Subgroup Techniques in Crystal and Molecular Physics

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The determination of the form of tensors and matrix elements is greatly simplified by using the smallest possible group of symmetry operations that is relevant. Whenever some indices are only permuted (aside from ± signs) by the symmetry operations, we show that complete symmetry information is contained in the subgroup of operations that leaves these indices invariant or exchanges them. For a particular tensor element T_{123} this is the group of the indices 123. For a tensor function of a vector $T_{\mu\nu}\cdots(\mathbf{E})$ this is the group of operations that leave the vector $\mathbf{E}$ invariant. For a force constant matrix $K_{\mu\nu\lambda}{}^{mn}$ this is the group of the bond mn. For an anharmonic force constant $K_{\mu\nu\lambda}{}^{mnp}$ this is the group of the triangle connecting the atoms mnp. For a matrix element $V^{\mathbf{kk'k''}}$ connecting three vectors $\mathbf{k},\mathbf{k'k''}$ of the Brillouin zone this is the common group of the wave vectors, i.e., the group G_s of elements that leave $\mathbf{k}$, $\mathbf{k'}$ and $\mathbf{k''}$ invariant (modulo a reciprocal lattice vector), in some cases augmented by the elements that permute $\mathbf{k}$, $\mathbf{k'}$ and $\mathbf{k''}$. The proper use of "exchange" elements is shown to be determined by the behavior of the operator V under time-reversal and Hermitian conjugation. The results are valid in the presence of spin-orbit interaction.

1. INTRODUCTION

THIS paper will show that if one asks specific, local, questions about a system possessing a large symmetry group G, that only a subgroup H of G is relevant to answering these questions.

For example, if we wish to calculate the number of independent force constants $K_{\mu\nu}{}^{mn}$ appropriate to a a particular pair of atoms m, n in a molecule, the relevant group H is the "group of the bond," namely, the subgroup of the group G of the molecule containing those elements R that restore the bond to itself. These include ordinary elements that restore the atoms to themselves

$$R(m)=m, \quad R(n)=n \quad \text{(ordinary)} \qquad (1.1)$$

and reversal elements that exchange the atoms

$$R(m)=n, \quad R(n)=m \quad \text{(exchange)}. \qquad (1.2)$$

Moreover, the exchange elements should only be used if the force constants obey a *symmetry relation*

$$K_{\mu\nu}{}^{mn}=fK_{\nu\mu}{}^{nm}, \quad f=\pm 1 \qquad (1.3)$$

closely related to *time reversal*.[1,2] (If $K_{\mu\nu}{}^{mn}$ represented the electric-dipole moment $M_\mu{}^m$ induced on atom m in Cartesian direction μ when atom n is given the displacement $u_\nu{}^n$ this symmetry would be absent.)

As a second example, we mention electronic or vibrational transitions in crystals involving a change of wave vector $\mathbf{k}$. The selection rules for such processes can be obtained by calculating the number of independent parameters (for fixed $\mathbf{k}$, $\mathbf{k'}$, $\mathbf{k''}$) among matrix elements of the form

$$V_{\mu\nu\lambda}{}^{\mathbf{kk'k''}}=\int \varphi_{\mathbf{k}\mu}{}^i(V_{\mathbf{k''}\lambda}{}^m)^*\psi_{\mathbf{k'}\nu}{}^i d\tau; \quad \mathbf{k''} \doteq \mathbf{k}+\mathbf{k'}, \qquad (1.4)$$

where $\doteq$ means congruent modulo a reciprocal lattice vector, and each factor transforms as a Bloch wave, e.g.,

$$R\varphi_{\mathbf{k}\mu}{}^i=\sum \varphi_{R\mathbf{k},\mu'}{}^i D_{\mu'\mu}{}^{iR\mathbf{k},\mathbf{k}}(R), \qquad (1.5)$$

where $\mathbf{k}$ is carried into $R\mathbf{k}\equiv \mathbf{R}\cdot\mathbf{k}$ where $\mathbf{R}$ is the rotational part of the complete space-group element $(\mathbf{R}\,|\,\mathbf{a})$. In this case, the relevant group G_s is the intersection of the three groups $G_{\mathbf{k}}$, $G_{\mathbf{k'}}$, $G_{\mathbf{k''}}$ of the corresponding wave vectors (the "common group of the wave vector"). In other words we select those R for which

$$R\mathbf{k}\doteq\mathbf{k}, \quad R\mathbf{k'}\doteq\mathbf{k'}, \quad R\mathbf{k''}\doteq\mathbf{k''}$$

or briefly

$$R(\mathbf{kk'k''})=\mathbf{kk'k''}. \qquad (1.6)$$

This is the group chosen by Elliott and Loudon.[3] (A slightly larger group was introduced by Lax and Hopfield[4] in order to permit the selection-rule calculation to proceed using only existing character tables. Moreover, the equivalence of the Lax-Hopfield procedure to that of Elliott and Loudon was established.[4])

If a special relation exists between $\mathbf{k}$ and $\mathbf{k'}$ *and* between the basis vectors:

$$\mathbf{k}\doteq Q\mathbf{k'} \quad \text{and} \quad \varphi_{\mathbf{k},\mu}{}^i\equiv Q\psi_{\mathbf{k'},\mu}{}^i, \qquad (1.7)$$

where Q is a space group element, then Lax[2] has shown, that one must also include exchange elements that obey

$$R(\mathbf{kk'k''})=\mathbf{k'kk''} \qquad (1.8)$$

so that the complete set of elements used is G_s+QG_s. One must then take a symmetric or antisymmetric product of the representation j with Qj according to the behavior of the perturbation operator V under *time-reversal* and Hermitian conjugation.[1,2]

In very special problems, all three basis vectors and wave vectors can be related, and it will be necessary to include *all possible exchange elements* such that

$$R(\mathbf{kk'k''})=\text{any permutation of } \mathbf{kk'k''}. \qquad (1.9)$$

[1] For a detailed discussion of time reversal, see the author's forthcoming book, Symmetry Principles in Solid State Physics.

[2] For a discussion of time reversal with specific application to selection rules connecting different points in the Brillouin zone see M. Lax, in *Report of the Exeter International Conference on The Physics of Semiconductors* (Institute of Physics and the The Physical Society, London, 1962), p. 395.

[3] R. J. Elliott and R. Loudon, J. Phys. Chem. Solids 15, 146 (1960).

[4] M. Lax and J. Hopfield, Phys. Rev. 124, 115 (1961).

An example of such a process is the use of a quartic anharmonic term in a face-centered cubic lattice to cause the decay of a $\Gamma=(0,0,0)$ photon into an $X=(1,0,0)$, a $Y=(0,1,0)$, and a $Z=(0,0,1)$ phonon where

$$(1,0,0)+(0,1,0)+(0,0,1)\equiv(1,1,1)\doteq(0,0,0).$$

Birman[5] and Zak[6] have criticized the Lax-Hopfield[4] and Elliott-Loudon[3] procedures because they do not make use of the full-space group. This criticism is misleading, however. The subgroup procedure attempts to calculate directly the number of independent constants in, for example, $V_{\mu\nu\lambda}^{\mathbf{kk'k''}}$ for fixed $\mathbf{k}$, $\mathbf{k'}$, $\mathbf{k''}$ whereas the use of full space-group-character formulas calculates the number of independent parameters in the complete set of matrix elements $V_{\mu\nu\lambda}^{R\mathbf{k}R\mathbf{k'}R\mathbf{k''}}$, a different question in principle. If the two results were to differ, the subgroup procedure would provide the correct (and the full group an incorrect) answer to the original question. The proof of the equivalence of the subgroup and full-group procedures given in Sec. 3, can be regarded then, not as a justification of the subgroup procedure, but rather a proof that the two sets of matrix elements have the same number of independent parameters.

Birman[5] also criticized the subgroup procedures of Lax-Hopfield and Elliott-Loudon on the grounds that they did not provide procedures for taking the symmetric or antisymmetric Kronecker product of representations. The character formulas for the symmetric and antisymmetric product formulas and the time-reversal considerations needed to determine which of these to use, have already been published.[2] However, Birman[7] has remained unconvinced that our subgroup procedures including time reversal are equivalent to the use of the full-space group including symmetric or antisymmetric products. It was thought worthwhile, therefore, to present an explicit proof in Sec. 3 that covers not only space groups, but a wide variety of cases in which subgroup procedures are useful.

Section 4 will develop the concepts of the group of the bond and the group of the triangle for dealing with harmonic and anharmonic force constants in molecules or crystals. Section 5 will specialize our general results to selection rules connecting different points in the Brillouin zone.

