# Electric Field Shift in Paramagnetic Resonance for Four Ions in a Calcium Tungstate Lattice

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The electric field shift in paramagnetic resonance has been studied for the rare-earth ions Ce, Nd, Er, and Yb in a $CaWO_4$ lattice by means of electron spin echoes. In each case the four coefficients of the electric effect tensor have been obtained. A simple way of visualizing the changes which occur in the spin resonance of a Kramers doublet when an electric field is applied has been given in terms of the $g$ ellipsoid. The symmetry of the paramagnetic site, and the possibility of observing electric spin resonance in suitable materials is discussed.

THE electron-echo method[1] has been used to study the effect of applying electric fields during paramagnetic resonance for the ions Ce, Nd, Er, and Yb in a $CaWO_4$ host lattice. In all four cases the lowest pair of levels consists of a Kramers doublet, and paramagnetic resonance, with or without applied electric fields, can be described in terms of a $g$ ellipsoid

$$g^2=\hat{r}\cdot\mathbf{A}\cdot\hat{r}, \tag{1}$$

where $\hat{r}$ is a unit vector parallel to the magnetic field. $\mathbf{A}$ is the $3\times3$ symmetric matrix obtained by squaring the matrix corresponding to the elements of the $g$ tensor, i.e.,

$$\mathbf{A}=\mathbf{g}\cdot\mathbf{g}. \tag{2}$$

The effect of applying an electric field is to introduce tilts and to make changes in the lengths of the principal axes of the ellipsoid. We shall begin by developing a description of the electric effect in geometrical terms, and show how this description is related to the more general formulation of the problem which can be made by adding electric field terms to the spin Hamiltonian. The advantage of such a geometrical formulation is that it makes it easy to visualize the changes which occur, and that it leads naturally to the representation of experimental data by simple trigonometrical expressions.

When an electric field is applied the matrix $\mathbf{A}$ is modified to $\mathbf{A}+\delta\mathbf{A}$. If the field components are $E_k$ $(k=x, y, z)$, then $\delta\mathbf{A}$ has the form

$$(\delta A)_{ij}=\sum_k B_{kij}E_k, \tag{3}$$

and the electric effect can be described in terms of a third-rank tensor $\{B\}$, which, in the general case, has 18 independent coefficients. Since $\mathbf{g}$ and $\mathbf{A}$ are symmetric matrices, the coefficients $\delta A_{ij}$ and $B_{kij}$ are symmetric under the interchange of $i$, $j$, and from Eqs. (1) and (3), we have that

$$\begin{aligned}\delta(g^2)&=\hat{r}\cdot\delta\mathbf{A}\cdot\hat{r}\\&=\sum_k E_k[B_{k11}l^2+B_{k22}m^2+B_{k33}n^2\\&\quad+(B_{k23}+B_{k32})mn+(B_{k13}+B_{k31})lm\\&\quad+(B_{k12}+B_{k21})ln]\\&=\sum_k E_k[B_{k11}l^2+B_{k22}m^2+B_{k33}n^2+2B_{k23}mn\\&\quad+2B_{k13}lm+2B_{k12}ln],\end{aligned} \tag{4}$$

where $l$, $m$, $n$, are the direction cosines of $\hat{r}$. $\{B\}$ has the same form and symmetry properties as the piezoelectric tensor.[2]

We may now reformulate the problem in terms of a spin Hamiltonian and show how the $B_{kij}$ may be related to the coefficients which appear in it. For a Kramers doublet in applied electric and magnetic fields

$$\mathcal{H}=\beta(\sum_{ij} g_{ij}H_iS_j)+\sum_{i,j,k} T_{kij}H_iS_jE_k. \tag{5}$$

