for all cases but the $\varphi_{\parallel}$ in Yb-$CaWO_4$) and tempt one to speculate on the significance of the actual angles we observe. The similarity in itself supports our general conclusion, that all effects save the $E_{\parallel}$ effect in Yb-$CaWO_4$ originate in the same way (i.e., are due to ionic displacement). It also suggests that, if $E_{\parallel}$ and $E_{\perp}$ are considered separately, the new crystal-field terms have the same form in all the host lattices. The values themselves acquire some significance if we note that, for a D_{2d} environment, the angles $\varphi_{\parallel}$ and $\frac{1}{2}\varphi_{\perp}$ define the orientation of the D_{2d} twofold axis. The nearest-neighbor oxygens, taken alone, subtend D_{2d} symmetry at the Ca site, the D_{2d} twofold rotation axes lying at 8° to the *a* axis in the *a*-*b* plane. The Ca and *W* atoms are likewise arranged with D_{2d} symmetry but for these the twofold axes are 45° to the *a* and *b* axes. The observed values of $\varphi_{\parallel}$ are therefore close to those which one would expect to find if the oxygen atoms were primarily responsible for the new crystal field components in the case of *c* axis displacements, while the value of $\varphi_{\perp}$ suggests that more remote atoms are important in the *a* axis displacement. It is interesting to compare this with our earlier conclusion that the two oxygens subtending the 74° angle (Fig. 1) provide the major restoring force in the *c* direction. The values for $\varphi_{\parallel}$ in Yb-$SrWO_4$ and Yb-$BaWO_4$ suggest that these oxygen atoms may also determine the form of the new crystal-field terms seen by the displaced ion.

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APPENDIX

Detailed descriptions of the equivalent even-field techniques and examples of its application to the effects of odd fields on the spin-Hamiltonian parameters are given elsewhere.[9,25] Here we briefly summarize the arguments as they apply to the case of the Yb^{3+} ion in a site of S_4 symmetry. We also extend the concept to cover odd field effects arising from the ionic motion. Although the ionic effects are physically distinct from the electronic case and, in particular, do *not* involve mixing of opposite parity states, they can be described in a manner which is formally similar.

We begin with the electronic effect. The states belonging to the $4f^{13}$ configuration of Yb^{3+} are all within 11 000 cm^{-1} of the ground doublet. The $4f^{12}\,5d$ states are all above ~50 000 cm^{-1}. In the ground manifold, states may be specified according to the familiar Russell-Saunders coupling scheme with *L*, *S*, *J* good quantum numbers. In fact, departures from the Russell-Saunders coupling and configuration interaction do not affect the validity of the following arguments. The crystal field may be expressed as a sum of spherical harmonics $\sum_{p,q}[(2p+1)/4\pi]A_p{}^qC_p{}^q(\theta,\varphi)$. For the case of S_4 point symmetry we have even-crystal-field terms ($p=2$, 4, or 6, $q=0$ or ± 4) and odd terms ($p=3$, 5 and $q=\pm 2$). The even crystal fields mix states within the f^{13} manifold so that *M*, the azimuthal component of angular momentum, is no longer a good quantum number. The odd field mixes states of opposite parity such as the $4f^{12}5d$ set into the ground manifold. According to second order perturbation theory the resulting interaction is given by

$$\sum_i \frac{\langle f^{13},j'|V_p{}^q|f^{12}d,i\rangle\langle f^{12}d,i|V_s{}^t|f^{13},j\rangle}{\Delta E_i}, \qquad \text{(A1)}$$

where *j* and *j'* are states belonging to the ground manifold [They must belong to different Kramers doublets for our odd electron case for the interaction (A1) to be nonzero.] The interaction terms $V_p{}^q$, $V_s{}^t$ are products of field strength parameters and the harmonics $C_p{}^q(\theta,\varphi)$, $C_s{}^t(\theta,\varphi)$. The sum is taken over all the states *i* of the $4f^{12}5d$ manifold and E_i is the energy of state *i*. The interaction terms can consist of odd-crystal-field terms such as $(7/4\pi)^{1/2}A_3{}^2C_3{}^2(\theta,\varphi)$, in which case the expression can be used to calculate modifications of the spin-Hamiltonian due to naturally occurring odd fields. We are however interested in the case where one of the terms is of the form $ErC_1{}^t(\theta,\varphi)$, representing the perturbation due to a laboratory applied field. This term, in conjunction with a naturally occurring odd-crystal-field term, leads to the linear electric shift (electronic case).