The reader who is not interested in the justification but the use of our procedures can proceed directly to Secs. 6–9 where applications are made in Sec. 6 to obtain the Herring criterion, in Sec. 7 to obtain two-phonon selection rules, in Sec. 8 to obtain harmonic

and anharmonic force constants in crystals and in Sec. 9 to obtain the form of tensors using the group of the indices, and the group of an external field vector or tensor. A discussion is also given of magnetic tensors such as piezomagnetic and magnetoelectric tensors since these illustrate the case in which time-reversal K is not a member of the group, but appears in some combination QK.

2. SELECTION OF THE RELEVANT SYMMETRY ELEMENTS

The displacement vectors in a molecular vibration $\mathbf{u}_\mu{}^m$ and the basis vectors for a space-group irreducible representation $\varphi_{\mathbf{k}\mu}{}^i$ are both described by parameters m or $\mathbf{k}$ that are simply permuted by the group operations, (and not taken into a linear combination of such objects). Thus a matrix element $K_{\mu\nu}{}^{mn}$ or $V_{\mu\nu\lambda}^{\mathbf{kk'k''}}$ can be written briefly in the form $V_s{}^\alpha$ where $\alpha=mn$ or $\alpha=\mathbf{kk'k''}$ is an index that suffers only permutations, and $s=\mu\nu$ or $\mu\nu\lambda$ are indices that need not have this special property. Thus, a symmetry requirement imposed by an arbitrary element R of the full group G takes the form

$$V_s{}^\alpha=RV_s{}^\alpha\equiv\sum_{\alpha's'}V_{s'}{}^{\alpha'}\delta(\alpha',R(\alpha))D_{s's}{}^{\alpha'\alpha}(R)$$

$$=\sum_s V_{s'}{}^{R(\alpha)}D_{s's}{}^{R(\alpha)\alpha}(R).\qquad(2.1)$$

If, therefore, we restrict our attention to the subgroup $H=G_\alpha$ defined by

$$R\epsilon H\quad\text{if}\quad R(\alpha)=\alpha,\qquad(2.2)$$

we obtain all the relations

$$V_s{}^\alpha=\sum_{s'}V_{s'}{}^\alpha D_{s's}{}^\alpha(R)\qquad(2.3)$$

between members of the set $V_s{}^\alpha$ (fixed α, varying s), where $D_{s's}{}^\alpha(R)=D_{s's}{}^{\alpha\alpha}(R)$ is the matrix representative of R in the subgroup G_α. Thus, these are the only elements *relevant* for fixing the relative sizes and number of independent parameters among the $V_s{}^\alpha$ (fixed α).

Once the $V_s{}^\alpha$ are determined, the $V_s{}^\beta$, $\beta\neq\alpha$ can be determined in terms of the $V_\mu{}^\alpha$ by choosing an R such that $R(\alpha)=\beta$ and inverting the matrix in (2.1). Thus the $V_\mu{}^\beta$ introduce no new parameters. The number of parameters N among all $V_\mu{}^{R(\alpha)}$ is then the same as the number N_α among $V_\mu{}^\alpha$ for *any one* fixed α. A corollary remark is then that N_α is independent of α since any one of the α could have been made our standard choice. These results constitute an informal proof that the questions posed in the subgroup and full group procedures are equivalent, and their answers identical. A direct proof of the latter statement will be given in the next section.

When α represents a compound set of symbols such as $\mathbf{kk'k''}$ and relations are available between $V^{\mathbf{kk'k''}}$ and $V^{\mathbf{k'kk''}}$ through time reversal[2] we can, in this section and the next interpret $\mathbf{k'kk''}$ as not distinct

[5] J. L. Birman, Phys. Rev. 127, 1093 (1962); 131, 1489 (1963). See also I. V. V. Raghavacharyulu, Report No. 116, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden (unpublished), for the derivation of selection rules using the full space-group and little-group theory.
[6] J. Zak, J. Math. Phys. 3, 1278 (1961).
[7] J. L. Birman, J. Phys. Chem. Solids, Suppl. I, 669 (1965); and discussion by M. Lax which follows this paper.

from $\mathbf{k}\mathbf{k}'\mathbf{k}''$, i.e., regard $R(\alpha)=\alpha$ for the elements that exchange $\mathbf{k}$ and $\mathbf{k}'$. In this way, the group G_α will include whatever exchange elements are needed. The matrix elements $D_{s's}{}^\alpha(R)$ that must be used for these exchange elements will contain certain symmetric or antisymmetric combinations, as discussed in Sec. 4, but the nature of this symmetrization process is parallel in the subgroup and full group procedures and will not disturb a comparison between these two.

3. FORMAL PROOF OF THE EQUIVALENCE OF THE SUBGROUP AND FULL-GROUP PROCEDURES

With a meaning for $R(\alpha)$ that includes exchange elements, the number of independent parameters among the set $V_s{}^\alpha$ for fixed α is given by[8]

$$N_\alpha = \frac{1}{g_\alpha} \sum_{R \in G_\alpha} \Phi^\alpha(R), \tag{3.1}$$

where g_α is the order of the subgroup G_α and

$$\Phi^\alpha(R) = \sum_s D_{ss}{}^{\alpha\alpha}(R) \tag{3.2}$$

is the character of the representation of R in the basis $V_s{}^\alpha$ (fixed α). The number N_α is given by (3.1) since (3.1) gives the number of times the identity representation is contained in the space spanned by the $V_s{}^\alpha$ (fixed α).

From the first part of (2.1), however, we can determine the character of R in the space of all $V_s{}^\alpha$ by setting $\alpha'=\alpha$, $s'=s$ in the matrix element and summing. The average of this character over the complete group G gives the number of parameters among all $V_s{}^\alpha$ (α varying as well):

$$N = \frac{1}{g} \sum_\alpha \sum_{R \in G} \delta(\alpha, R(\alpha)) \Phi^\alpha(R)$$

$$= \frac{1}{g} \sum_\alpha g_\alpha \left[\frac{1}{g_\alpha} \sum_{R \in G_\alpha} \Phi^\alpha(R) \right]$$

$$= \frac{1}{g} \sum_\alpha g_\alpha N_\alpha. \tag{3.3}$$

We shall show, below, that g_α and N_α independent of α (see also the remarks in Sec. 2). The number of terms in the sum is then g/g_α, and we find

$$N = N_\alpha \tag{3.4}$$

which was to be established.

To see that g_α is independent of α, we note that if $X\alpha=\beta$ or $X^{-1}\beta=\alpha$ and if $R \in G_\alpha$ then $XRX^{-1}\beta=XR\alpha=X\alpha=\beta$ so that

$$G_\beta = XG_\alpha X^{-1} \tag{3.5}$$

is a conjugate subgroup with $g_\beta=g_\alpha$.

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[8] See Chap. 4 of Ref. 1.

Since there is a certain amount of arbitrariness in the choice of basis vectors in the conjugate subspaces, we can choose for convenience

$$V_s{}^\beta = XV_s{}^\alpha \tag{3.6}$$

from which we learn that

$$\Phi^\beta(R) = \sum_s (XV_s{}^\alpha, RXV_s{}^\alpha) = \Phi^\alpha(X^{-1}RX) \tag{3.7}$$

a trace result that is independent of our arbitrary choice (3.6). By the group rearrangement theorem, we can now write

$$\sum_{R \in G} \Phi^\alpha(R)\delta(\alpha, R\alpha) = \sum_{R \in G} \Phi^\alpha(X^{-1}RX)\delta(\alpha, X^{-1}RX\alpha)$$

$$= \sum_{R \in G} \Phi^\beta(R)\delta(\beta, R\beta),$$

or

$$g_\alpha N_\alpha = g_\beta N_\beta, \tag{3.8}$$

where we have used $\delta(\alpha, X^{-1}R\beta) = \delta(X\alpha, R\beta) = \delta(\beta, R\beta)$. Thus $g_\alpha N_\alpha$ (and hence N_α) is independent of α.

Our proof of (3.4) and the identity of the subgroup and full-group answers is now complete.

