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Electric Field Effect in Paramagnetic Resonance for Mn^{2+} in $SrWO_4$

A. Kiel
Bell Telephone Laboratories, Holmdel, New Jersey 07733

and

W. B. Mims
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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The electric field shifts in the paramagnetic resonance (EPR) for Mn^{2+} in $SrWO_4$ have been measured to be 104 and 225 for $R_\perp$ and $R_\parallel$, respectively, in units of Hz per V/cm. Comparison is made with the corresponding results obtained earlier for Mn^{2+} in $CaWO_4$. The experimental evidence indicates that the magnitude of the shifts depends on the ease with which the Mn^{2+} ion is displaced by the applied electric field, i.e., on the looseness of the ion in its substitutional site. In an earlier study involving the Yb^3 ion in the same host lattices, it was found that "ionic-motion" effects of this kind could be explained in terms of new even crystal field components seen by the displaced ion. In the present case, however, the observed magnitudes were too large to be attributed to the motion-induced crystal field components. The polarization of the Mn^{2+} ion induced by the applied field appears to be the primary mechanism giving rise to the electric field EPR shifts; the ease of ionic displacement of the impurity ion entering into the result insofar as it enhances the magnitude of the electric field is actually seen at the Mn^{2+} site. This result is especially surprising in view of the fact that in the previous Yb^{3+} study, we found that polarization effects of the larger and better-fitting Yb ion were, by and large, negligibly small. It is suggested here that the classification of electric field effects as ionic or electronic is liable to be misleading and that it is more appropriate to distinguish electric shifts which involve odd-even-state interactions from those which do not. In either case, motion of the ions will play an important role.

I. INTRODUCTION

In a recent study[1] of the electric field *g* shifts for Yb^{3+} in the series of scheelite lattices $CaWO_4$, $SrWO_4$, and $BaWO_4$, we found evidence that the shifts were due primarily to an electric-field-induced motion of the Yb^{3+} ion in their substitutional sites. This movement was larger than the movement of the cations in the normal scheelite lattice and was strongly dependent on the ratio between the size of Yb^{3+} and the size of the ions (Ca^{2+}, Sr^{2+}, and Ba^{2+}) replaced by it. This increased motion of the substituent ion was due in part to the extra positive charge of Yb^{3+}. The principal reason lay, however, in the considerable reduction in the short-range repulsive forces which occurs when a smaller loose-fitting ion is substituted for a larger ion in a crystal lattice.

These results have prompted us to reconsider the interpretation of an earlier set of experiments[2] in which the paramagnetic electric shifts of Mn^{2+} in $CaWO_4$ were measured. We have also made new measurements on the electric shifts of Mn^{2+} in $SrWO_4$ in order to find out whether the same pattern of behavior would be followed in this case as in the parallel case of Yb^{3+}. Unfortunately we were not able to extend the comparison to the case of Mn^{2+} as a substituent for Ba^{2+} because of the dominant tendency for Mn to form $(MnO_4)^{2+}$, $(MnO_4)^{3+}$ ions in the $BaWO_4$ lattice. This would otherwise have constituted an interesting case since calculations suggest that the Mn^{2+} ion should become unstable and switch to off-center positions[3] here.

The spectroscopic interpretations of the paramagnetic electric shift for Mn^{2+} (an *S*-state ion) and for Yb^{3+} (a Kramers-doublet ground state) are different in detail, but the results confirm our earlier conclusion that the magnitudes are essentially proportional to the elastic restoring forces which act on the ions in the different lattices. However, we have been forced to modify our earlier view that the paramagnetic electric effects can, like the dielectric constants, be clearly resolved into electronic and ionic components.

II. EXPERIMENTAL

The sample of Mn-doped $SrWO_4$ was grown by Linde Air Products, Inc.[4] The concentration was not determined but we estimate it as $\sim 10^{-5}$ Mn^{2+} per Sr^{2+}. Measurements of the electric-field-effect parameters were made by the electron-spin-echo method[5] at a temperature of 4.2 °K. The principal effect of the applied electric field is to add a term $H_E = E_i R_{ijk} S_j S_k$ to the spin Hamiltonian of the Mn^{2+} ion, i.e., to add terms of the "D" and "E" type. For S_4 point symmetry H_E reduces to the form

$$\begin{aligned} H_E = {} & E_a[R_{14}(S_yS_z + S_zS_y) + R_{15}(S_xS_z + S_zS_x)] \\ & + E_b[-R_{15}(S_yS_z + S_zS_y) + R_{14}(S_xS_z + S_zS_x)] \\ & + E_c[R_{11}(S_x^2 - S_y^2) + R_{36}(S_xS_y + S_yS_x)] \;, \end{aligned} \tag{1}$$

where $E_a = E_1$, $E_b = E_2$, and $E_c = E_3$ are electric field components[6] along the a, b, and c axes of the scheelite crystal and where R_{ijk} has been rewritten in the contracted Voigt notation.[7] As is pointed out in Ref. 2, the four independent numerical parameters can be rewritten as two magnitudes[8]

$$R_\perp = (R_{14}^2 + R_{15}^2)^{1/2}, \quad R_\parallel = (R_{31}^2 + R_{36}^2)^{1/2} \tag{2a}$$

and two angles

$$\phi_\perp = \arctan(R_{15}/R_{14}), \quad \phi_\parallel = \tfrac{1}{2}\arctan(R_{31}/R_{36}) \; . \tag{2b}$$

