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Group-Theoretical Selection Rules in Inelastic Neutron Scattering within the Rigid-Molecule Model

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The model-independent technique of Elliott and Thorpe (ET) is extended to apply to a class of models in which molecular units undergo translational vibrations with respect to each other and also librations, but in which the internal vibronics of the molecules are neglected. Within the model we find that the ET "structure function" $F^{(\gamma)}(\vec{k})$, associated with irreducible representation γ and momentum transfer $\vec{k}$, can be written in the form $F^{(\gamma)}(\vec{k}) = F^{(\gamma)}(\vec{k}\,|\,R) + F^{(\gamma)}(\vec{k}\,|\,\theta)$, where R and θ signify translational and rotational oscillations. Moreover, the translational part is identical to that of ET except that the atomic scattering lengths a_n which appear in their result are to be replaced by $\vec{k}$-dependent molecular form factors $a_n(\vec{k}')$. $F^{(\gamma)}(\vec{k}\,|\,\theta)$ contains a vector form factor equal to $i\nabla_{\vec{k}} \cdot a_n(\vec{k}')$, where $\vec{k}'$ is related to $\vec{k}$ via a rotation. Mathematically, their result is contained in ours as a special case. Physically, we indicate how to use both procedures in concert, thereby aiding in the identification of γ as well as in separating the internal from external vibrations and among the latter, the translational and rotational parts thereof. At the Brillouin-zone boundary we employ the so-called multiplier representations, thereby achieving a simplification both of our results and theirs. By significantly reducing the number of phonon modes to be considered in complex molecular crystals, we have likewise increased the diagnostic power of this method which requires no detailed knowledge of force constants. It is hoped that our results will receive wide application in the identification of phonons in such crystals.

I. INTRODUCTION AND QUALITATIVE CONCLUSIONS

Several years ago Elliott and Thorpe[1] (ET) introduced an elegant *model-independent* technique to aid in identifying phonon branches group theoretically[2] in inelastic neutron scattering experiments. Despite its potential power, their method has been applied rather sparingly,[3] one reason being perhaps that for sufficiently complex crystals the number of modes is so large that other more or less model-dependent assumptions must be introduced *a posteriori* to help resolve possible ambiguities in the assignments. (Another reason, of course, lies in the fact that only recently have molecular crystals come under intensive experimental study.) It is our purpose here to narrow the field of possibilities considerably while retaining as much as possible the generality of their approach. We do so by extending their analysis to apply to the well-known rigid-molecule model within which the internal degrees of freedom of each molecular unit are neglected.[4] Within this model or, better, *class* of models, our procedure is completely general in that details regarding force constants, etc., are left wholly unspecified, as in the original ET work.

As will be seen, the extension of their analysis to the rigid-molecule model involves the resolution of several points of principle, notably, ascertaining the correct transformation properties of the polarization "vectors" $\xi_\lambda^{\vec{\alpha}j}(\vec{\rho}_n\,|\,\theta)$ appearing in the normal-mode expansion of the (moment-of-inertia weighted) angular displacements about the principal axes of inertia in equilibrium. Neither the $\xi_\lambda^{\vec{\alpha}j}(\vec{\rho}_n\,|\,\theta)$ nor the weighted nor unweighted angular displacements mentioned above have simple transformation properties such as possessed by vector or axial-vector fields. Rather, one must revert to a more general set of coordinates which qualify

as simple-vector and axial-vector displacement fields, but in terms of which even the kinetic-energy term in the small vibration Lagrangian has nondiagonal parts in the angular velocity components. This competition between achieving simplicity in the transformation properties and ease in solving the dynamics results in considerable computational complexity. Nevertheless, when carried through to completion, the results are amazingly simple: The ET structure function $F^{(r)}(\vec{k})$, associated (in our notation) with irreducible representation r and momentum transfer $\vec{k}$, consists of two additive terms,

$$F^{(r)}(\vec{k}) = F^{(r)}(\vec{k}\,|\,R) + F^{(r)}(\vec{k}\,|\,\theta) \ . \tag{1}$$