4. GROUP OF THE BOND

The potential energy of vibration of a molecule or crystal

$$V = \frac{1}{2} \sum_{mn} \mathbf{u}^m \cdot \mathbf{K}^{mn} \cdot \mathbf{u}^n = \frac{1}{2} \sum_{mn\mu\nu} u_\mu{}^m K_{\mu\nu}{}^{mn} u_\nu{}^n \tag{4.1}$$

is assumed to be invariant under the (possibly inhomogeneous) space-group operations $(S|\mathbf{v})$ that take the equilibrium positions $\mathbf{X}^m$ into new equilibrium positions

$$\mathbf{X}^{m'} = (\mathbf{X}^m)' = \mathbf{S} \cdot \mathbf{X}^m + \mathbf{v} \equiv \mathbf{X}^{S(m)}, \tag{4.2}$$

where $m' = S(m)$ is the name of the new position and $\mathbf{S}$ is the 3×3 matrix of the rotation. The complete positions are carried into

$$(\mathbf{X}^m + \mathbf{u}^m)' = \mathbf{S} \cdot (\mathbf{X}^m + \mathbf{u}^m) + \mathbf{v} \tag{4.3}$$

or

$$\mathbf{X}^{S(m)} + \mathbf{u}'^{S(m)} = \mathbf{X}^{S(m)} + \mathbf{S} \cdot \mathbf{u}^m,$$
$$\mathbf{u}'^{S(m)} = \mathbf{S} \cdot \mathbf{u}^m, \tag{4.4}$$

i.e., the rotated vector $\mathbf{S} \cdot \mathbf{u}^m$ is the displacement deposited at the new position $S(m)$. The new potential energy is then

$$V' = \frac{1}{2} \sum (\mathbf{S} \cdot \mathbf{u}^m) \cdot \mathbf{K}^{S(m)S(n)} \cdot (\mathbf{S} \cdot \mathbf{u}^n) \tag{4.5}$$

or

$$S_{\mathrm{op}} K_{\mu\nu}{}^{mn} = K'_{\mu\nu}{}^{mn} = \sum_{\mu'\nu'} K_{\mu'\nu'}{}^{S(m)S(n)} S_{\mu'\mu} S_{\nu'\nu}$$

$$= \sum K_{\mu'\nu'}{}^{m'n'} \Delta_{m'n'\mu'\nu'; mn\mu\nu}(S), \tag{4.6}$$

where

$$\Delta_{m'n'\mu'\nu'; mn\mu\nu}(S) = \delta(m', S(m))\delta(n', S(n)) S_{\mu'\mu} S_{\nu'\nu} \tag{4.7}$$

in complete analogy with our more abstract Eq. (2.1). If we make no use of $K_{\mu\nu}{}^{mn} = K_{\mu\nu}{}^{nm}$, the character of

any element of the group of the molecule (crystal) is

$$\chi(S) = \sum_{m,n} \delta(m,S(m))\delta(n,S(n))\Phi^{mn}(S), \quad (4.8)$$

where

$$\Phi^{mn}(S) = [\Phi(S)]^2 = (\sum_\mu S_{\mu\mu})^2 \quad (4.9)$$

is the character that results if restrict our attention to the bond mn, i.e., to the $K_{\mu\nu}{}^{mn}$ for a fixed mn.

If $K_{\mu\nu}{}^{mn}$ has a known symmetry under the operation F ("flip") that flips the indices,

$$FK_{\mu\nu}{}^{mn} = K_{\nu\mu}{}^{nm} = fK_{\mu\nu}{}^{mn}; \quad f = \pm 1, \quad (4.10)$$

then an operator R that exchanges m and n can be combined with F to yield a relation between $K_{\mu\nu}{}^{mn}$ and other members $K_{\mu'\nu'}{}^{mn}$ of the same set:

$$RFK_{\mu\nu}{}^{mn} = RK_{\nu\mu}{}^{nm} = \sum K_{\mu'\nu'}{}^{m'n'}\delta(m',R(n))$$
$$\times \delta(n',R(m))R_{\mu'\nu}R_{\nu'\mu} \quad (4.11)$$

using Eq. (4.6). The character can be obtained by setting $m'=m$, $n'=n$, $\mu'=\mu$, $\nu'=\nu$ and summing:

$$\chi(RF) = \sum_{m,n} \delta(m,R(n))\delta(n,R(m))\Phi^{mn}(R), \quad (4.12)$$

$$\Phi^{mn}(R) = \Phi(R^2) = \sum R_{\mu\nu}R_{\nu\mu}. \quad (4.13)$$

Equations (4.8) and (4.12) can be used for any element R, or S in the full group of the molecule (or crystal). The structure of these formulas indicate that for a given mn, the only relevant elements are those that have the bond invariant, or exchange the ends. The general procedure of Sec. 3 (which has been carried out in detail for this application[9]) shows that one can work directly with the group of the bond, including its exchange elements. If Q is a particular reversal element, we can use the abbreviation

$$\begin{aligned} J(R) &= \delta(m,R(m))\delta(n,R(n)), \\ J(RQ) &= \delta(m,R(n))\delta(n,R(m)), \end{aligned} \quad (4.14)$$

and write the number of force constants in bond mn via (3.1) in the simplest possible form:

$$N_{mn} = \frac{1}{g_{mn}} \sum_{R\epsilon G_{mn}} \{[\Phi(R)]^2 J(R) + f\Phi(R^2)J(RQ)\}, \quad (4.15)$$

where the factors $J(R)$, $J(RQ)$ insure that the first sum contains only ordinary elements, and the second sum only exchange elements.

For the special case in which $m=n$, there is no distinction between ordinary and exchange elements, and the two representation Eqs. (4.7) and (4.11) are not independent. The average of these two equations yields the usual result

$$N_{mm} = \frac{1}{2}\frac{1}{g_m} \sum_{R\epsilon G_{mm}} \{[\Phi(R)]^2 + f\Phi(R^2)\} \quad (4.16)$$

[9] See Chap. 5 of Ref. 1.

for the symmetric $(f=+1)$ or antisymmetric $(f=-1)$ product representations. This is the same result as we would have gotten if we had simply used (4.15) and divided the result by 2. The factor of 2 arises because $K_{\mu\nu}{}^{11}$ and $K_{\nu\mu}{}^{11}$ are not independent whereas $K_{\mu\nu}{}^{12}$ and $K_{\nu\mu}{}^{12}$ are independent basis functions in constructing our representation.

The extension of these ideas to a third-rank tensor $K_{\mu\nu\lambda}{}^{mnp}$ that is symmetric $(f=1)$ on all interchanges $m\mu \rightleftarrows n\nu$, $m\mu \rightleftarrows p\lambda$, $n\nu \rightleftarrows p\lambda$, or antisymmetric $(f=-1)$ on such pair exchanges can be obtained immediately by writing

$$RK_{\mu\nu\lambda}{}^{mnp} = K_{\mu'\nu'\lambda'}{}^{R(m)R(n)R(p)}R_{\mu'\mu}R_{\nu'\nu}R_{\lambda'\lambda} \quad (4.17a)$$

$$= fK_{\nu'\mu'\lambda'}{}^{R(n)R(m)R(p)}R_{\mu'\mu}R_{\nu'\nu}R_{\lambda'\lambda} \quad (4.17b)$$

$$= fK_{\lambda'\nu'\mu'}{}^{R(p)R(n)R(m)}R_{\mu'\mu}R_{\nu'\nu}R_{\lambda'\lambda} \quad (4.17c)$$

$$= fK_{\mu'\lambda'\nu'}{}^{R(m)R(p)R(n)}R_{\mu'\mu}R_{\nu'\nu}R_{\lambda'\lambda} \quad (4.17d)$$

$$= K_{\nu'\lambda'\mu'}{}^{R(n)R(p)R(m)}R_{\mu'\mu}R_{\nu'\nu}R_{\lambda'\lambda} \quad (4.17e)$$

$$= K_{\lambda'\mu'\nu'}{}^{R(p)R(m)R(n)}R_{\mu'\mu}R_{\nu'\nu}R_{\lambda'\lambda}. \quad (4.17f)$$