$R_\parallel$, $\phi_\parallel$ and $R_\perp$, $\phi_\perp$ are parameters determined by applying electric fields parallel to and perpendicular to the crystal c axis, and are analogous to the quantities $B_\parallel$, $\phi_\parallel$ and $B_\perp$, $\phi_\perp$ obtained in connection with the g shifts of a Kramers-doublet ion.[1] Some ambiguity in the signs of $\phi_\parallel$ and $\phi_\perp$ arises from the indeterminacy of the sign of the electric field shift in "inversion image" crystals such as the scheelites.[9] For the simpler D_{2d} symmetry, which, for example, is subtended by the nearest-neighbor oxygen atoms in the scheelite, $\phi_\parallel$ and $\frac{1}{2}\phi_\perp$ are equal and define the orientation of the D_{2d} twofold axes.

The electric-field-effect parameters for Mn^{2+} in $SrWO_4$ and for Mn^{2+} in[2] $CaWO_4$ are shown together in Table I for the purpose of comparison.[10] $R_\parallel$, $R_\perp$ are in units of MHz per 100 kV/cm of applied field. In order to derive the R_{ij} for Mn^{2+} in $SrWO_4$ from the experimental data, it was also necessary to measure some of the parameters which characterize the spin Hamiltonian in the absence of applied electric fields. These results are shown in Table II together with the corresponding results for Mn^{2+} in $CaWO_4$ as reported by Hempstead and Bowers.[11] The error is (as in Ref. 10) given as three standard deviations.

TABLE I. Electric-field-effect parameters for Mn^{2+} in two scheelite lattices. The $CaWO_4$ results are from a previous publication (Refs. 2 and 10). $R_\perp$, $R_\parallel$ are given in units of MHz per 10^5 V/cm of applied field.

	$CaWO_4$	$SrWO_4$
$R_\perp$	5.8	10.4
$R_\parallel$	12.6	22.5
$\lvert\varphi_\perp\rvert$	40°	25°
$\lvert\varphi_\parallel\rvert$	3°	8°

TABLE II. The larger terms appearing in the spin Hamiltonian of Mn^{2+} in two scheelite lattices. The $CaWO_4$ values are from Hempstead and Bowers (Ref. 11). A, B, and D are given in MHz units.

	$CaWO_4$	$SrWO_4$
$g_\parallel$	1.99987	1.970 ± 0.0002
$g_\perp$	1.99980	1.970 ± 0.0002
A	-266.8 ± 0.3	-271.2 ± 0.2
B	-268.6 ± 0.3	-270.5 ± 0.9
D	-413 ± 1	-326.6 ± 0.3

III. INTERPRETATION OF RESULTS

A. Ionic Motion

Before entering into details we should like to draw attention to the way in which the electric effects and ionic radii appear to be related in some of the scheelite crystals which we have examined (Refs. 1, 2, and present work). The Mn^{2+} ion is a loose-fitting substitute for Ca^{2+} and Sr^{2+} to much the same degree that the Yb^{3+} ion is a loose-fitting substitute for Sr^{2+} and Ba^{2+}. We can see this by taking ratios of ionic radii. According to Pauling,[12] we have the ionic radii Ca^{2+}: 0.99, Sr^{2+}: 1.13, Ba^{2+}: 1.35, Mn^{2+}: 0.80, and Yb^{3+}: 0.94 for which the relevant ratios are Mn^{2+}/Ca^{2+}: 0.81, Mn^{2+}/Sr^{2+}: 0.71, and Yb^{3+}/Sr^{2+}: 0.82, Yb^{3+}/Ba^{2+}: 0.69. If the magnitudes of the electric effect give us a measure of the elastic forces, we should therefore expect these magnitudes to change in much the same way in proceeding from $CaWO_4$ + Mn to $SrWO_4$ + Mn as they do when we proceed from $SrWO_4$ + Yb to $BaWO_4$ + Yb. This is very roughly the case. The ration $(R_\parallel)_{SrWO_4}/(R_\parallel)_{CaWO_4}$ and the similar ratio for $R_\perp$ are both ~ 1.8 (Table I). The corresponding ratios between the values of $R_\parallel$ and $R_\perp$ for Yb^{3+} in $SrWO_4$ and $BaWO_4$ are 2.3 and 1.7, respectively.[1] On this basis alone it would indeed appear that the ionic restoring forces undergo a slightly larger change in the Yb case than in the Mn case—a result which we might anticipate from the ratios of the ionic radii quoted above.