$F^{(r)}(\vec{k}\,|\,R)$ is associated with translations of the molecular center of mass (c.m.) and $F^{(r)}(\vec{k}\,|\,\theta)$, with rotations about the c.m. Either or both may or may not contain contributions to the differential cross section $d\sigma/d\Omega$ at fixed $\vec{k}$, r, and ω, the energy ($\hbar = 1$) of the emitted or absorbed phonon. Moreover, the translational term is identical in form with the result of ET except that their (mass and Debye–Waller-factor weighted) Fermi scattering length $\bar{a}_n$ for a point molecule is to be replaced with a $\vec{k}$-dependent molecular form factor $\bar{a}_n(\alpha^{-1}\vec{k})$, where

$$\bar{a}_n(\vec{k}) = \sum_i \bar{a}_{ni}\, e^{-i\vec{k}\cdot\vec{b}(n,i)} \ , \tag{2}$$

and where α is the rotational part of the Seitz operator $(\alpha\,|\,\vec{a}) = (\alpha\,|\,\vec{v}_\alpha + \vec{t})$. [Here, $\vec{b}(n, i)$ is the position relative to the molecular c.m. of the ith atomic nucleus in the nth molecule in the unit cell, $\bar{a}_{ni}$ is its corresponding Fermi scattering length (again weighted by a Debye–Waller factor and the *molecular* mass), and $\vec{a}$ is a translation, composed of a fractional ($\vec{v}_\alpha$) and full ($\vec{t}$) lattice translation.] The rotational term $F^{(r)}(\vec{k}\,|\,\theta)$ contains multiplicatively a *vector* form factor $\vec{h}(n, \alpha^{-1}\vec{k})$, where

$$\vec{h}(n, \vec{k}) = i\vec{\nabla}_{\vec{k}}\bar{a}_n(\vec{k}) \ . \tag{3}$$

We remark that our result contains the ET result as a special case for point molecules (atoms) as may be seen from Eq. (2), where the sum on i is to be restricted to a single term ($i = 1$) for which $\vec{b}(n, i) = 0$, whence $\bar{a}_n(\vec{k}) = \bar{a}_{n1}$. The absence of $F^{(r)}(\vec{k}\,|\,\theta)$ follows from Eq. (3) and the fact that $\bar{a}_n(\vec{k})$ does *not* depend on $\vec{k}$ for this special case.

Moreover, our analysis simplifies the treatment of Brillouin-zone boundary effects by avoiding use of the Herring factor group $G^{\vec{q}}/T^{\vec{q}}$ employed by ET. By utilizing the so-called "multiplier" (pseudo-) representations $\tau^{(r)}(\alpha)$ cataloged by Kovalev,[5] we are able to give a unified treatment of the zone boundary and interior. $\{G^{\vec{q}}$ is the little group of the reduced wave vector $\vec{q}$ associated with the momentum transfer $\vec{k}$ via

$$\vec{k} = \vec{q} + \vec{K} \ , \tag{4}$$

where $\vec{K}$ is a principal vector of the reciprocal lattice. In the zone interior the irreducible representation (IR) $D^{(\vec{q}r)}[(\alpha\,|\,\vec{a})]$ of the little group may be written

$$D^{(\vec{q}r)}[(\alpha\,|\,\vec{a})] = e^{-i\vec{q}\cdot\vec{a}} d^{(r)}(\alpha) \ , \tag{5}$$

where $d^{(r)}(\alpha)$ is the rth IR of the point group $G_0^{\vec{q}}$ associated with $G^{\vec{q}}$. At the zone boundary,

$$D^{(\vec{q}r)}[(\alpha\,|\,\vec{a})] = e^{-i\vec{q}\cdot\vec{a}} \tau^{(r)}(\alpha) \ , \tag{6}$$

where $\tau^{(r)}(\alpha)$ is the rth "multiplier representation."} Since our result contains that of ET as a special case, this aspect of our work represents a simplication of their method as applied to their original problem.