The form (4.17b), for example, yields restrictive information on K^{mnp} only if $R(n)=m$, $R(m)=n$, the last, (4.17f), only if $R(p)=m$, $R(m)=n$, $R(n)=p$. The detailed form of the matrix is obtained by using just these ordinary and exchange elements of the *group of the mnp triangle*. With respect to this group, the character associated with (4.17) is obtained by permuting the dummy indices μ', ν', λ' until each K has the form $K_{\mu'\nu'\lambda'}$, setting now $\mu'\nu'\lambda' = \mu\nu\lambda$ and summing the diagonal elements:

$$\Phi^{mnp}(R) = J_1(R)[\Phi(R)]^3 + fJ_2(R)\Phi(R^2)\Phi(R)$$
$$+ J_3(R)\Phi(R^3), \quad (4.18)$$

where

$$J_1(R) = \delta(m,R(m))\delta(n,R(n))\delta(p,R(p)) \quad (4.19)$$

selects the ordinary elements,

$$\begin{aligned} J_2(R) = &\delta(m,R(n))\delta(n,R(m))\delta(p,R(p)) \\ &+ \delta(m,R(p))\delta(n,R(n))\delta(p,R(m)) \\ &+ \delta(m,R(m))\delta(n,R(p))\delta(p,R(n)) \end{aligned} \quad (4.20)$$

selects those elements that interchange any pair of atoms, and

$$\begin{aligned} J_3(R) = &\delta(m,R(n))\delta(n,R(p))\delta(p,R(m)) \\ &+ \delta(m,R(p))\delta(n,R(m))\delta(p,R(n)) \end{aligned} \quad (4.21)$$

selects those elements that produce cyclic exchanges. The number of independent parameters if K is invariant under the group operation is

$$N_{mnp} = \frac{1}{g_{mnp}} \sum_R \Phi^{mnp}(R). \quad (4.22)$$

The special case $m=n=p$ can be handled directly by taking the average of the right-hand sides of Eq. (4.17) since the K's with different superscripts are no longer independent. The result is

$$\Phi^{mmm}(R)=\frac{1}{3!}\{[\Phi(R)]^3+3f\Phi(R^2)\Phi(R)$$
$$+2\Phi(R^3)\}J(R), \quad (4.23)$$

where

$$J(R)=\delta(m,R(m))$$

simply restricts us to that subgroup of elements that leaves the atom m invariant. For $f=+1$, (4.23) is recognizable as the usual triple symmetry product.

For the case $m=n\neq p$, the last four lines of Eq. (4.17) do not contribute since any interchange of m (or n) and p changes K^{mmp} into K^{ppm} and leads one out of the space of the $K_{\mu\nu\lambda}{}^{mmp}$ (fixed mmp) in which we take the character. The average of the first two terms then leads to

$$\Phi^{mmp}(R)=\frac{1}{2}\{[\Phi(R)]^2+f\Phi(R^2)\}$$
$$\times\Phi(R)\delta(m,R(m)\delta(p,R(p)). \quad (4.24)$$

For contrast with (4.18) and (4.24) let us write the character for the case

$$K_{\mu\nu\lambda}{}^{mnp}=fK_{\nu\mu\lambda}{}^{nmp} \quad (4.25)$$

and K possesses no particular symmetry under the interchange of m and p or of n and p. In this case

$$\Phi^{mnp}(R)=\{[\Phi(R)]^2\delta(m,R(m))\delta(n,R(n))+\Phi(R^2)$$
$$\times\delta(m,R(n))\delta(n,R(m))\}\Phi(R)\delta(p,R(p)) \quad (4.26)$$

is simply the product of the representation generated by $K_{\mu\nu}{}^{mn}$ with that generated by $K_\lambda{}^p$.

To apply these results to lattice vibrations, we must replace m by a double index αi where α is the "name" of the particle in the cell, and i is the cell index. The pure lattice translation $(\varepsilon|t)$ simply tells us that

$$K_{\mu\nu}{}^{\alpha i\beta j}=(\varepsilon|t)K_{\mu\nu}{}^{\alpha i\beta j}=K_{\mu\nu}{}^{\alpha i+t,\beta j+t}=K_{\mu\nu}{}^{\alpha\beta}(j-i)$$

is a function only of the difference in cell indices. Once this is accepted, the operator $(S|v+t)$ yields the same end result as $(S|v)$. Thus character sums over all group elements including translations will simply yield a factor N (the order of the translation group), but this N also appears in the order of the relevant group and cancels. One can thus take sums simply over the representative elements $(S|v)$, and then divide by the number of such representative elements.

Since all calculations are done modulo an arbitrary lattice translation, conditions such as $\delta(m,R(n))$ will be replaced by $\delta(\alpha,S(\beta))$ where β is carried into $S(\beta)$ by $(S|v)$, but not necessarily in the same cell. With this understanding, all of the formulas of this section can be applied directly to lattices.

5. SELECTION RULES CONNECTING DIFFERENT POINTS IN THE BRILLOUIN ZONE

The matrix element (1.4) transforms under R as

$$RV_{\mu\nu\lambda}{}^{kk'k''}=\sum_{\mu'\nu'\lambda'}V_{\mu'\nu'\lambda'}{}^{Rk,Rk',Rk''}D_{\mu'\mu}{}^{iRk,k}(R)$$
$$\times D_{\nu'\nu}{}^{jRk',k'}(R)D_{\lambda'\lambda}{}^{mRk'',k''}(R)^* \quad (5.1)$$

since each factor transforms as in (1.5). Thus, the character generated by this representation is

$$\chi(R)=\chi^{ik}(R)\chi^{jk'}(R)\chi^{mk''}(R)^*J(R), \quad (5.2)$$

where

$$J(R)=\delta(k,Rk)\delta(k',Rk')\delta(k'',Rk''), \quad (5.3)$$

where $\chi^{ik}(R)$ is the character of R in representation, i in G_k, the group of the wave vector k, etc. If $\chi(R)$ were to be regarded as a character in the full-space group, the right-hand side of of (5.2) would have to be summed over all the points in the stars of k, k', and k''. Since, however, we are interested in matrix elements involving the particular k, k', and k'', we must restrict ourselves to the elements of G_s, the intersection of G_k, $G_{k'}$, and $G_{k''}$. These are the elements for which $J(R)$ is unity.

An element $(S|v+t)$ has a character χ that differs from that of $(S|v)$ by a factor $\exp[i(k+k'-k'')\cdot t]$. A sum over all t merely yields the selection rule $k+k'\doteq k''$, which we have assumed from the start. With this choice, the sum over t yields a factor N which also appears in the denominator, when we divide by the order of the group. Hence we can, as in the case of the group of the bond, take all group sums over the set of representative elements $(S|v)$.

If k and k' are two points of the same star, $k\doteq Qk'$ and i and j are descriptions of the same irreducible representation of the full-space group,[10] i.e.,

$$\varphi_{k\mu}{}^i=\psi_{k\mu}{}^j\equiv Q\psi_{k',\mu}{}^j \quad (5.4)$$

then we would expect in the full-space group to use either the symmetric or the antisymmetric product representation. Which of these is appropriate depends on the behavior of $V_\lambda{}^m$ under time reversal, and whether the $\psi_{k\mu}{}^j$ is a spinor or not.

We shall assume[11] that Q obeys $Qk''\doteq k''$ and also that $Qk=k'$ so that Q^2 is in G_s. The matrix element (1.4) can be rewritten in the form

$$(K\varphi_{k\mu}{}^i,V\psi_{k'\nu}{}^j)=(QK\psi_{k'\mu}{}^j,V\psi_{k'\nu}{}^j), \quad (5.5)$$

where we write V briefly for $(V_{k''\lambda}{}^m)^*$, and the left-hand side transforms identically as (1.4), since $K\varphi_\mu{}^i$ transforms as $D_{\mu'\mu}(R)^*$ because of the antilinear nature of

[10] In general, of course, $Q\psi_{k',\mu}{}^j$ can be some linear combination of $\psi_{k,\mu}{}^j$, but it is always possible to choose the base vectors in accord with (5.4). The final character will depend only on the spaces spanned and not on how the basis vectors of each space are labeled.

[11] If the full-space group contained no such element, it would be impossible to relate $V^{kk'k''}$ to $V^{k'kk''}$ and hence to itself by time reversal (see below). The character formula (5.2) would then provide complete information, and the use of symmetric products would lead to nothing new.

the time-reversal operator K, and $D^i(R)^*$ is restored to $D^i(R)$ when it is removed from the left-hand side ("bra position") of the closed product. The form (5.5) of the matrix element is valid in the presence of spin-orbit coupling. The antiunitary property of K permits the right-hand side of (5.5) to be rewritten as

$$(KV\psi_\nu{}^j, KQK\psi_\mu{}^j) = K^2(K\psi_\nu{}^j, \bar{V}Q\psi_\mu{}^j), \quad (5.6)$$

where the (omitted) subscript $\mathbf{k}'$ is now understood to be automatically associated with j, and

$$\bar{V} = (KVK^{-1})^\dagger = KV^\dagger K^{-1} \equiv FVF^{-1}. \quad (5.7)$$

The operator F represents the combined action of Hermitian conjugation and time reversal. If V depends only on position and momentum its action can be written in Dirac notation as

$$V\psi(\mathbf{r}) = \int \langle \mathbf{r}|V|\mathbf{r}'\rangle d\mathbf{r}'\psi(\mathbf{r}') \equiv \int V(\mathbf{r},\mathbf{r}')d\mathbf{r}'\psi(\mathbf{r}'). \quad (5.8)$$

In this case, time reversal reduces to complex conjugation and $\bar{V} = (V^\dagger)^* = \hat{V}$, i.e.,

$$FV(\mathbf{r},\mathbf{r}')F^{-1} \equiv \bar{V}(\mathbf{r},\mathbf{r}') = V(\mathbf{r}',\mathbf{r}), \quad (5.9)$$

so that F flips the indices $\mathbf{r}$, $\mathbf{r}'$ here, just as it flipped the indices mn in K^{mn}.