$\{T\}$ is a third-rank tensor with 18 independent coefficients. Its relation to $\{B\}$ can be shown as follows. If the changes in $\mathcal{H}$ due to the second term in Eq. (5) are represented as changes $\delta g_{ij}$ in the $g$ tensor, we have that

$$\delta g_{ij}=(1/\beta)\sum_k E_kT_{kij}. \tag{6}$$

Differentiating (2) we obtain

$$\delta A_{ij}=g_{iq}\delta g_{qj}+\delta g_{iq}g_{qj}. \tag{7}$$

Eliminating $\delta g_{ij}$ between (6) and (7) and comparing with (4) we have

$$(1/\beta)\sum_{k,q} E_k(g_{iq}T_{kqj}+T_{kiq}g_{qj})=\sum_k B_{kij}E_k,$$

and therefore

$$B_{kij}=(1/\beta)(g_{iq}T_{kqj}+T_{kiq}g_{qj}). \tag{8}$$

$B$, $g$, and $T$ are symmetric in the suffixes $i$ and $j$, and it is convenient when writing out expressions at length to adopt the condensed notation in which $g_{11}=g_1$, $g_{22}=g_2$, $g_{33}=g_3$, $g_{23}=g_{32}=g_4$, $g_{13}=g_{31}=g_5$, $g_{12}=g_{21}=g_6$,

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

[2] A table showing which coefficients vanish for various symmetries is given by C. S. Smith, Solid State Phys. 6, 229 (1958).

etc. In this notation Eq. (4) becomes

$$\delta(g^2)=\sum_k E_k(B_{k1}l^2+B_{k2}m^2+B_{k3}n^2+2B_{k4}mn+2B_{k5}ln+2B_{k6}lm), \quad (9)$$

and Eq. (8) gives the relations

$$\begin{aligned}
B_{k1}&=(2/\beta)[g_1T_{k1}+g_5T_{k5}+g_6T_{k6}],\\
B_{k2}&=(2/\beta)[g_2T_{k2}+g_4T_{k4}+g_6T_{k6}],\\
B_{k3}&=(2/\beta)[g_3T_{k3}+g_5T_{k5}+g_6T_{k6}],\\
B_{k4}&=(1/\beta)[g_6T_{k5}+g_5T_{k6}+g_2T_{k4}+g_4T_{k2}+g_4T_{k3}+g_3T_{k4}],\\
B_{k5}&=(1/\beta)[g_5T_{k3}+g_3T_{k5}+g_1T_{k5}+g_5T_{k1}+g_6T_{k4}+g_4T_{k6}],\\
B_{k6}&=(1/\beta)[g_5T_{k4}+g_4T_{k5}+g_1T_{k6}+g_6T_{k1}+g_6T_{k2}+g_2T_{k6}]. \quad (10)
\end{aligned}$$

## EXPERIMENTAL

The experiments were conducted by establishing a right-angled axis system, in this case the *a*, *b*, *c* axes of the $CaWO_4$ crystal, then applying the electric field along one axis and varying the magnetic field direction in a plane containing any two axes. The frequency shifts were measured, converted into changes $\delta(g^2)$ and fitted to the specific form of Eq. (9) containing the appropriate $B$ coefficients. For example, if we apply the electric field along the $z$ axis and move the magnetic field in the $xy$ plane, $k=3$, $n=0$, and

$$\begin{aligned}
\delta(g^2)&=E_3(B_{31}l^2+B_{32}m^2+2B_{36}lm)\\
&=E_3[\tfrac{1}{2}(B_{31}+B_{32})+\{\tfrac{1}{4}(B_{31}-B_{32})^2+B_{36}^2\}^{1/2}\sin(2\varphi-2\varphi_3)],
\end{aligned}$$

where

$$\tan2\varphi_3=(B_{32}-B_{31})/B_{36}, \quad (11)$$

and $\varphi$ is the angle of the magnetic field with respect to the $x$ axis. Similar expressions may be written down for all nine possible experiments of this kind. If, however, we assume that the rare-earth ions are situated at calcium sites, and that $S_4$ symmetry of these sites is not changed by the substitution, there are only four independent $B$ coefficients as given by

$$\left(\begin{array}{ccc|ccc}
B_{11} & B_{12} & B_{13} & B_{14} & B_{15} & B_{16}\\
B_{21} & B_{22} & B_{23} & B_{24} & B_{25} & B_{26}\\
B_{31} & B_{32} & B_{33} & B_{34} & B_{35} & B_{36}
\end{array}\right)
=\left(\begin{array}{ccc|ccc}
0 & 0 & 0 & B_{14} & B_{15} & 0\\
0 & 0 & 0 & -B_{15} & B_{14} & 0\\
B_{31} & -B_{31} & 0 & 0 & 0 & B_{36}
\end{array}\right) \quad (12)$$

and only three experiments are needed. Axis 3 of the tensor is the $S_4$ fourfold axis, and axes 1, 2, and 3 are the *a*, *b*, and *c* axes of the $CaWO_4$ crystal. With $E$ along the *c* axis (or *z* axis) and $H$ in the *ab* plane