The calculation can be greatly simplified if one can assume that the energy separation is essentially the same for all states in the excited $4f^{12}5d$ configuration. Closure techniques[9,25] may then be employed and the expression

$$\sum_i \frac{V_p{}^q|f^{12}d,i\rangle\langle f^{12}d,i|V_s{}^t}{E_i} \qquad \text{(A2)}$$

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[24] R. J. Quigley and T. P. Das, Phys. Rev. **177**, 1340 (1969); **164**, 1185 (1967).

[25] B. R. Judd, Phys. Rev. **127**, 750 (1962).

may be replaced by an equivalent operator $\sum_u D_u{}^v C_u{}^v \times(\theta,\varphi)$, where $v=t+q$ and u equals one of the integers in the range $|p-s|$, $|p-s+2|$, $\ldots$, $p+s$. The expression for the coefficient $D_u{}^v$ is a complicated combination of $3j$ and $6j$ symbols which we will not give here (see Refs. 9 and 25). It is important to note that, since p and s are both odd, the $D_u{}^v C_u{}^v(\theta,\varphi)$ are, of necessity, even tensor operators. They constitute an *equivalent even field* whose effects on the resonance intervals and on the spin-Hamiltonian may be computed by the familiar methods. If both fields in (A2) are the naturally occurring odd fields, the resulting equivalent even field merely consists of additions to those spherical harmonics which were already represented. These additions would constitute a modification of the crystal-field parameters obtained in a point-charge calculation, but would produce no effects on the spin-Hamiltonian which are phenomenologically distinguishable from the effect of the even field. If, on the other hand, one of the odd fields is the applied electric field, new crystal field terms can be generated. For example, an electric field along the c axis [harmonic $C_1{}^0(\theta,\varphi)$] in combination with the $C_3{}^2$ odd crystal harmonic in S_4 symmetry produces an equivalent field which has the form[26] $C_1{}^0 C_3{}^2 \simeq a C_2{}^2 + b C_4{}^2$. (This corresponds to a reduction of the point symmetry from S_4 to C_2 by elimination of the reflection plane.)

In the ionic effect, the applied field causes a displacement of the Yb ion relative to its surroundings. In its new position the Yb^{3+} ion "sees" a different crystal field which may include new crystal-field components. Initially, let us take the Yb^{3+} ion at the origin with the electron position defined by the vector $\mathbf{r}$ with neighbor j, charged Z_j is defined by the vector $\mathbf{R}_j$. Under the influence of the electric field $\mathbf{E}$, there is a relative displacement $\mathbf{u}^{(j)}$. The change in the crystal field potential, to terms linear in $\mathbf{u}$, is given by the dipole term $\delta V^{(j)}=Z_j e^2(\mathbf{u}^{(j)}\cdot\nabla)|\mathbf{R}_j-\mathbf{r}|^{-1}$. For convenience we take the entire relative displacement to be due to motion of the Yb ion. The gradient is therefore taken only over the electron coordinates r, θ, φ while coordinates of the jth ion, R_j, θ_j, φ_j, are unaffected. The quantity $|R_j-r|^{-1}$ can be expressed by the usual multipole expansion $\sum_k (r^k/R^{k+1})P_k(\cos\omega)$ and using the spherical harmonic addition theorem (p. 63 of Ref. 23) we have, for the new crystal-field terms,

$$\delta V^{(j)}=Z_j e^2(\mathbf{u}^{(j)}\cdot\nabla)\sum_{k,q}\frac{r^k}{R_j{}^{k+1}}C_k{}^q(\theta,\varphi)C_k{}^q(\theta_j,\varphi_j). \quad \text{(A3)}$$