If the Hamiltonian of the problem commutes with K (and hence F) then F can be diagonalized

$$\bar{V} = fV, \quad f = \pm 1. \quad (5.10)$$

The proof that follows, however, requires only that QK commute with the Hamiltonian; K need not.

Insertion of the exchange operator R (a member of QG_s) into the right-hand side of (5.6) and comparison with (5.5) yields

$$(QK\psi_\mu{}^j, V\psi_\nu{}^j) = K^2(RK\psi_\nu{}^j, V(RF)RQ\psi_\mu{}^j), \quad (5.11)$$

where

$$V(RF) \equiv R\bar{V}R^{-1} = R(\bar{V}_\lambda{}^m)^*R^{-1}$$
$$\equiv \sum (V_{\lambda'}{}^m)^* D_{\lambda'\lambda}(RF)^*, \quad (5.12)$$

$$RQ\psi_\mu{}^j = \sum \psi_{\nu'}{}^j D_{\nu'\mu}{}^j(RQ), \quad (5.13)$$

$$R\psi_\nu{}^j = \sum Q\psi_{\mu'}{}^j D_{\mu'\nu}{}^j(Q^{-1}R), \quad (5.14)$$

since RQ and $Q^{-1}R$ are members of G_s [Eq. (5.14) can be verified by multiplying it by Q^{-1} on the left]. We insert (5.12)–(5.14) into (5.11) to find the matrix generated by RF:

$$(QK\psi_\mu{}^j, (V_\lambda{}^m)^*\psi_\nu{}^j) = \sum (QK\psi_{\mu'}{}^j, (V_{\lambda'}{}^m)^*\psi_{\nu'}{}^j)$$
$$\times \Delta_{\mu'\nu'\lambda'\mu\nu\lambda}(RF), \quad (5.15)$$

$$\Delta_{\mu'\nu'\lambda'\mu\nu\lambda}(RF) = K^2 D_{\mu'\nu}{}^j(Q^{-1}R)D_{\nu'\mu}{}^j(RQ)$$
$$\times D_{\lambda'\lambda}{}^m(RF)^*, \quad (5.16)$$

where the right-hand side of (5.15) contains the same set of matrix elements as the left, because we have used $R\epsilon QG_s$. The character in this representation can

therefore be written

$$\chi(RF) = K^2\chi^{jk'}(R^2)\chi^{mk''}(RF)^*J(RQ), \quad (5.17)$$

where

$$J(RQ) = \delta(\mathbf{k}, R\mathbf{k}')\delta(\mathbf{k}', R\mathbf{k})\delta(\mathbf{k}'', R\mathbf{k}''). \quad (5.18)$$

The number of independent constants among the $V_{\mu\nu\lambda}{}^{Qjk',jk',mk''}$ is then

$$N = \frac{1}{2g_s}\sum_R \left[\chi^{ik}(R)\chi^{jk'}(R)\chi^{mk''}(R)^*J(R)\right.$$
$$\left. + K^2\chi^{jk'}(R^2)\chi^{mk''}(RF)^*J(RQ)\right], \quad (5.19)$$

and the relation (5.4) implies that

$$\chi^{ik}(F) = \chi^{jk'}(Q^{-1}RQ). \quad (5.20)$$

If we specialize to the case in which K commutes with the Hamiltonian so that F can be diagonalized, then

$$\chi^{mk''}(RF)^* = f\chi^{mk''}(R)^*. \quad (5.21)$$

By setting V equal to the identity operator, we see that the representation generated by $(QK\psi_\mu{}^j)^\dagger\psi_\nu{}^j$ has the character

$$\chi(R) = \chi^j(Q^{-1}RQ)\chi^j(R) \quad R\epsilon G,$$
$$\chi(RF) = K^2\chi^j(R^2) \quad\quad R\epsilon QG,$$

a result that can also be established directly using $(QK\psi_\mu{}^j)^\dagger\psi_\nu{}^j$ as basis functions.[12]

6. THE HERRING CRITERION

Since Q and K both reverse $\mathbf{k}$, it follows that $QK\psi_{\mathbf{k}\mu}{}^j$ provide a set of states of wave vector $\mathbf{k}$ that are degenerate with $\psi_{\mathbf{k}\nu}{}^j$. If these states are independent of $\psi_{\mathbf{k}\nu}{}^j$, additional degeneracy at $\mathbf{k}$ due to time reversal will be produced. These states will be independent if $(QK\psi_\mu{}^j, \psi_\nu{}^j) = 0$, a selection rule, Eq. (5.5), in which the perturbation operator V is unity, so that $f = 1$, $\chi^m(R) = 1$, and

$$N = \tfrac{1}{2}(A + K^2 b), \quad (6.1)$$

where

$$A = \frac{1}{g_\mathbf{k}}\sum_R \chi^{jk}(Q^{-1}RQ)\chi^{ik}(R)\delta(\mathbf{k}, R\mathbf{k}), \quad (6.2)$$

$$b = \frac{1}{g_\mathbf{k}}\sum_R \chi^{jk}(R^2)\delta(-\mathbf{k}, R\mathbf{k}). \quad (6.3)$$

The values of A, b and N for the three types of (irreducible) representations are[12]:

Type of representation	A	b	$K^2=1$ N	$K^2=-1$ N	
1	1	1	1	0	
2	1	−1	0	1	(6.4)
3	0	0	0	0.	

If $QK\psi^j$ and ψ^j are orthogonal because they belong to

[12] See Ref. 1, Chap. 10.

inequivalent representations then $\chi^j(Q^{-1}RQ)^*$ and $\chi^j(R)$ are orthogonal, i.e., $A=0$. In this case b and N must also vanish.[12] Added degeneracy due to time reversal is therefore produced when $b=0$ and when $bK^2=-1$, i.e., type-2 representations without spin, and type-1 representations with spin.

The classification of representations into three types by $b=+1$, -1, or 0 was shown by Herring[13] to be equivalent to direct application of the usual Frobenius criterion to the full-space group.

7. TWO-PHONON SELECTION RULES

Lax and Burstein[14] using inversion symmetry demonstrated that electric-dipole absorption in diamond with the creation of a pair of identical phonons is forbidden. They overlooked the same selection rule in NaCl crystal because considerable care is needed in a direct proof which will be presented in Appendix A.

The diamond problem has been reconsidered recently by Birman[5] using the full-space group of the diamond lattice, without realizing that inversion and time reversal are sufficient to guarantee the selection rule at any $\mathbf{k}$. Birman indeed establishes this two-phonon selection rule in zincblende (in the absence of inversion) at points of high symmetry. An approximate selection rule is then probably valid at general $\mathbf{k}$ for this structure, but an absolute selection rule at general $\mathbf{k}$ in any structure is guaranteed only by inversion and time reversal. Burstein, Johnson, and Loudon[15] have applied similar techniques to the rocksalt structure, and Szigeti[16] has applied elementary parity arguments to the rocksalt structure. Loudon,[17] realizing that inversion was the key element provided an argument valid for all crystals possessing inversion symmetry. But Loudon made use of all the wave vectors in the star, and of all translational elements. Moreover, he stated that his conclusion was valid at general wave vectors, but not at $\mathbf{k}$ of special symmetry.

It may be worthwhile, therefore, stating our result as a theorem, in the most general possible form:

Theorem 7.1: In a crystal possessing a center of inversion, a phonon at *any* vector $\mathbf{k}$ and its *time-reverse* phonon (at $-\mathbf{k}$) yield a product representation at $\mathbf{k}=0$ that is even under the operation IF, where I is inversion and F is the combination of Hermitian conjugation with time reversal. Since the electric moment is even under F and odd under I it is forbidden. Magnetic dipole radiation is also forbidden since it is odd under F and even under I. The electric-quadrupole moment, or the polarizability that enters the Raman effect are both even under I and F and are thus allowed.