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

where

$$\tan2\varphi_3=-B_{31}/B_{36}. \quad (13)$$

With $E$ along the axis (the $x$ axis) and $H$ in the *ac* plane

$$(1/E_x)\delta(g^2)=B_{15}\sin2\theta, \quad (14)$$

and for $E$ along the *a* axis and $H$ in the *bc* plane

$$(1/E_x)\delta(g^2)=B_{14}\sin2\theta. \quad (15)$$

No additional measurements with $E$ along the *b* axis are needed since the *b* axis is equivalent to the *a* axis under inversion and 90° rotation. When $E$ is along the *a* axis it is, however, sometimes useful to vary $H$ in an arbitrary direction. For this case, by combining (14) and (15) we have that

$$(1/E_x)\delta(g^2)=(B_{14}^2+B_{15}^2)^{1/2}\sin2\theta\sin(\varphi-\varphi_1),$$

where

$$\tan\varphi_1=-B_{15}/B_{14}. \quad (16)$$

The $S_4$ $g$ tensor is determined by only two independent quantities, and, in the system of axes used above, $g$ is diagonal with components $g_\perp$, $g_\perp$, and $g_\parallel$. By Eq. (10) the relations between the $B$ and $T$ coefficients are therefore as follows:

$$\begin{aligned}
\beta B_{31}&=2g_\perp T_{31},\\
\beta B_{36}&=2g_\perp T_{36},\\
\beta B_{14}&=(g_\perp+g_\parallel)T_{14},\\
\beta B_{15}&=(g_\perp+g_\parallel)T_{15}.
\end{aligned} \quad (17)$$

Since $\mathbf{g}$ is diagonal, $\mathbf{A}$ is also diagonal and has elements $g_\perp^2$, $g_\perp^2$, and $g_\parallel^2$. The $g$ ellipsoid is the spheroid $g^2=g_\parallel^2\times\cos^2\theta+g_\perp^2\sin^2\theta$. The changes in the geometry of the ellipsoid which occur when an electric field is applied can be visualized as follows. An electric field along the *c* axis produces no rotation of the ellipsoid and no change in the length of the $g_\parallel$ axis, but it breaks the degeneracy $g_1=g_2=g_\perp$ and gives new principal axes in the *ab* plane which differ from $g_\perp$ by $\delta g_\perp$, where $2g_\perp\delta g_\perp=(B_{31}^2+B_{36}^2)^{1/2}E_z$. The new axes are at angles of $\frac{1}{2}\arctan(B_{36}/B_{31})$ to the *a* and *b* axes. An electric field along the *a* axis produces no changes in the axis lengths but tilts the ellipsoid by an angle $(B_{14}^2+B_{15}^2)^{1/2}E_x/(g_\perp^2-g_\parallel^2)$ about a line in the *ab* plane at an angle of $\arctan(B_{15}/B_{14})$ to the *a* axis. (A field along the *b* axis causes a similar tilt, but in the opposite sense, about a line similarly located with respect to the *b* axis.)

The measurements were made at a frequency of 9.42 Gc/sec and, except in the case of (Ca,Er)$WO_4$ crystals or of mixed crystals containing Er, all results were obtained at 4.2°K.[3] There are two types of paramagnetic sites, the one being obtained from the other by inversion of the environment through the Ca lattice point. In ordinary paramagnetic resonance these sites are indistinguishable, but an applied electric field shifts the resonance frequencies of the two sites by equal

[3] Rapid lattice relaxation causes the phase memory to be too short in (Ca,Er)$WO_4$ at 4.2°K. Shortening of the phase memory occurs for other ions also if Er is present in the crystal.