We now turn to the problem of interpreting these results in more specific terms. The case of Yb^{3+} in the scheelite lattices has already been discussed in Ref. 1. It is shown there that the calculated electronic effect is too small by an order of magnitude or more[13] to account for the results, and an attempt is made to interpret the observed g shifts in terms of ionic motion. Somewhat better agreement is obtained in this way (although the calculated values now tend to exceed the measured values). According to the model considered in Ref. 1, the g shifts are caused by[14] new *even* crystal fields V_{2K}^{Q} which arise as a result of the ionic displacement u. These even fields mix states in the ground manifold of Yb^{3+}, and the electric effects calculated in this way do not, therefore, involve the opposite-parity manifold.[15]

Since $V_{2K}^{Q} \propto u = qE/k$ (where q is the ionic charge and k the force[16] constant), this model at first suggests that it should be possible to compare force constants in the various scheelite lattices by comparing electric effects. Unfortunately, however, the situation in the case of the Yb^{3+} ion is not quite as straightforward as we might wish. As we proceed from one scheelite lattice to a larger one, the spacing between the Yb^{3+} Kramers doublets may be expected to diminish, and the g tensor of the ground-state doublet will, as a result, be more easily influenced by the new crystal field terms which are introduced by the ionic displacement. Thus, although the electric effect increases in proceeding to a larger host lattice, it may increase nonlinearly. The Mn^{2+} ion is not likely to show this kind of nonlinearity since the separations of the $^4P_{5/2}$ and $^5D_{5/2}$ levels which are involved in the perturbation calculations are largely determined by the Coulomb and exchange fields of the Mn^{2+} ion and are relatively insensitive to a scaling up or down of the lattice parameters. It should therefore afford us a better means of comparing the force constants—that is, providing we can confirm our assumption that the electric effects are due to ionic motion.

In order to calculate the ionic effect, we first need to know the ionic displacement which is caused by the applied field. This involves estimating the magnitude of the internal electric field $E_{\text{int}} = \sigma E_{\text{app}}$ which causes the ionic motion and finding values for the force constants k in the expression $u = qE_{\text{int}}/k$. Both σ and k would be better described by second-rank tensors and characterized by parameters $\sigma_\parallel$, $\sigma_\perp$, $k_\parallel$, and $k_\perp$ (for a site of S_4 symmetry). We can, however, adopt an approximate isotropic value for σ [for example, the value $\sigma = \frac{1}{3}(\epsilon + 2)$ which appears in the Lorentz formula for the internal field] and derive an average force constant k by applying the Born model of repulsive forces.

As shown in Ref. 1, the quantity $k_{\text{ratio}} = k(\text{Mn}^{2+})/k$ (normal divalent cation) depends principally on the ionic size mismatch $\Delta r = r$(substitutional cation) $- r$(normal cation).[17] Following the procedure outlined in Ref. 1, we obtain

$$\begin{aligned} &k_{\text{ratio}}(\text{Mn in CaWO}_4) = 0.4\ , \\ &k_{\text{ratio}}(\text{Mn in SrWO}_4) = 0.17\ . \end{aligned} \tag{3}$$

Absolute values for $k(\text{Mn}^{2+})$ can be inferred from (3) by estimating the force constants for Ca in $CaWO_4$ and Sr in $SrWO_4$. This estimate can be obtained directly from the ionic portion of the dielectric constant $\epsilon(\text{ionic}) = \epsilon(0) - \epsilon(\text{optical})$ as follows. If the lattice of Ca^{2+} (or Sr^{2+}) ions is assumed to move relative to a stationary lattice of $(WO_4)^{2-}$ ions in an applied field, then the polarization $P = nqu = \epsilon(\text{ionic})E_{\text{app}}$, where n is the number of Ca^{2+} ions/cm^3. The displacement $u = qE_{\text{int}}/k = q\sigma E_{\text{app}}/k$. Hence, eliminating E_{app} and u, we have the result $k = nq^2\sigma/\epsilon(\text{ionic})$. Inserting the numerical values $n = 1.26 \times 10^{22}$ ions/cm^3, $\epsilon(\text{ionic}) = 5$, $q = 2e = 9.6 \times 10^{-10}$ esu, and $\sigma = \frac{1}{3}(\epsilon + 2) = 3.67$, we thus obtain $k = 1.1 \times 10^4$ dyn/cm. An alternative estimate based on the TO phonon frequency ω_T via the relationship[18] $k = \mu\omega_T^2$ (μ is the reduced mass of the two types of ion) yields the result $k = 4 \times 10^4$ dyn/cm (see Ref. 1, footnote 21). It is not entirely clear how this discrepancy arises. The two estimates can be made to agree either by setting $\sigma = 1$ (as implied in the treatment given in Ref. 18) or, alternatively, by introducing a local-field correction factor into the relationship $k = \mu\omega_T^2$. We can, however, avoid this difficulty, and pass over the question of what value to assign to k(Ca in $CaWO_4$), if we are prepared to assume that the *local-field correction factor* σ *is the same for the impurity ion* Mn^{2+} *as for the normal cations* Ca^{2+} *and* Sr^{2+}. We can then write