If a matrix element vanishes because of some symmetry element (or group of elements) the conditions that lead to the vanishing must still be obeyed even if additional group elements are added. Thus at *any* point $\mathbf{k}$, we can see what vanishings are produced by inversion symmetry alone—even if other symmetry operations are available. The proof of our theorem is now a trivial application of our character formula (5.19). The only elements available are the identity, and inversion as an element that exchanges $\mathbf{k}$ and $-\mathbf{k}$ so that (5.19) reduces to

$$N=\tfrac{1}{2}[\chi^m(E)+\chi^m(IF)], \qquad (7.1)$$

where $\chi^m(R)$ is the character under R of the representation m generated by the electric moment, magnetic moment, polarizability tensor, etc. Thus a Hermitian operator will yield a nonvanishing matrix element only if it is even under the combination of inversion and time reversal.

The trivial nature of this proof, as compared to the use of the full-space group, was emphasized by the use of this very example, at the Copenhagen Conference on Lattice Dynamics.[7]

8. FORCE CONSTANTS IN CRYSTALS

The third-neighbor force constants in a diamond structure provide a nontrivial application of our method of the group of the bond. (The first- and second-neighbor force constants have been previously discussed.[18]) If one atom is at the origin, a typical third neighbor can be placed at $(\tfrac{1}{4}a)(-1,-1,-3)$ where a is the edge of the cubic cell. The only symmetry element that leaves this atom invariant is the reflection plane $\varrho_{\bar{x}y}$. (We follow here the notation of Herring[19] and of Lax and Hopfield.[4]) The inversion element $(\mathbf{i}|\boldsymbol{\tau})$ is an element that interchanges the diamond sublattices, i.e., aside from an irrelevant lattice translation, it reverses the bond. So does $(\mathfrak{s}_{2\bar{x}y}|\boldsymbol{\tau})$, the product of $(\mathbf{i}|\boldsymbol{\tau})$ with $\varrho_{\bar{x}y}$. Thus our character formula (4.15) yields

$$N=\tfrac{1}{4}\{[\Phi(\varepsilon)]^2+[\Phi(\varrho)]^2+\Phi(\mathbf{i}^2)+\Phi(\mathfrak{s}_2{}^2)\}$$
$$=\tfrac{1}{4}\{3^2+1^2+3+3\}=4. \qquad (8.1)$$

Indeed, the reflection plane $\varrho_{\bar{x}y}$ requires our quadratic form to be symmetric under the interchange of x and y, i.e., to have the form

$$\begin{bmatrix} \mu & \nu & \delta \\ \nu & \mu & \delta \\ \theta & \theta & \lambda \end{bmatrix} \qquad (8.2)$$

with 5 parameters. We shall show that inversion requires $\delta=\theta$. Indeed, we can show that for any odd-neighbor interaction, the matrix must be symmetric. With the sublattices labeled by $\bar{1}$ and 1, inversion yields the

[13] C. Herring, Phys. Rev. **52**, 361 (1937).

[14] M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955).

[15] E. Burstein, F. A. Johnson, and R. Loudon, Phys. Rev. (to be published).

[16] B. Szigeti, Proc. Roy. Soc. (London) **A252**, 217 (1959).

[17] R. Loudon, Phys. Rev. **137**, 1784 (1965).

[18] See Ref. 1, Secs. 9.3 and 9.4.

[19] C. Herring, J. Franklin Inst. **233**, 525 (1942).

TABLE I. $\Phi(R)$ = character of R in three space for elements of C_{3v}.

R	$\Phi(R)$	$\Phi(R^2)$	$\frac{1}{2}\{[\Phi(R)]^2 + \Phi(R^2)\}\Phi(R)$	n_c
ε	3	3	18	1
$\delta_{3xyz}, \delta_{3xyz}{}^{-1}$	0	0	0	2
$\varrho_{\bar{x}y}, \varrho_{y\bar{z}}, \varrho_{\bar{z}x}$	1	3	2	3

relation

$$K_{\mu\nu}{}^{\bar{1}i1j} = K_{\mu\nu}{}^{1\bar{1}\bar{1}j} = K_{\nu\mu}{}^{\bar{1}j1\bar{1}} \tag{8.3}$$

or

$$K_{\mu\nu}{}^{\bar{1}1}(\mathbf{j}-\mathbf{i}) = K_{\nu\mu}{}^{\bar{1}1}(\mathbf{i}-\mathbf{j}) = K_{\nu\mu}{}^{\bar{1}1}(\mathbf{j}-\mathbf{i}), \tag{8.4}$$

where the second step uses the symmetry of K under F, Eq. (4.10), and Eq. (8.4) utilizes translational invariance. The desired symmetry in $\mu\nu$ has been established.

As a second example, let us consider cubic anharmonic interactions between first neighbors in a diamond structure that are linear in the displacements (u,v,w) of the atom at the origin, and quadratic in the displacements (x,y,z) of the atom at $(\frac{1}{4}a)(1,1,1)$. The group that preserves this bond is the subgroup C_{3v} with threefold axis δ_{3xyz} in the [111] direction, and the three reflection planes $\varrho_{\bar{x}y}$, $\varrho_{\bar{y}z}$, $\varrho_{\bar{z}x}$. The number of independent parameters can be computed immediately with the help of (4.24) and Table I

$$N = \frac{1}{6}[18 \times 1 + 0 \times 2 + 2 \times 3] = 4. \tag{8.5}$$

As is evident in Eq. (4.24) no exchange elements enter, but the symmetry of the quadratic form has been used. It is easy enough to write down cubics that are symmetric, i.e., $xy = yx$ and invariant under the cyclic exchanges δ_{3xyz}, $\delta_{3xyz}{}^{-1}$, and the pair interchanges $\varrho_{\bar{x}y}$, $\varrho_{\bar{y}z}$, $\varrho_{\bar{z}x}$. The result is

$$a(ux^2 + vy^2 + wz^2) + b[u(y^2 + z^2) + v(z^2 + x^2) + w(x^2 + y^2)]$$
$$+ c[(u+v)xy + (v+w)yz + (w+u)zx]$$
$$+ d[uyz + vzx + wxy]. \tag{8.6}$$

Having found four invariants, we can stop.

9. THE FORM OF TENSORS

1. Group of the Indices

Let a tensor $T_{\mu\nu\lambda}\cdots$ be invariant with respect to a group G containing a subgroup H of all elements that simply permute the indices $\mu\nu\lambda\cdots$ (aside from sign). Then all information in H concerning the vanishing of a particular set of elements $T_{\mu\nu\lambda}\cdots$ (fixed $\mu\nu\lambda$, other indices $\cdots$ may vary) is contained in a subgroup of H we shall call the group of the indices,[8] namely, those elements that leave $\mu\nu\lambda$ invariant.

For example, let us consider a third-rank tensor $\sigma_{\mu\nu\lambda}$ invariant under the tetrahedral group T. Does the element σ_{122} vanish? To test this we need only use that subgroup of T that leaves 1 and 2 invariant, namely the group D_2. Under a twofold rotation C_{2y} about the y axis, (one element of D_2), x and z change sign, thus

$\sigma_{122} = -\sigma_{122} = 0$. For an arbitrary element $\sigma_{\mu\nu\lambda}$, C_{2y} tells us that

$$\sigma_{\mu\nu\lambda} = (-1)^{n_1 + n_3}\sigma_{\mu\nu\lambda}, \tag{9.1}$$

where n_1 is the number of 1's and n_3 the number of 3's among $\mu\nu\lambda$. Since $n_1 + n_2 + n_3 = 3$, we can conclude that $\sigma_{\mu\nu\lambda} = 0$ unless 2 appears an odd number of times. The use of C_{2x} tells us that 1 must appear an odd number of times. The use of C_{2z} tells us that 3 must appear an odd number of times. Thus, with respect to D_2 the possible nonvanishing components are $(\sigma_{123}, \sigma_{231}, \sigma_{312})$ and $(\sigma_{213}, \sigma_{321}, \sigma_{132})$. The elements of $T - D_2$ cannot cause any elements to vanish, but the threefold rotations show that the first three constants are equal to one another, and the second three constants are equal to one another.

If $\sigma_{\mu\nu\lambda}$ is known to be symmetric with respect to $\mu\nu$, (as it would be for the piezoelectric tensor) only one independent constant remains. In the presence of such a symmetry, one can use elements that interchange μ and ν to get a vanishing. There are no such elements in T, but for the group 0 we could use the element C_{2xy} that carries xyz into yxz to obtain

$$\sigma_{123} = -\sigma_{213} \tag{9.2}$$

so that $\sigma_{\mu\nu\lambda}$ is necessarily antisymmetric in $\mu\nu$ and the piezoelectric tensor must vanish for the octahedral group 0.

We see then, that when a tensor has known symmetries under interchange of certain indices, the *group of the indices* must be augmented to include the *appropriate exchange elements*.