amounts in opposite directions. The method of measurement has already been described in some detail with $(Ca,Ce)WO_4$ as an example,[1] so that here it will only be necessary to consider the accuracy of the present experiments, and to discuss some problems arising from ambiguities in determining the sign of the tensor coefficients. The measurement gives directly $1/\delta f$, which is the reciprocal of the shift in the Larmor frequency of each spin packet in the resonance line. Since $g$ can be measured more precisely than $\delta f$ there is no loss of accuracy in converting this to $\delta(g^2)$ by means of the relation $\delta(g^2)=2g\delta g=2g^2\delta f/f$, and the results can be fitted to sine curves as in Eqs. (13)–(15). Examples are shown in Figs. 1 and 2. It can be seen from the figures that the quantities most readily derived from the experiments are the amplitudes $(B_{31}^2+B_{36}^2)^{1/2}$, $B_{14}$, $B_{15}$, and the angle of zero shift $\varphi_3$. The amplitude $(B_{31}^2+B_{36}^2)^{1/2}$ is sensitive to the accuracy with which the time $1/\delta f$ and the electric field $E_z$ are measured, but is insensitive to the orientation of the magnetic field. $\varphi_3$ is, on the other hand, a purely angular measurement depending on the precision with which the crystal is aligned. $B_{14}$, $B_{15}$ depend on field measurements, time measurements, and on orientation of the magnetic field, but these factors may be separated from one another by deriving an amplitude $(B_{14}^2+B_{15}^2)^{1/2}$ and an angle $\varphi_1$ as in Eq. (16). The angle $\varphi_1$, which defines a plane of zero $\delta g$ (the plane of intersection of the original $g$ ellipsoid and the ellipsoid produced by applying an electric field along the $a$ axis) can also be located by making a suitable rotation of the Zeeman field. For some of the rare earths the Zeeman field required only a small rotation out of the $ac$ or $bc$ planes in which the frequency shifts were being measured, and in these cases the angle $\varphi_1$ was determined directly and checked against the value of $\arctan(-B_{15}/B_{14})$. Errors in the alignment of the electric field are

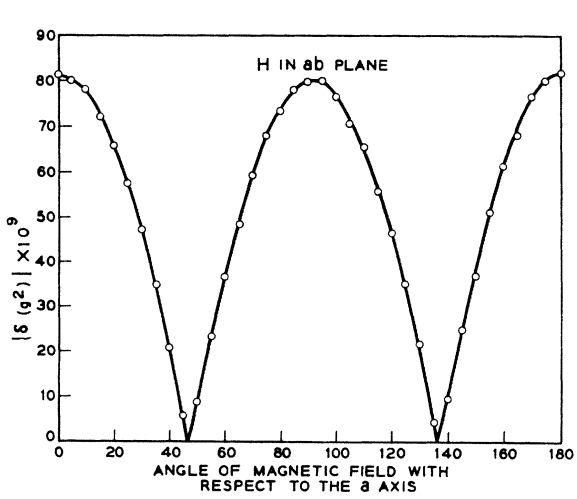


FIG. 1. $|\delta(g^2)|\times10^9$ for an electric field of 1 V/cm along the $c$ axis in $(Ca,Yb)WO_4$. $H$ is varied in the $ab$ plane. The angle at which $\delta(g^2)$ is zero, is given by $\varphi_3=\frac{1}{2}\arctan(-B_{31}/B_{36})$. The maximum amplitude of the curve is $(B_{31}^2+B_{36}^2)^{1/2}$.

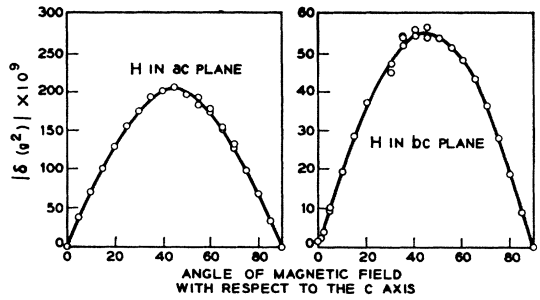


FIG. 2. $|\delta(g^2)|\times10^9$ for an electric field of 1 V/cm along the $a$ axis in $(Ca,Yb)WO_4$. For $H$ in the $ac$ plane the maximum amplitude of the curve gives $B_{15}$. For $H$ in the $bc$ plane the maximum amplitude gives $B_{14}$.