$$u(\text{Mn in CaWO}_4)/u(\text{Ca in CaWO}_4) = k_{\text{ratio}}(\text{Mn in CaWO}_4)$$

and derive u(Ca in $CaWO_4$) from the ionic dielectric constant ϵ(ionic) as above. In this way we obtain

$$\begin{aligned} u(\text{Mn in CaWO}_4)/E_{\text{app}} &\simeq 2 \times 10^{-16}\ \text{cm/V}\ , \\ u(\text{Mn in SrWO}_4)/E_{\text{app}} &\simeq 4.7 \times 10^{-16}\ \text{cm/V}\ . \end{aligned} \tag{4}$$

This gives the displacement u in an applied field according to a simple isotropic model.

Let us now consider the new even crystal fields introduced by the displacement and their effect on the Mn^{2+} spin Hamiltonian. $E_\parallel$ will give rise to the new terms[14] $V_2^{\pm 2} = b_2^{\pm 2} C_2^{\pm 2}$ and $E_\perp$ to the new terms $V_2^{\pm 1} = b_2^{\pm 1} C_2^{\pm 1}$. New even fields of higher order will also appear but these will not give rise to terms of the $R_{jk}S_jS_k$ type (i.e., to new terms of the E and D type) and can be ignored in interpreting the electric-field-effect data. The changes in the spin Hamiltonian which are induced by the addition of these new even fields could be calculated from first principles using the point-charge model. We have not done this here. Instead, we have tried to eliminate some

TABLE III. Calculated electric-field-effect parameters for Mn^{2+} assuming a pure ionic effect. $R_{\parallel}$ and $R_{\perp}$ are in units of MHz per 10^5 V/cm of applied field. The angle φ_d defines the orientation of the D_{2d} twofold axis implicit in the combination of the crystal field terms $B_3^{\pm 2}C_3^{\pm 2}(\theta, \varphi)$.

	$CaWO_4$	$SrWO_4$
$R_{\perp}$	0.13	0.25
$R_{\parallel}$	0.13	0.25
$\varphi_{\perp}$	$2\varphi_d$	$2\varphi_d$
$\varphi_{\parallel}$	φ_d	φ_d

of the errors which arise in point-charge calculations by a ratio procedure in which the new fields V_2^q are related to the crystal field[14] $V_2^0 = B_2^0 C_2^0$ which is responsible for the D term in the absence of applied electric fields. It is assumed here that any screening correction $\chi = D/B_2^0$ will affect both in the same way. Thus, if B_2^0 and b_2^q are crystal field parameters calculated from the point-charge model, and D and R are the corresponding parameters in the spin Hamiltonian, we assume that[19] $R_{\parallel}/D = \sqrt{\frac{2}{3}}\,|b_2^2|/B_2^0$ and $R_{\perp}/D = \sqrt{\frac{2}{3}}\,|b_2^1|/B_2^0$. (The factor $\sqrt{\frac{2}{3}}$ arises from the rotation which is implied in the comparison.) In Ref. 1, Appendix A, we showed that the point-charge values of any new terms $|b_k^q|$ created by a displacement $\vec{u}$ (components u_μ, $\mu = 0, \pm 1$) are related to the point-charge value of a previously existing term B_2^0 by the expression

$$b_K^Q = \frac{u_\mu}{R}\,\alpha\eta(K, Q)B_2^0\,, \tag{5a}$$

where

$$\eta(K, Q) = (-)^{K+Q}\left[(2K+3)(2K+1)(K+1)\right]^{1/2} \times \begin{pmatrix} K & 1 & K+1 \\ -Q & \mu & Q-\mu \end{pmatrix}. \tag{5b}$$

The symbol on the right-hand side of (6b) is the $3j$ symbol,[20] R is the unit cell size ~ 10.5 Å, and α is a parameter equal to the geometric factor

$$\textstyle\sum_j C_3^2(\theta_j, \phi_j) / \sum_j C_2^0(\theta_j, \phi_j)\,,$$

the summation being over the lattice points. Combining Eqs. (4) and (5) with $\alpha \simeq 0.6$ we obtain

($CaWO_4$):

$$|b_2^2| \simeq |b_2^1| \simeq 4\times 10^{-9} B_2^0\ [\mathrm{cm}^{-1}/(\mathrm{V/cm})]\,, \tag{6a}$$

($SrWO_4$):

$$|b_2^2| \simeq |b_2^1| \simeq 9.4\times 10^{-9} B_2^0\ [\mathrm{cm}^{-1}/(\mathrm{V/cm})]\,. \tag{6b}$$