The number of independent parameters in such tensors can be evaluated by well-known character techniques.[8] We shall therefore illustrate the use of these techniques in the less well-known magnetic tensors.

2. Magnetic Tensors (Odd Under Time Reversal)

Cobalt fluoride (CoF_2), a rutile structure,[20] belongs to space group[21] $D_{4h}{}^{14} = P4_2/mnm$ from the point of view of x-ray crystallography. However, when the antiferromagnetic order[22] displayed in Fig. 1 is taken into account, the fourfold screw axis 4_2 and the mirror plane m_{xy} do not restore the crystal to itself unless the spins are simultaneously reversed, i.e., the complete magnetic space group[23] is $P4_2'/mnm'$ where the prime indicates an ordinary element combined with time reversal. (This group also applies to MnF_2 and FeF_2.) We should like to show that under the corresponding point group, $4'/mmm'$, *piezomagnetism* is allowed.[23]

[20] See, for example, T. Nagamiya, K. Yosida, and R. Kubo, Advan. Phys. 4, 1 (1955) for a discussion of the structure and magnetic properties of iron group fluorides. Also J. Nakamura and H. Taketa, Progr. Theoret. Phys. (Kyoto) 13, 129 (1955).

[21] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers Inc., New York, 1963), Vol. 1.

[22] R. A. Erickson, Phys. Rev. 90, 779 (1953).

[23] I. E. Dzialoshinski, Zh. Eksperim. i Teor. Fiz. 33, 1454 (1958) [English transl.: Soviet Phys.—JETP 6, 1120 (1958)].
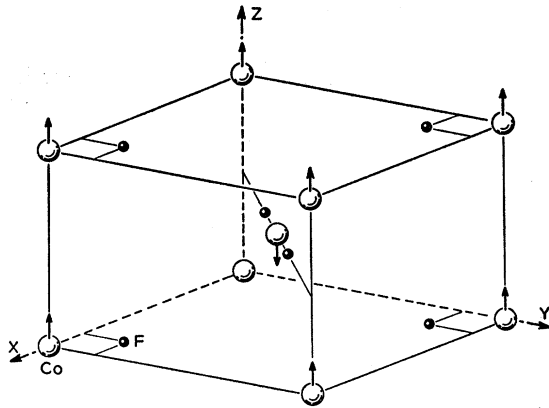
FIGS. 1. The magnetic structure of CoF_2 (and MnF_2, and FeF_2) is displayed. The x-ray structure is tetragonal with principal axis in the z direction. The fluorines (black balls) are nonmagnetic. The cobalt atoms (white balls) have spin up at the vertices of the unit cell, and spin down at the body center. The magnetic fourfold screw axis $4_z'$ is parallel to the z direction through an origin halfway between a pair of equivalent cobalts, e.g., through $(a/2,0,0)$.

Since the piezomagnetic tensor $\epsilon_{\mu\nu\lambda}$ is even under inversion, symmetric in $\mu\nu$ and odd under time reversal, the character generated by an arbitrary element R is

$$\chi(R)=\tfrac{1}{2}\{[\Phi(R_1)]^2$$
$$+\Phi(R_1{}^2)\}\Phi(R_1)[J(R)-J(RQ)], \quad (9.3)$$

where R_1 is the proper rotation that corresponds to R, $J(R)=1$, 0 according as R is or is not an ordinary symmetry element, and Q is one element associated with time reversal, e.g., $4_z=C_{4z}$ in the present example. If we write

$$D_{4h}=D_{2h}+C_{4z}\cdot D_{2h} \quad (9.4)$$

then the last factor $J(R)-J(RQ)$ is plus one for the elements of D_{2h} and minus one for the ("reversal") elements of $C_{4z}\cdot D_{2h}$. Indeed, we can ignore inversion although, since it places no restriction on $\epsilon_{\mu\nu\lambda}$ and consider instead the smaller group

$$D_4=D_2+C_{4z}\cdot D_2, \quad (9.5)$$

where, of course, our formula (9.3) accounts for the fact that the latter elements are to be used with time reversal.

Since $\Phi(R)=-1$ for $R=$ any twofold rotation, the number of independent parameters in $\epsilon_{\mu\nu\lambda}$ is

$$N=\tfrac{1}{8}[\chi(1)+3\chi(2_z)-2\chi(4_z)-2\chi(2_{xy})]$$
$$=\tfrac{1}{8}\times\tfrac{1}{2}\{(9+3)3+3(1+3)(-1)$$
$$-2(1-1)-2(1+3)(-1)\}=2. \quad (9.6)$$

Under D_2 above, we saw that a third-rank tensor symmetric on its first two indices reduces to three independent parameters

$$\epsilon_{123}=\epsilon_{213}, \quad \epsilon_{231}=\epsilon_{321}, \quad \epsilon_{312}=\epsilon_{132}.$$

Under time reversal

$$K\epsilon_{231}=-\epsilon_{231}, \quad (9.7)$$

but time reversal is not a group element in this magnetic material, or else $\epsilon_{\mu\nu\lambda}$ would vanish identically. Thus

$$\epsilon_{231}=4_z{}'\epsilon_{231}=4_zK\epsilon_{231}=-4_z\epsilon_{231}=\epsilon_{132}. \quad (9.8)$$

Thus the three independent parameters are reduced to two.

A recently grown crystal[24] $GaFeO_3$ is unusual in that it is piezoelectric,[24,25] ferrimagnetic[24,26] (specifically, it has a canted antiferromagnetic order) and magneto-electric[26]: an applied electric field generates a magnetic moment, and an applied magnetic field induces an electric polarization. Wood[27] has established the x-ray space group to be $C_{2v}{}^9=Pc2_1n$, and Abrahams, Reddy and Bernstein[28] have established the structure. The space group $Pc2_1n$ is compatible with four possible magnetic space groups: $Pc2_1n$, $Pc2_1'n'$, $Pc'2_1n'$, $Pc'2_1'n$. The first group is ruled out because the point group $C_{2v}=m2m$ (with no magnetic elements) can have no net magnetic moment.[29] Since the net magnetization is along the c axis of the crystal, and such a magnetic vector can exist normal to a mirror plane m, but not normal to m', a mirror plane combined with time reversal, Abrahams and Reddy[30] were able to conclude that the magnetic space group is $Pc'2_1'n$, and the corresponding magnetic point group[31] is $m'2'm$ with elements 1, m_x', $2_y'$, m_z (as deduced by Rado).

Since the magnetoelectric tensor Q_{ij} transforms as E_iH_j, i.e., it is odd under time reversal, and behaves as the product of an ordinary and pseudovector, the character generated by Q_{ij} is

$$\chi(R)=\Phi(R)\Phi(R_1)[J(R)-J(RQ)] \quad (9.9)$$

and the number of independent elements is

$$N=\tfrac{1}{4}[\Phi(1)\Phi(1)+\Phi(m_z)\Phi(2_z)-\Phi(m_x)\Phi(2_x)$$
$$-\Phi(2_y)\Phi(2_y)]$$
$$=\tfrac{1}{4}[3\cdot3+1\cdot(-1)-(1)(-1)-(-1)^2]=2, \quad (9.10)$$

where $J(R)$ has selected the ordinary elements with $+$ sign, and $J(RQ)$ the primed elements with $-$ sign. The symmetry element m_z reverses H_1 and H_2 but not H_3, and thus reduces $Q_{ij}\sim E_iH_j$ to the form

$$\begin{bmatrix} 0 & 0 & Q_{13} \\ 0 & 0 & Q_{23} \\ Q_{31} & Q_{32} & 0 \end{bmatrix} \quad (9.11)$$

[24] J. P. Remeika, J. Appl. Phys. 31, 263S (1960).
[25] D. L. White, Bull. Am. Phys. Soc. 5, 189 (1960).
[26] G. T. Rado, Phys. Rev. Letters 13, 335 (1964); The Proceedings of the International Conference on Magnetism, Nottingham, 1964, Proc. Phys. Soc. Suppl. (to be published).
[27] E. A. Wood, Acta Cryst. 13, 682 (1960).
[28] S. C. Abrahams, J. M. Reddy, and J. E. Bernstein, J. Chem. Phys. (to be published).
[29] See Ref. 1, Sec. 4.2.
[30] S. C. Abrahams, J. M. Reddy, Phys. Rev. Letters 13, 688 (1964).
[31] Rado, Ref. 26 stated his point group as $2'm'm$ but it would have been written $m'2'm$ if the conventional abc order of the operators had been followed.

and $Q_{ij}=m_x{}'Q_{ij}=-m_xQ_{ij}$ yields the condition

$$\begin{bmatrix} 0 & 0 & Q_{13} \\ 0 & 0 & Q_{23} \\ Q_{31} & Q_{32} & 0 \end{bmatrix}$$

$$=-\begin{bmatrix} 0 & 0 & Q_{13} \\ 0 & 0 & -Q_{23} \\ Q_{31} & -Q_{32} & 0 \end{bmatrix}=\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & Q_{23} \\ 0 & Q_{32} & 0 \end{bmatrix} \quad (9.12)$$

leaving the desired two constants. The form of this tensor is in agreement with Rado's experimental results.

