A Note on the Paramagnetoelectric Effect

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When an external magnetic field is applied to the crystals that contain paramagnetic ions like transition metal ions or rare earth ions, local symmetries around the ions in the zero field is no longer present and the time reversal invariance is also lost. However, in analogy with the magnetic symmetry group,\(^1\) certain symmetry elements in the absence of the field may be new symmetry elements under the field if the time reversal operator is combined with them. In fact, it may be shown\(^2\) in the case of the \(C_{3h}\) symmetry crystal with a transverse magnetic field that the one-ion Hamiltonian

\[
H = H_0 + V - \mu_B [H_s (L_s + 2S_s) + H_v (L_v + 2S_v)],
\]

(1)

where \(H_0\) is the free ion Hamiltonian and \(V\) the \(C_{3h}\) symmetry crystal field potential, has the symmetry element \(O T; \ [H_0 O T] = 0.\) Here \(T\) is the time reversal operator and \(O\) the \(C_{3h}\) group generator.\(^3\) The Zeeman energy in (1) will be denoted by \(H_Z.\)

The existence of such a new symmetry element leads\(^5\) to very useful relations for transition matrix elements in optical absorption. They provide some prescription between relative phases of initial and final states in transitions, and can be assumed as the new selection rules. The purposes of the present note are to indicate that the selection rules can predict the presence of the paramagnetoelectric effect\(^4\) and to calculate a detailed form of this effect in rare earth crystals with the \(C_{3h}\) symmetry.

In absence of magnetic field each energy level is either doubly degenerate or non-degenerate in the \(C_{3h}\) symmetry crystal. Let crystal eigenstates with the crystal field quantum numbers \(\mu_s\)satisfy the following equations:\(^3\)

\[
O \psi(\mu) = \exp(i\pi\mu/3) \psi(\mu) ;
\]
\[
T \psi(\mu) = \eta(\mu) \psi(\bar{\mu}) ;
\]

(2)

with \(\eta(\mu) = \pm 1,\) where \(\psi(\mu)\) and \(\psi(\bar{\mu})\) are states degenerate each other and, if \(\psi(\mu)\) is a nondegenerate state, \(\psi(\mu) = \psi(\mu).\) The parity mixing is present in \(\psi(\mu)\) because of the absence of the inversion symmetry. The basis functions for a doubly degenerate state were taken\(^3\) to diagonalize \(H_Z\) in this manifold; \(\psi((\mu \bar{\mu})_s) = 2^{-1/2} \times \left[ \psi(\mu) + se^{i\phi_m} \psi(\bar{\mu}) \right],\) where \(s = \pm 1\) and \(f\) is a function of the angle \(\phi_m\) which specifies...
Letters to the Editor

1039

the direction of $\mathbf{H}$ measured from the $x$-axis defined in reference 3). The operation $O_{y}^{2}T\psi$ on this function yields

$$O_{y}^{2}T\psi = \exp(i\lambda)\psi$$

(3)

with $\exp(i\lambda) = (-1)^{n} \eta(\mu) \exp(-if)$, where the equalities $\eta(\mu) \eta(n) = \exp[i\pi(n-\mu)] = (-1)^{n}$ were used. The basis function for a nondegenerate state may be taken as $\psi(\mu)$. Operation of $O_{y}^{2}T$ on this yields

$$0_{y}^{3}r'=\exp(i\lambda')r'$$

(3)

with $\exp(i\lambda) = (-1)^{n} \eta(\mu)$. These eigenvalues $\exp(i\lambda)$ depend on internal phases.* For the functions that satisfy Eq. (3) the following equality holds:

$$-\left(\frac{1}{r_{2}}\right)\psi_{1}(\mu_{2}) = \exp[i(\lambda_{2}-\lambda_{1})]\psi_{1}(\mu_{2})$$

(4)

where $A$ is an operator. From (4) and the relation $(O_{y}^{2}T)H_{x}(O_{y}^{2}T)^{-1} = H_{x}$, it can be shown that complete perturbed wave function also satisfy (3) with the same eigenvalue $\exp(i\lambda)$ that is obtained for the zeroth order function. Therefore, (4) also holds for the complete perturbed functions.

Now, take $P = \Sigma(-v)\gamma_{1}$ or $M = \mu_{k}(L+2\mathbf{S})$ for $A$ in (4). It holds that $(O_{y}^{2}T)P_{x}(O_{y}^{2}T)^{-1} = -P_{x}$ and $(O_{y}^{2}T)M_{x}(O_{y}^{2}T)^{-1} = -M_{x}$ while $P_{x}$, $P_{y}$, $M_{x}$ and $M_{y}$ do not change sign by this transformation. Therefore, one gets

$$\langle\psi_{1}|A|\psi_{2}\rangle^{*} = \exp[i(\lambda_{1}-\lambda_{2})]\langle\psi_{1}|(O_{y}^{2}T)A(O_{y}^{2}T)^{-1}|\psi_{2}\rangle,$$