Taken in conjunction with the previously established relationships $R_{\parallel}/D = \sqrt{\frac{2}{3}}\,|b_2^2|/B_2^0$, etc., and with the D values in Table II, Eqs. (6) yield the result

($CaWO_4$):

$$R_{\parallel} = R_{\perp} = \sqrt{\tfrac{2}{3}} \times 4\times 10^{-9} \times 413\ [\mathrm{MHz}/(\mathrm{V/cm})]\,, \tag{7a}$$

($SrWO_4$):

$$R_{\parallel} = R_{\perp} = \sqrt{\tfrac{2}{3}} \times 9.4\times 10^{-9} \times 326\ [\mathrm{MHz}/(\mathrm{V/cm})]\,. \tag{7b}$$

The results of this calculation are shown in Table III.

By comparing Tables I and III we see that the calculated ratios R(Mn in $SrWO_4$)/R(Mn in $CaWO_4$) ~ 1.9 are in very good agreement with experiment. Since these ratios arise from our treatment of the restoring force acting on impurity ions, we assume that this part of the analysis is substantially correct. The calculated values of R itself are, however, ~ 100 times too small. Even if the crystal field screening effect for the new forms b_2^q and for the previously existing term B_2^q differ, rendering our assumption $R_{\parallel}/D \sim b_2^q/B_2^0$ incorrect, it is difficult to see how such a large discrepancy could arise. We are therefore forced to abandon our interpretation of the electric effect for Mn in the scheelites in terms of new even-field components and return to the possibility that odd-field polarization of the Mn^{2+} ion (i.e., the "electronic effect") is involved. We do this in spite of the observation that *ionic radii play an important part in determining the electric shifts*. As we shall see, ionic motion effects can enhance the electronic polarization induced by an externally applied field. We first, however, summarize the calculation of the electronic effect for Mn^{2+} as given in detail in Ref. 2.

B. Electronic Effect

The electronic contribution to the electric effects in Mn^{2+} can arise in two ways, both involving high-order perturbations (see Fig. 1). One kind of perturbation (perturbation A) is related to that which is used to calculate the D term. An equivalent even field[21] formed from the product of the laboratory applied field and the odd crystal field terms $V_3^{\pm 2}$ mixes the ${}^4P_{5/2}$ and ${}^4D_{5/2}$ excited states in the d^5 manifold, and the effect is transmitted to the ground state via spin-orbit coupling. The $E_{\mathrm{odd}} - E_{\mathrm{even}}$ energy denominator appears only once in the computation of the equivalent even field.[22] In the second kind of perturbation (perturbation B), spin-orbit coupling mixes states in the d^4p odd manifold, the effect being transmitted to the ground state via the laboratory applied field and via the odd crystal field terms $V_3^{\pm 2}$. The $E_{\mathrm{odd}} - E_{\mathrm{even}}$ energy denominator appears twice here, but the resulting electric effect is not necessarily negligible since the perturbation itself is of a lower order. The matrix elements involved in these two perturbations are indicated on the diagrams in Fig. 1.

Calculations of the electric effect via perturbation A are described in Ref. 2. The result, assuming the Lorentz value $\frac{1}{3}(\epsilon + 2)$ for the internal-field correction factor σ, is $R_{\parallel}$(Mn in $CaWO_4$)

$=R_\perp$(Mn in $CaWO_4$) = 0.6 MHz per 10^5 V/cm of applied field. A similar calculation for the case of Mn in $SrWO_4$ gives 0.43 MHz per 10^5 V/cm, the reduction in the case following from the generally smaller value of the crystal field components in the more spacious $SrWO_4$ lattice. (This is also evidenced by the smaller value of D for Mn^{2+} in $SrWO_4$.) Calculations via perturbation B were not attemped in Ref. 2 since a detailed knowledge of the structure of the d^4p manifold, needed in order to calculate matrix elements 3 and 4 in Fig. 1(b), was not available. (A closure method involving integration over the whole d^4p manifold can be used in perturbation A, thus avoiding this difficulty.) Perturbation B could conceivably be as large as perturbation A, and the values for the electronic effect calculated via perturbation A only should therefore be regarded as lower limits.