liable to affect the values of the angles $\varphi_1$ and $\varphi_3$, and also the amplitudes $(B_{14}^2+B_{15}^2)^{1/2}$ and $(B_{31}^2+B_{36}^2)^{1/2}$. These errors were minimized by aligning the specimens with an x-ray goniometer and by carefully machining the parallel faces which constitute the electrodes. Typical dimensions were 0.22 cm×0.45 cm×0.45 cm, the electrodes being placed on the 0.45 cm×0.45 cm faces. Since low applied fields of not more than a few kilovolts/cm are quite adequate when the electron-echo method is used to determine electric field shifts, there is no need to use a very thin specimen, and the electrodes can be taken all the way to the edge of the crystal faces without risk of breakdown. Consideration of the magnitudes involved shows that it is not likely that errors in the alignment of the electric field limited the over-all accuracy except in the case of $(Ca,Er)WO_4$ where the coefficients for the $z$ axis field are much larger than those for an $x$ axis field, and a small $E_z$ component can make an appreciable difference in an $E_x$ experiment. In experiments with different specimens the amplitudes $(B_{14}^2+B_{15}^2)^{1/2}$ and $(B_{31}^2+B_{36}^2)^{1/2}$ were repeatable to within 10%, and the angles $\varphi_1$ and $\varphi_3$ to within 2°, except in the case of the angle $\varphi_1$ and the amplitude $(B_{14}^2+B_{15}^2)^{1/2}$ in $(Ca,Er)WO_4$. In most instances the whole of the angular error can be attributed to errors in the mounting of the crystal in the cavity, it being possible for any given assembly of the apparatus to repeat measurements of the zero shift angle to within a fraction of a degree.[4] Errors of 2° in angle may of course imply quite large uncertainties in a particular tensor coefficient. For example if the angle $\varphi_1$ for $Ca,CeWO_4$ were to be changed from 3° to 1°, this would alter $B_{15}$ by a factor of 3.

Each individual measurement gives the magnitude but not the sign of the electric field shift, and a set of isolated measurements of $B$ coefficients would, therefore, leave a considerable degree of ambiguity in the electric effect tensor. It is, however, possible to reduce

[4] It is often possible to detect some shift even at a zero. This is probably caused by inhomogeneity in the line. For $(Ca,Er)WO_4$ the zero shift occurred at slightly different angles $\varphi_3$ in the center and on the wings of the line, indicating that some of the observed inhomogeneity is due to irregularities in the alignment of crystal fields in the sample.

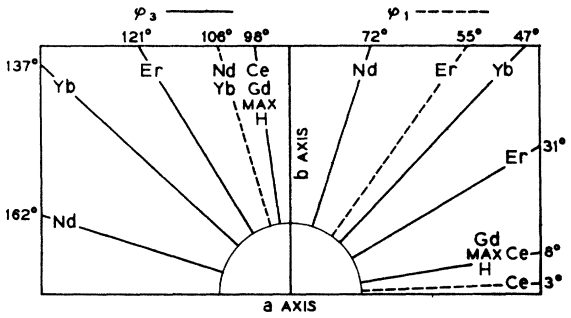


FIG. 3. Diagram showing the relation between characteristic azimuthal angles.

$\varphi_1 = \arctan(-B_{15}/B_{14})$ and $\varphi_3 = \frac{1}{2}\arctan(-B_{31}/B_{36})$.