(4)

and the expressions with $M_{x,y}$ and $M_{x}$ in places of $P_{x,y}$ and $P_{x}$ respectively. They provide the selection rules in the electric and the magnetic dipole transitions. If $\psi_{2}$ is set equal $\psi_{1}$ in (5), $\langle\psi_{1}|P_{x}|\psi_{2}\rangle = \langle\psi_{1}|M_{x}|\psi_{2}\rangle = 0$ from hermiticity, while $\langle\psi_{1}|P_{x,y}|\psi_{2}\rangle$ and $\langle\psi_{1}|P_{x}|\psi_{2}\rangle$ may not be equal to zero. These indicate the presence of the paramagnetoelectric effect: electric polarization is induced by a magnetic field.

Detailed expressions for the electric polarization is obtained by calculating $\langle P_{z}\rangle_{AV}/N = Z^{-1}\mathrm{Tr} P \exp[-\beta(H_{0}+V+H_{2})]$, where $Z = \mathrm{Tr} \exp[-\beta(H_{0}+V+H_{2})]$ and $N$ is the number of rare earth ions. By use of the perturbation expansion of $H_{2}$ and of the matrix elements given in reference 3), one gets

$$\langle P_{z}\rangle_{AV}/N = -Z_{0}e^{-2\mu_{0}}$$

$$\times \Sigma\{(F_{210}-F_{221})\eta(1)\eta(2)\} \langle P_{z}\rangle_{AV}$$

$$\times \{F_{0}+F_{2}+F_{21}\} \langle P_{z}\rangle_{AV} - F_{22} \langle P_{z}\rangle_{AV}$$

$$+ (F_{10}+F_{20}) \langle P_{z}\rangle_{AV} - F_{210} \langle P_{z}\rangle_{AV}$$

(6)

for crystals containing rare earth ions with odd number of electrons and

$$\langle P_{z}\rangle_{AV}/N = -Z_{0}e^{-2\mu_{0}}$$

$$\times \Sigma\{(F_{210}+F_{20})\eta(1)\eta(2)\} \langle P_{z}\rangle_{AV}$$

$$\times \{F_{211}+F_{212}\} \langle P_{z}\rangle_{AV} - F_{221} \langle P_{z}\rangle_{AV}$$

$$- F_{222} \langle P_{z}\rangle_{AV}$$

(7)

for those with even number of electrons, where all numbers are the $\mu$-quantum numbers and the sum is taken for other necessary quantum numbers. In (6) and (7), $P_{z} = P_{z}^{+}+iP_{z}^{-}$, $Z_{0} = \Sigma \exp(-\beta E_{m})$, $E_{m}$ being eigenvalues of $H_{0}+V$, $H_{nm} = \langle n|H_{0}(\mathbf{H}/\mathbf{x})|m\rangle$, and

$$F_{n}\left[\frac{1}{1-E_{m}}\right]$$

$$\times \exp(-\beta E_{m}) - \exp(-\beta E_{m})$$

$$\frac{E_{m} - E_{n}}{E_{m} - E_{n}}$$

(8)

$\langle P_{z}\rangle_{AV}$ and $\langle P_{z}\rangle_{AV}$ are given from (6) and (7) by taking their real and imaginary parts, respectively. Equations (6) and (7) show the $H^{2}$-dependence in contrast to the linear dependence in magnetic substances, and this is the consequence of the time reversal property. Hou and Bloembergen has observed this sort of effect in NiSO$_{4}$6H$_{2}$O. Rare earth ethylsulfates, for instance, have the $C_{5v}$ symmetry and the present expressions must be applicable. A macroscopic
polarization may, however, be unobservable in this substance, because there are two rare earth ions in a unit cell and they have opposite sign in the odd parity crystal field potential and hence in the matrix elements of \( P_+ \) in (6) and (7). Nevertheless, if there are some rare earth compounds which should exhibit the macroscopic effect, the polarization may be quite appreciable. This is due to the fact that two energy denominators in \( F_{mn} \) can be quite small or even can be degenerate, while the corresponding denominators in the 3d ions are quite large (cf. Eq. (14) of reference 4)). The observation of this effect may be useful to get information about the odd parity potential, which reflects in the matrix elements of \( P_+ \), as in the observation of the Stark effect.\(^6\) The author would like to thank Professor S. Sugano, Professor Y. Tanabe, and Professor I. Tsujikawa for stimulating discussions.


\(*\) The eigenvalues are dependent on the choice of total phase factors and the expressions in reference 2) correspond to a special choice of these. However, the final result is independent of this.


**Note added in proof:** The author also expresses his thanks to Prof. R.H. Good for helpful discussions. He has pointed out to the author that a macroscopic electric polarization may possibly be observed in mixed crystals like \( Y \cdot R \)-ethylsulfates \((R = \text{rare earth ions})\), if the \( R \)-ions occupy two kinds of lattice points with unequal weights.