C. Ionic Motion and the Local-Field Correction Factor

In earlier calculations little attention was paid to the relationship between the applied electric field and the field seen by the ion, $\sigma E_{\rm app}$. It seemed to us that inaccuracies arising from crystal field calculations would outweigh inaccuracies in estimating σ. It was also supposed that any resulting error would cancel out when comparisons were made between ions in the same or in similar lattices. These rough assumptions can lead, however, to conclusions which are qualitatively wrong. A comparatively trivial illustration of this is the assumption of the isotropy of σ which leads to the prediction (as in Sec. III B above) that the electronic effects $R_\parallel$ and $R_\perp$ will be the same. More serious, however, is the assumption that σ will be the same for an impurity ion as for the normal unsubstituted cation. We now attempt to illustrate the manner in which σ may be enhanced for a "loose ion" and the way in which it will vary according to the ionic restoring forces. Let us break down the internal field into components by writing

$$E_{\rm int}=E_{\rm app}+E_{p_1}+E_{p_2}+E_{p_3}\ ,$$

where E_{p_1} is the internal field at the cation site due to the polarization of the surrounding lattice, and E_{p_2} and E_{p_3} are the fields which are seen by the cation as a result of its own individual electronic polarization and motion, respectively. E_{p_2} gives rise to a shielding (or antishielding) factor which would probably be small for the case considered, and would, in any case, be the same for Mn^{2+} in both lattices. The last term is approximately given by $E_{p_3}=2mqu/R^3$, where R is the anion to cation spacing, $q=2e$ is the ionic charge, u is the displacement of the impurity cation, and m is a numerical factor $\gtrsim 1$ obtained by summing over nearby lattice points. If we take $R\sim 4$ Å and substitute the expressions for u given in Eq. (4), we find that $E_{p_3}\simeq 4mE_{\rm app}$ for Mn in $CaWO_4$ and $E_{p_3}\simeq 9.5mE_{\rm app}$ for Mn in $SrWO_4$. In the unsubstituted lattice, $E_{p_3}\simeq 1.6mE_{\rm app}$ [see Eq. (3)]. It should be noted that although the field component E_{p_3} cannot be a major factor determining the ionic motion itself (unless the ion is unstable), it is quite well able to polarize the electron charge cloud and thus enhance the electronic effect. The above argument suggests that the estimates of the electronic effect given in Table IV should be increased by a factor ~ 2.5 in the case of Mn in $CaWO_4$ and by a factor ~ 6 in the case of Mn in $SrWO_4$, thus causing the electronic effect for Mn in $SrWO_4$ to be ~ 1.7 times as large as electronic effects for Mn in $CaWO_4$ instead of ~ 0.7 times the $CaWO_4$ result as suggested at the end of Sec. III B. An appropriately revised set of calculated values for the electronic effects are shown in Table IV. The ratio between the coefficients R(Mn in $SrWO_4$) and R(Mn in $CaWO_4$) agrees with the experiments, but, as was pointed out in Sec. III A, this merely

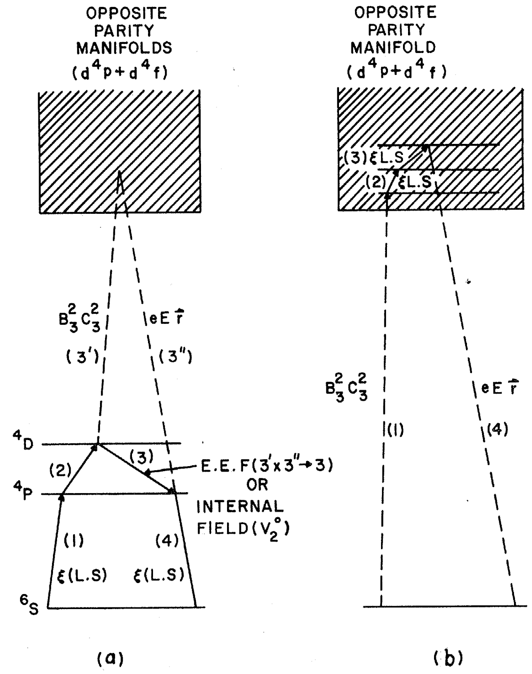

FIG. 1. Schematic representation of odd-field interactions for Mn^{2+} in scheelites. In (a) the combined effect of the odd-crystal-field matrix element (3′) and the matrix element for the applied electric field (3″) are represented by (3), the matrix element for the equivalent even field (EEF) (Ref. 21). In computing the EPR parameter D according to this scheme, the axial crystal field V_2^0 replaces the EEF (3). Similarly, in the case of ionic movement, the resulting V_2^q replaces the EEF. The spin-orbit interactions (1), (2), and (4) are identical in each case, leading to the same parameter (Ref. 22) $\chi\equiv D/B_2^0$. In (b) a different perturbation scheme for the electronic effect is depicted. This case requires a more detailed summation over odd states. There is no equivalent to (b) for the existing axial field V_2^0.

TABLE IV. Calculated electric-field-effect parameters for Mn^{2+} assuming electronic polarization of the Mn^{2+} ion and taking ionic motion into account in estimating the internal electric field. $R_{\parallel}$ and $R_{\perp}$ are in units of MHz per 10^5 V/cm of applied field. The equivalent even-field method (perturbation A) has been used. The angle ϕ_d defines the orientation of the D_{2d} twofold axes implicit in the combination of the crystal field terms V_3^2, as in Table III.