For a recent thorough discussion of crystalline tensors, including "magnetic" tensors, the reader is referred to Birss.[32] Magnetic space groups are discussed by Opechowski and Guccione.[33]

3. Tensor Function of a Vector

The conductivity tensor, $\sigma_{\mu\nu}$ of a cubic material is isotropic: $\sigma_{\mu\nu}=\sigma\delta_{\mu\nu}$. This is no longer true if the electric field is strong. In this case, the invariance requirement takes the form

$$\sigma_{\mu\nu}(\mathbf{E})=\sigma_{\mu'\nu'}(\mathbf{R}\cdot\mathbf{E})R_{\mu'\nu}R_{\nu'\nu} \quad (9.13)$$

and the study of $\sigma_{\mu\nu}(\mathbf{E})$ for fixed $\mathbf{E}$ and arbitrary $\mu\nu$ is facilitated by using the *group of the vector* $\mathbf{E}$, namely those rotations for which $\mathbf{R}\cdot\mathbf{E}=\mathbf{E}$. Thus if $\mathbf{E}$ is in the z or 3 direction of a cubic crystal, the appropriate subgroup of O is the group C_{4v} with axis in the z direction, and $\sigma_{\mu\nu}(E_3)$ will have the form of the usual conductivity tensor in a material of tetragonal symmetry namely:

$$\begin{bmatrix} \sigma_{11}(E_3) & 0 & 0 \\ 0 & \sigma_{11}(E_3) & 0 \\ 0 & 0 & \sigma_{33}(E_3) \end{bmatrix}. \quad (9.14)$$

Threefold rotations in O can cause no vanishings, but provide relationships of the form

$$\sigma_{11}(E_1,E_2,E_3)=\sigma_{22}(E_3,E_1,E_2)=\sigma_{33}(E_2,E_3,E_1) \quad (9.15)$$

for an arbitrary $\mathbf{E}=(E_1,E_2,E_3)$, or more specifically

$$\sigma_{11}(0,0,E)=\sigma_{22}(E,0,0)=\sigma_{33}(0,E,0) \quad (9.16)$$

for the case under discussion.

In the presence of strain $\boldsymbol{\varepsilon}$, electric and magnetic fields, we can replace[f] (9.13) by a more general relation

$$\sigma_{\mu\nu}(\boldsymbol{\varepsilon},\mathbf{E},\mathbf{B})=\sigma_{\mu'\nu'}(\mathbf{R}\boldsymbol{\varepsilon}\mathbf{R}^{-1}, \mathbf{R}\cdot\mathbf{E}, \mathbf{R}\cdot\mathbf{B})R_{\mu'\mu}R_{\nu'\nu}. \quad (9.17)$$

Vanishes can then only be produced by rotations such that $\mathbf{R}\boldsymbol{\varepsilon}\mathbf{R}^{-1}=\boldsymbol{\varepsilon}$ (the group of the strain tensor), $\mathbf{R}\cdot\mathbf{E}=\mathbf{E}$, $\mathbf{R}\cdot\mathbf{B}=\mathbf{B}$ simultaneously.

[32] R. R. Birss, Rept. Progr. Phys. 26, 307 (1963).
[33] W. Opechowski and Rosalia Guccione, in *Magnetism*, edited by G. Rado (Academic Press Inc., New York, 1965, to be published), Vol. 2, Part A; and W. Opechowski (to be published).

APPENDIX A: TWO-PHONON ELECTRIC-DIPOLE ABSORPTION

The second-order electric moment $\mathbf{M}$ can be written briefly as a power expansion in the displacements[14] $\mathbf{u}^{\alpha i}$ (of particle α in cell i)

$$\mathbf{M}=\sum \mathbf{C}^{\alpha i\beta j}\mathbf{u}^{\alpha i}\mathbf{u}^{\beta j} \quad (A1)$$

or explicitly as

$$M_\lambda=\sum C_{\mu\nu\lambda}{}^{\alpha i\beta j}u_\mu{}^{\alpha i}u_\nu{}^{\beta j}. \quad (A2)$$

Under the space-group operation $(\mathbf{R}|\mathbf{v})$ we have

$$R\mathbf{M}=\sum \mathbf{C}^{\alpha i\beta j}\mathbf{R}u^{R^{-1}(\alpha i)}\mathbf{R}u^{R^{-1}(\beta j)}$$
$$=\sum \mathbf{C}^{R(\alpha i)R(\beta j)}\mathbf{R}u^{\alpha i}\mathbf{R}u^{\beta j}, \quad (A3)$$

which leads to the condition

$$C_{\mu\nu\lambda}{}^{\alpha i\beta j}=C_{\mu'\nu'\lambda'}{}^{R(\alpha i)R(\beta j)}R_{\mu'\mu}R_{\nu'\nu}R_{\lambda'\lambda}. \quad (A4)$$

If normal coordinates $q_{k,t}$ are introduced by the transformation[1,14]

$$\mathbf{u}^{\alpha i}=N^{-1/2}\sum_{k,t} q_{k,t}\mathbf{b}_t{}^\alpha(k) \exp[i\mathbf{k}\cdot\mathbf{X}^{\alpha i}], \quad (A5)$$

where $\mathbf{X}^{\alpha i}$ is the equilibrium position of particle αi, then the second-order moment takes the form[14]

$$\mathbf{M}=\sum_{t;\,\ell k} q_{k,t'}{}^*q_{k,t}\mathbf{H}_{t't}{}^k, \quad (A6)$$

where

$$H_{t't}{}^k=\sum_{\alpha,\beta} \mathbf{b}_{t'}{}^\alpha(\mathbf{k})^*\cdot\mathbf{S}^{\alpha\beta}(\mathbf{k})\cdot\mathbf{b}_t{}^\beta(\mathbf{k}) \quad (A7)$$

and

$$\mathbf{S}^{\alpha\beta}(\mathbf{k})=\sum_j \mathbf{C}^{\alpha i\beta j} \exp[i\mathbf{k}\cdot(\mathbf{X}^{\beta j}-\mathbf{X}^{\alpha i})]. \quad (A8)$$

The symmetry condition (A4) on C can be translated into a corresponding symmetry condition on $\mathbf{S}(\mathbf{k})$:

$$S_{\mu\nu\lambda}{}^{\alpha\beta}(\mathbf{k})=S_{\mu'\nu'\lambda'}{}^{R(\alpha)R(\beta)}(\mathbf{R}\cdot\mathbf{k})R_{\mu'\mu}R_{\nu'\nu}R_{\lambda'\lambda}. \quad (A9)$$

Applying the inversion operator we obtain

$$S_{\mu\nu\lambda}{}^{\alpha\beta}(\mathbf{k})=-S_{\mu\nu\lambda}{}^{\bar\alpha\bar\beta}(-\mathbf{k})=-S_{\mu\nu\lambda}{}^{\bar\alpha\bar\beta}(\mathbf{k})^*$$
$$=-S_{\nu\mu\lambda}{}^{\bar\beta\bar\alpha}(\mathbf{k}), \quad (A10)$$

where the second step uses complex conjugation (i.e., time reversal) and the last step uses the Hermitian nature of S. The final relationship has thus used the operator IF.

If we choose the phases of our symmetry vectors to obey[1]

$$b_{t\nu}{}^\beta(\mathbf{k})=b_{t\nu}{}^{\bar\beta}(\mathbf{k})^* \quad (A11)$$

(i.e., to be diagonal under IK) and insert (A10) into (A7) we obtain

$$H_{t't\lambda}{}^k=-\sum b_{t\nu}{}^\beta(\mathbf{k})S_{\nu\mu\lambda}{}^{\bar\beta\bar\alpha}(\mathbf{k})b_{t'\mu}{}^\alpha(k)^*$$
$$=-H_{tt'\lambda}{}^k. \quad (A12)$$

Thus $H_{tt}=0$, i.e., the term $q_{k,t}{}^*q_{k,t}$ which creates a phonon at $\mathbf{k}$ and destroys one at $\mathbf{k}$ (or creates one at $-\mathbf{k}$) is absent.