$\varphi$(Gd max$H$) serves as a reference angle. It denotes the angle at which the $-\frac{3}{2} \leftrightarrows -\frac{1}{2}$ interval is least when normal paramagnetic resonance of (Ca,Gd)$WO_4$ is observed with $H$ in the $ab$ plane.

this ambiguity by comparing the angles $\varphi_1$ and $\varphi_3$ with one another in the same specimen and by relating their sign to some other property of the crystal which shows a variation in the $ab$ plane. $\varphi_3$ establishes the sign of the ratio $B_{31}/B_{36}$ and $\varphi_1$ the sign of the ratio $B_{15}/B_{14}$. A different type of experiment in which the electric field direction was gradually varied would give the sign of one more ratio, e.g., $B_{31}/B_{14}$, but no such experiment was attempted here. One final ambiguity, the sign in front of the whole $B$ tensor, cannot be resolved by any method for a crystal such as $CaWO_4$ which contains inversion image sites, since there is no way of labeling one particular site of the pair. The signs of $\varphi_1$ and $\varphi_3$ were found as follows. An individual crystal was marked in accordance with an arbitrarily assigned right-handed axis system and used in two experiments, one with $E$ along the $c$ axis and one with $E$ along the $a$ axis. The Zeeman field was rotated in appropriate manner, changes in $\delta f$ were noted, and the relative signs of $\varphi_1$ and $\varphi_3$ were thus obtained for a particular rare-earth ion. Measurements were then made on crystals containing two or more types of ion in order to compare signs for different rare earths. Finally, the sign of $\varphi_3$ was compared with the sign of the angle $\varphi_{Gd}$ at which the energy levels of the $Gd^{3+}$ ion have a maximum or minimum separation when the normal paramagnetic resonance (Ca,Gd)$WO_4$ is studied in the $ab$ plane,[5] by making measurements on a (Ca,Ce,Gd)$WO_4$ mixed crystal. The angular relations are shown diagrammatically in Fig. 3. The amplitudes $(B_{31}^2+B_{36}^2)^{1/2}$, $(B_{14}^2+B_{15}^2)^{1/2}$ and angles $\varphi_1$, $\varphi_3$ are given in Table I.

## DISCUSSION

A detailed analysis of the results in terms of crystal-field theory is being undertaken by A. Kiel, and the discussion here will be confined to two topics: the use of the electric-effect measurements in determining site symmetry, and some experimental indications that transitions were caused by the microwave electric field. We have so far assumed that the rare-earth ions substitute for calcium in the $CaWO_4$ lattice and that they are situated in a crystalline field with $S_4$ point symmetry. This assumption is based on prior knowledge of the $CaWO_4$ crystal structure obtained by x-ray diffraction, on reasonable guesses as to the likely substitution site and as to the limits of possible distortions caused by the substitution, and on information contained in the $g$ tensor. Although there is little reason to doubt these assumptions here, it may be of interest, if only as an illustration of the way in which electric-effect measurements can contribute to the solution of more complex problems, to show how the $S_4$ site symmetry may be established from resonance data only. Let us therefore assume that we have no prior knowledge regarding the host and its crystalline axes. The observation of a $g$ tensor with two distinct principal values restricts consideration to the trigonal, tetragonal, and hexagonal systems, and establishes one unique axis, the $g_{II}$ axis, which in the notation of Ref. 2 is axis number 3. Only the 13 point groups belonging to these systems and lacking inversion symmetry need be considered, i.e., $C_3$, $D_3$, $C_{3v}$, $C_4$, $D_4$, $C_{4v}$, $S_4$, $D_{2d}$, $C_6$, $D_6$, $C_{6v}$, $C_{3h}$, and $D_{3h}$. In all experiments with $E$ and $H$ both along the $g_{II}$ axis the electric effect was zero, hence all symmetries having a third-rank tensor with a 33 element can be deleted, leaving $D_3$, $D_4$, $S_4$, $D_{2d}$, $D_6$, $C_{3h}$, and $D_{3h}$. However, in experiments with the electric field along the $g_{II}$ axis, effects were noted at some orientations of $H$ in the perpendicular plane. Therefore the 31, 32, and 36 elements cannot simultaneously be zero, and all symmetries but $S_4$ and $D_{2d}$ are ruled out. Since the $g$ tensor does not define any unique axes in the perpendicular plane, axes 1 and 2 are not known, and we cannot draw the final conclusion by mere inspection of the data. Certain relations between the characteristic angles $\varphi_1$ and $\varphi_3$ of Eqs. (16) and (13) will, however, hold for a $D_{2d}$ symmetry and not for $S_4$. If the