A simple method for evaluating[27] the gradient terms is given on p. 79 of Ref. 23. The method consists of directly evaluating $\nabla_z Y_k{}^0(\theta,\varphi)$. Noting that ∇ transforms like a first-rank spherical tensor, we can immediately obtain the general $\nabla_\mu Y_k{}^q$ in terms of standard $3j$ symbols,[23] where μ is the component of the electric field in spherical coordinates.[22] The change in potential energy due to an electric field component E_μ is given by

$$\begin{aligned}\delta V_\mu{}^{(j)}&=u_\mu\sum_{k,q}\left[\frac{r^{k-1}}{R_j{}^{k+1}}Z_j e^2 C_k{}^q(\theta_j,\varphi_j)\right]\\&\qquad\times\eta(k-1,\,q+\mu)C_{k-1}{}^{q+\mu}(\theta,\varphi)\,,\\ \eta(k-1,\,q+\mu)&=(-)^{k-1+q+\mu}[k(2k-1)(2k+1)]^{1/2}\\&\qquad\times\begin{pmatrix}k-1 & 1 & k\\ -(q+\mu) & \mu & q\end{pmatrix}.\end{aligned}\quad \text{(A4)}$$

At this stage it is convenient to sum over all lattice points j and to write the results in terms of the spherical harmonic components $k-1$, $q+\mu$. We obtain

$$\delta V_\mu(k-1,\,q+\mu)=u_\mu\eta(k-1,\,q+\mu)F_k{}^q C_{k-1}{}^{q+\mu}(\theta,\varphi)\,, \quad \text{(A5)}$$

where $F_k{}^q$ is the term in brackets in Eq. (A4) summed over all lattice points j. $F_k{}^q$ has the *exact angular form* of the crystal field parameter $A_k{}^q$ but the radial factor appears only to the $k-1$ power rather than as r_k. This fact introduces a complication into the determination of δV. Before dealing with this, some brief qualitative comments are in order.

If δV is to produce a significant first-order effect, it must be an even harmonic ($k-1$ must be an even integer). Hence k must be an odd number. This is, of course, a manifestation of the fundamental rule that first order electric shifts occur only for crystals without a center of symmetry. It is also important to note the $\delta V(k-1,\,q+\mu)$ is nonzero only when the k,q correspond to an odd-crystal-field component present in the host material in zero applied electric field.

The dominant odd field term in CaWO$_4$ is the component $(7/4\pi)A_3{}^2C_3{}^2(\theta,\varphi)$; therefore we need to calculate

$$F_3{}^2=\sum Z_u e^2(r^2/R_j{}^4)C_3{}^2(\theta_j,\varphi_j)\,. \quad \text{(A6)}$$

At first sight it may seem that $F_3{}^2$ can be determined by using the values of $A_3{}^2=1500$ cm^{-1} (Sec. III) in the expression for $F_3{}^2$. Unfortunately, this conceals the fact that the odd field component $A_3{}^2C_3{}^2$ is used to generate the second-degree fields $C_2{}^q$ seen by the displaced ion. For the second-degree terms, the point-charge model is notoriously unreliable, with large errors the usual result of such calculations. It is therefore preferable to use the empirically known second-degree crystal-field parameter $A_2{}^0\simeq 750$ cm^{-1}, in determining $F_3{}^2$. In essence we define $F_3{}^2=(\alpha/R)A_2{}^0$, where $\bar{R}$ is an average distance between the Yb and its neighbors and α is a proportionality constant which we expect to be of the order of unity since the $C_k{}^q$ are of the same order numerically. α is in fact related to the ratio of the sums $\sum[C_3{}^2(\theta_j,\varphi_j)+C_3{}^{-2}(\theta_j,\varphi_1)]/2R_j{}^3$ and $\sum C_2{}^0(\theta_j)/R_j{}^3$.

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[26] The Kramers doublets for Yb^{3+} in CaWO$_4$ are already widely separated (>100 cm^{-1}) because of the crystal field. Small off-diagonal terms like $C_2{}^2(\theta,\varphi)$, $C_4{}^2(\theta,\varphi)$ will not cause any first-order changes in these splittings. They do produce first-order changes in the state compositions with which we are concerned when calculating g. For evaluation of direct tensor products see Ref. 23, p. 63.

[27] There is a misprint in the expression for $\sin\theta\partial/\partial\theta$ on p. 79 of Ref. 23. The factor $l(l-1)$ in the second term on the right should read $l(l+1)$.