	$CaWO_4$	$SrWO_4$
$R_{\perp}$	1.5	2.6
$R_{\parallel}$	1.5	2.6
$\phi_{\perp}$	$2\phi_d$	$2\phi_d$
$\phi_{\parallel}$	ϕ_d	ϕ_d

confirms the approximate validity of our treatment of the restoring-force problem. The absolute magnitudes are now, on the average, within a factor of ~ 6 of the experimental values. This discrepancy could arise either from our ignoring perturbation B in calculating the electronic effect or from numerous simplifications which have been made in the theory. The result is, however, much closer than the result calculated by considering only the new even-field terms due to ionic displacements.

We conclude, therefore, that the electric effect for Mn^{2+} in the scheelite lattices is predominantly electronic in origin, but that ionic motion must be considered in order to obtain the proper local-field correction factor. In view of this result it seems that the distinction between ionic and electronic effects should be abandoned and should be replaced by a distinction between (i) an even-state electric effect which is independent of odd-state mixing and which can only arise from ionic motion, and (ii) an effect due to odd-state mixing which may also depend on the degree of ionic motion.

D. Comparison with Result Obtained for Yb^{3+}

These conclusions seem at first to be in conflict with those which we reached in considering the case of the Yb^{3+} ion. There the even-state ionic-motion effect was found to give the best interpretation. Here, on the other hand, we find it necessary to invoke odd-state mixing, in spite of the fact that the two situations have many features in common. The reason probably lies in the very different situation in regard to the Yb^{3+} and Mn^{2+} ground states. Yb^{3+} has three other Kramers-doublet states nearby separated by an interval ~ 100 cm^{-1}, and is relatively sensitive to even fields. Mn^{2+} is an S-state ion and is only influenced by even fields in high-order perturbation. Effects due to the mixing of the odd-state manifold are thus at less of a disadvantage for Mn^{2+} than for Yb^{3+}. It is interesting to note that the ratios of parallel and perpendicular electric shifts, which would have been impossible to explain in a consistent manner if the even-state "ionic motion" effect were predominant for both ions, become more intelligible when the effects are assigned to a different origin. In Yb^{3+} the experimental evidence indicated that the force constant $k_{\parallel}$ was greater than $k_{\perp}$, a conclusion which seemed reasonable since motion along the c axis in the scheelites is restricted by two closely spaced oxygen atoms (see Fig. 2 of Ref. 1). If the ratio $R_{\parallel}/R_{\perp}$ ~ 2, which is observed for Mn^{2+}, were to be explained in like manner, it would suggest that on the contrary $k_{\perp} > k_{\parallel}$. The difficulty is partly resolved, however, if we remember that when the ion is moved along the c axis toward the closely spaced oxygen the polarizing field E_{p_3} will be larger than it would be for an equivalent motion in the ab plane. According to our view, this component E_{p_3} will be the most important single factor determining the internal field E_{int} which polarizes the Mn^{2+} ion. The component E_{p_3}, which results from the motion of the impurity ion, cannot, however, contribute to the field causing this ion motion and does not therefore, lead to any enhancement of the "even-state effect" which is dominant in the case of Yb^{3+}.

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[1] A. Kiel and W. B. Mims, Phys. Rev. B 1, 2935 (1970).

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

[3] This has been observed to happen for Li^+ in certain halide crystals [R. J. Quigley and T. P. Das, Phys. Rev. 164, 1185 (1967); 177, 1340 (1969)].

[4] The crystal of Mn-doped $BaWO_4$, in which the Mn^{2+} ion did not appear to substitute for Ba, was also grown by Linde Air Products, Inc.

[5] W. B. Mims, Phys. Rev. 133, A835 (1964).

[6] The electric fields specified here are obtained by dividing the voltage between two parallel electrodes attached to the sample by the distance between the electrodes. The results are not adjusted in any way for dielectric-constant effects.

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

[8] In Ref. 2, $R_{\perp}$, $R_{\parallel}$, $\varphi_{\perp}$, and $\varphi_{\parallel}$ are wirtten as $R_{\perp}$, R_3, $\varphi_{\perp}$, and φ_3, respectively. We use the $\parallel$ and $\perp$ subscripts here as in Ref. 1 for mnemonic convenience.

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

[10] The angle $\varphi_{\perp}$ was incorrectly given as 50° in Ref. 2. The correct value $\varphi_{\perp} = 40°$ is shown here.

[11] C. F. Hempstead and K. D. Bowers, Phys. Rev. 118, 131 (1960).

[12] Linus Pauling, *Nature of the Chemical Bond*, 3rd ed. (Cornell U. P., Ithaca, N. Y., 1960). Several other sources for the ionic radii exist, some of which take coordination numbers into account. Although the sizes of ions quoted by separate authors vary somewhat, the differences in radii of any two ions [e.g., $r(\text{Ba}) - r(\text{Yb})$] are nearly identical.