TABLE I. $g$ values and electric-field-effect coefficients for four ions in $CaWO_4$. Amplitudes $(B_{14}^2+B_{15}^2)^{1/2}$ and $(B_{31}^2+B_{36}^2)^{1/2}$ are in units of $\delta(g^2)$ per V/cm times $10^9$, and are accurate to within 10%. Angles $\varphi_1$ and $\varphi_3$ are accurate to within 2°. $\varphi_1$ repeats every 180° and $\varphi_3$ every 90°. $\varphi_1 = \arctan(-B_{15}/B_{14})$, $\varphi_3 = \frac{1}{2}\arctan(B_{31}/B_{36})$. Errors in the coefficients $B_{14}$, $B_{15}$, $B_{31}$, $B_{36}$, depend on the particular values of $\varphi_1$ and $\varphi_3$ in each case. Ambiguities of sign are discussed in the text.

| Ion | $Ce^{3+}$ | $Nd^{3+}$ | $Er^{3+}$ | $Yb^{3+}$ |
|---|---|---|---|---|
| $g_{II}$ | 2.92 | 2.03 | 1.2 | 1.05 |
| $g_{\perp}$ | 1.43 | 2.52 | 8.3 | 3.93 |
| $(B_{14}^2+B_{15}^2)^{1/2}$ | 170 | 209 | 1800 | 212 |
| $(B_{31}^2+B_{36}^2)^{1/2}$ | 87 | 37 | 11 000 | 81 |
| $\varphi_1$ | 3° | 106° | 55° | 106° |
| $\varphi_3$ | 8° | 72° | 31° | 47° |
| $\lvert B_{14}\rvert$ | 170 | 58 | 1060 | 58 |
| $\lvert B_{15}\rvert$ | 9 | 201 | 1470 | 204 |
| $\lvert B_{31}\rvert$ | 24 | 22 | 9700 | 81 |
| $\lvert B_{36}\rvert$ | 84 | 30 | 5200 | 6 |

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

twofold axes are axes 1 and 2, then the third-rank tensor for $D_{2d}$ symmetry assumes the form

$$\left(\begin{array}{ccc|ccc} 0 & 0 & 0 & B_{14}' & 0 & 0 \\ 0 & 0 & 0 & 0 & B_{14}' & 0 \\ 0 & 0 & 0 & 0 & 0 & B_{36}' \end{array}\right).$$

Rotation of the twofold axes by an arbitrary angle $\varphi'$ in the 12 plane gives a tensor or the same form as the $S_4$ tensor [Eq. (12)], with the coefficients

$$B_{14}=B_{14}'\cos 2\varphi', \quad B_{15}=B_{14}'\sin 2\varphi',$$
$$B_{36}=B_{36}'\cos 2\varphi', \quad B_{31}=B_{36}'\sin 2\varphi'.$$

These coefficients, if substituted in Eqs. (16) and (13), would give characteristic angles $\varphi_1$ and $\varphi_3$ related to $\varphi'$ as follows: $\varphi_1=2\varphi'+n\pi$ and $\varphi_3=\varphi'+\frac{1}{2}m\pi$. The test for $D_{2d}$ symmetry is therefore that $\varphi_3-\frac{1}{2}\varphi_1=0+\frac{1}{2}m\pi$; and, in the event that this condition is satisfied, the angles $\varphi_3$ or $\frac{1}{2}\varphi_1$ will give the twofold axes characteristic of the local $D_{2d}$ crystal field. The values of $\varphi_3-\frac{1}{2}\varphi_1$ in the cases of Ce, Nd, Er, and Yb are 6°, −19°, 4°, and −6°, respectively. These discrepancies are considerably smaller than the maximum possible discrepancy of ±45°, but they lie outside experimental error and indicate that the point symmetry is indeed $S_4$ and cannot be approximated by $D_{2d}$.

These results may be contrasted with results obtained in conventional spin-resonance experiments on the ions $Mn^{2+}$ and $Gd^{3+}$ in $CaWO_4$.[5] For these $S$-state ions the angular dependence of the spectrum and the symmetry of the Hamiltonian was found to be closely related to the $D_{2d}$ axes of the nearest-neighbor oxygen atoms, which have been determined by x-ray measurements[6] to lie at an angle of 8.4° to the $a$ and $b$ axes in the $ab$ plane. The Mn and Gd spectra showed maximum and minimum separation between levels when the magnetic field was at 9°±2° to the $a$ or $b$ axes. Of the electric-effect parameters on the other hand, only those belonging to Ce show any correlation with this angle. For the remaining ions it is apparent from Fig. 3 that the angles $\frac{1}{2}\varphi_1$ and $\varphi_3$ are spread out over a considerable range, and that a wide assortment of distortions would have to be invoked to force the results to fit an approximate $D_{2d}$ symmetry. This, and the clear evidence for $S_4$ as distinct from $D_{2d}$ symmetry, indicates that at least three out of the four rare-earth ions studied here interact strongly with the more remote atoms in the crystal as well as with the eight oxygen nearest neighbors.

During experiments with (Ca,Er)$WO_4$ crystals it was observed that, for certain orientations of the Zeeman field in the $ab$ plane, the echo-signal strength changed rapidly as a function of Zeeman field angle in a manner very reminiscent of the sharp variation of the electric effect near a point of zero shift. The electric effect in (Ca,Er)$WO_4$ is exceptionally large, and suggests the possibility that an electric microwave resonance, as distinct from a magnetic microwave resonance, might have been observed. Consideration of the magnitudes involved will show that such an observation would be unlikely in a simple $TE_{110}$ cavity and that it must be attributed here to an unexpectedly large distortion of microwave fields in the cavity, arising, possibly, from a nearby resonance in the electrode structure.[7] It would, however, be easy to design a cavity to concentrate the oscillating electric field inside the sample and to give a strong microwave electric resonance signal for a material such as (Ca,Er)$WO_4$. Since the electric effect consists of a modulation of $g$, such an electric resonance would be increasingly easy to observe at higher Larmor frequencies. To illustrate the relations which exist between the field vectors required to give electric and magnetic resonance let us take a particular case in which the only magnetic field is a Zeeman field $H_0$ in the $x$ direction and the only electric field an oscillating field $E_z$ in the $z$ direction. For $S_4$ point symmetry the Hamiltonian (5) then reduces to

$$\mathcal{H}=g_\perp\beta H_0 S_x+T_{31}H_0E_zS_x+T_{36}H_0E_zS_y. \qquad (18)$$

This may be compared with the Hamiltonian for the case when there is a Zeeman field in the $x$ direction, no electric field, and an oscillating magnetic field $H_y$ in the $y$ direction

$$\mathcal{H}=g_\perp\beta H_0 S_x+g_\perp\beta H_y S_y. \qquad (19)$$

By comparing (18) and (19) it can be seen that the oscillating electric field term $T_{36}H_0E_zS_y$ plays a role equivalent to that of an oscillating magnetic field term $g_\perp\beta H_yS_y$. Equating the two we find the ratio between electric and magnetic field intensities which would give the same resonance effects

$$E_z/H_y=(g_\perp\beta)/(T_{36}H_0)=2g_\perp^2/(B_{36}H_0). \qquad (20)$$

For (Ca,Er)$WO_4$ $B_{36}=5.2\times10^{-6}$ per V/cm, $g_\perp=8.3$, and at a resonance frequency of 9.42 Gc/sec, $H_0=810$ G. The microwave electric field with an effect equivalent to 1 G magnetic field is therefore 33 000 V/cm (i.e., $E_z/H_y$ is over 100 times larger than the ratio which exists between the peak amplitudes of electric and magnetic fields in an empty $TE_{110}$ cavity). It may be noted that the coefficient $B_{36}$ has one sign for half the sites in $CaWO_4$ and the opposite sign for the other half. This is of no consequence so long as there is only an electric oscillating field, but it implies that electrically generated echoes will not couple with a microwave magnetic field and vice versa, and may give rise to interference effects in mixed fields.

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[6] A. Zalkin and D. H. Templeton, J. Chem. Phys. 40, 501 (1964).

[7] Figure 6 in Ref. 1. This interpretation is consistent with the fact that no such effect has been observed with $CaErWO_4$ in a cavity without electrodes.