[13] Yb^{3+} in $CaWO_4$ is not a loose ion to the same degree as the others mentioned here and forms an exception to

this generalization. The ratio of ionic radii Yb^{3+}/Ca^{2+} is 0.95. The $R_{\parallel}$ coefficient for Yb^{3+} in $CaWO_4$ is much smaller than any of the other electric shift parameters observed in this series of experiments and is within a factor of 2 of the value calculated for the electronic effect.

[14] The crystal field terms V_K^Q are often expressed as $A_K^Q Y_K^Q(\theta, \varphi)$, where $Y_K^Q(\theta, \varphi)$ are the conventional normalized spherical harmonics. In recent years, many papers on this subject use the related harmonic

$$C_K^Q(\theta, \varphi) = [(2K+1)/4\pi]^{1/2} Y_K^Q(\theta, \varphi),$$

hence

$$V_K^Q = B_K^Q C_K^Q(\theta, \varphi) = [4\pi/(2K+1)]^{1/2} A_K^Q C_K^Q(\theta, \varphi).$$

We shall use the C_K^Q harmonic in this paper. When B_K^Q is a term induced by the applied electric field, we will use the lower-case symbol b_K^Q to conform to Ref. 1.

[15] It is still essential, however, that the undisplaced ion should be at a site which lacks inversion symmetry. If this is not so, the new even-field terms will be quadratic in the displacement u.

[16] In the case of a linear chain, if the force constant is k, the restoring force is proportional to $2k$. (In Ref. 1, we set $\beta = 2k$.) This duplicity of notation seems to be extravagant and we will define k as the *restoring force* throughout this paper.

[17] Other parameters of less importance here are "ρ," the hardness parameter, and β_{+-}, a charge distribution parameter, as presented in the treatment of the Born model by Mario Tosi, in *Solid State Physics*, Vol. 1b, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1965), p. 1.

[18] Charles Kittel, *Introduction to Solid State Physics*, 2nd ed. (Wiley, New York, 1956), p. 167.

[19] We use moduli $|B_K^Q C_K^Q|$ instead of the actual combinations $B_K^Q C_K^Q + B_K^{-Q} C_K^{-Q}$, etc., in order to obtain estimates of the magnitudes $R_{\parallel}$ and $R_{\perp}$. The phases of the spherical harmonics determine $\phi_{\parallel}$ and $\phi_{\perp}$.

[20] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1959).

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

[22] It is important to note that interaction assumed in perturbation A [Fig. (a)] is intended primarily to be representative of the types of perturbations leading to the D term in $Mn^{2+}:SrWO_4$. Another sequence of matrix elements, which is particularly appropriate to nearly cubic crystals, is described in R. R. Sharma, T. P. Das, and R. Orbach, Phys. Rev. 149, 257 (1966). The exact form is immaterial, however, since we use the observed $\chi = D/B_2^0$ [see discussion leading to Eq. (5)], which should be independent of which perturbation term dominates.

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Brehmsstrahlung Spectrum of Energetic β Particles Traversing Single Crystals in Lattice-Directed Trajectories

Hans C. H. Nip and J. C. Kelly
Materials Irradiation Group, Department of Physics, University of New South Wales, Sydney, Australia 2033

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For lattice-directed trajectories, the Fourier spectrum of the interaction between an energetic ($\gtrsim 10^5$eV) β particle and the lattice atoms is different from the Fourier spectrum of the interaction with randomly distributed target atoms by significant terms of frequencies near $(sv/2a)$. Here s is an integer, v is the velocity of the β particle parallel to the low-index crystallographic direction, and $2a$ is the interatomic spacing in this low-index direction in the reference frame of the β particle. It is suggested that these frequencies will dominate the brehmsstrahlung spectrum of an energetic β particle traversing a single crystal in a lattice-directed trajectory. This effect is considered in terms of the quantal time-dependent perturbation theory. Its magnitude is estimated using the classical theory of radiation.

I. INTRODUCTION

During the last decade, appreciable interest has been focused on the lattice-directed trajectories of energetic positive[1-4] and negative[3-5] particles. In a lattice-directed trajectory, the direction of motion of the projectile particle is aligned with the lattice atoms in a simple crystallographic direction. Therefore, the Fourier spectrum of the interaction between the lattice atoms and the projectile particle will contain significant terms of frequencies around integral multiples of the interaction frequency. These terms have to be considered in the derivation of the transition probabilities between the various quantum states of the energetic projectile particle.[6-10] If we consider the projectile particle free except for the periodic perturbation of the interaction with the lattice atoms, we can apply quantal time-dependent perturbation theory to obtain these transition probabilities. As is well known,[11] we will obtain a strongly increased transition probability to states which differ in energy from the initial state by an amount $sh\gamma$, where s is an integer, h is Planck's constant, and γ is the frequency of the interaction.

For channelled or blocked heavy ions, these energies $sh\gamma$ will be of the same order of magnitude as the energy differences between electronic ex-