We stress that, excepting the modification just noted, our solution for the rigid-molecule model class and its application are not intended to supplant the *exact* individual-atom selection rules of Ref. 1. Whereas our solution for the rigid-molecule model is itself exact and therefore contains the earlier work mathematically as a special case in the way discussed above, *physically*, of course, *the model is itself an approximation*, the precision of which depends upon the degree to which the internal vibronics of a molecule are decoupled from its external cooperative motions. Thus, instead of replacing Ref. 1, our results are to be used *in conjunction with* those contained there to answer the following: (a) Which IR, r contributes to scattering with momentum transfer $\vec{k}$? (b) Is the mode associated predominantly with external or internal molecular motion? (c) Is the contribution from the external mode ($\vec{q}r$) translational, rotational, or both? We give an example of employing both techniques in concert: If, for a given r and $\vec{k}$, $F^{(r)}(\vec{k}) = 0$ in the rigid-molecule approximation, whereas in the individual-atom treatment $F^{(r)}(\vec{k}) \neq 0$, then we conclude that the contribution to $d\sigma/d\Omega$ comes mainly from internal molecular vibrations, generally expected to contribute strongly to neutron scattering *only from relatively high-energy modes* and only weakly, if at all, to scattering from low-energy modes.

We close the present discussion with an explanation of the remaining undefined symbols in the polarization "vector" $\xi_\lambda^{\vec{q}j}(\vec{\rho}_n\,|\,\theta)$ introduced earlier. The quantity $\vec{\rho}_n$ denotes the equilibrium position of the c.m. of the nth molecule relative to cell position $\vec{L}$, i.e.,

$$\vec{x}_{Ln} = \vec{L} + \vec{\rho}_n \ , \tag{7}$$

where $\vec{x}_{Ln}$ is the equilibrium position of the c.m. of the nth molecule in the Lth cell relative to an arbitrary origin. The subscript $\lambda (= 1, 2, 3)$ specifies

a Cartesian coordinate and j labels the mode associated with the frequency $\omega_{\vec{q}j}$. The symbol j denotes a composite entity

$$j=(r,\ \mu,\ \gamma)\ , \tag{8}$$

where μ denotes the row of the rth IR and γ is a "principal quantum number" used to label distinct solutions of the dynamical problem belonging to the same r and μ.

In Sec. II we briefly state the basic notions introduced by ET and (in our notation) give their fundamental result, incorporating the modifications introduced by utilizing Eqs. (5) and (6). Section III contains the derivation of our main results for the rigid-molecule model. Section IV is a summary and outlook.

II. ELLIOTT-THORPE METHOD

The inelastic neutron scattering amplitude is calculated in Born approximation with the Fermi potential[6]

$$V_F(\vec{x})=\frac{2\pi}{m}\sum_{Ln} a_n\delta[\vec{x}-(\vec{x}_{Ln}+\vec{u}_{Ln})]\ , \tag{9}$$

where the λth component of the displacement $\vec{u}_{Ln}$ is given by the expression

$$u_\lambda(\vec{x}_{Ln})=\sum_{\vec{q}j}[2\omega_{\vec{q}j}M(n)N]^{-1/2} \times[a_{\vec{q}j}e^{i\vec{q}\cdot\vec{L}}\,\xi_\lambda^{\vec{q}j}(\vec{\rho}_n)+\text{H. c.}]\ . \tag{10}$$

The usual expansion to first order in the exponent of the quantity $\exp[-i\vec{k}\cdot\vec{u}(\vec{x}_{Ln})]$, which occurs along the way, is made and, accounting for the kinematics in standard fashion, one obtains for the differential cross section

$$\frac{d\sigma(\vec{k},r,\gamma)}{d\Omega}=N\bar{\rho}(\vec{k},r,\gamma)\sum_{\mu=1}^{l_r}|\vec{k}\cdot\vec{g}^{\,j}(\vec{k})|^2 \times\begin{cases} n_{\vec{q}j}+1 & \text{phonon emission}\\ n_{\vec{q}j} & \text{phonon absorption}\end{cases}\ . \tag{11}$$

Of the undefined quantities above, m is the neutron mass; $\vec{x}$ its position; a_n the unweighted scattering length of atom n; $M(n)$ the atomic mass; N the number of unit cells; $a_{\vec{q}j}$ the annihilation operator for the phonon mode $(\vec{q}j)$; $n_{\vec{q}j}$ its average occupation number; l_r the dimension of the $(\vec{q}r)$th IR of $G^{\vec{q}}$; and the quantities $\bar{\rho}$ and $\vec{g}^{\,j}(\vec{k})$ are given below:

$$\bar{\rho}(\vec{k},r,\gamma)=|\vec{p}_f/\vec{p}_i|\{(2\omega_{\vec{q}r\gamma})[1\pm(m/|\vec{p}_f|^2)\vec{p}_f\cdot\vec{\nabla}_{\vec{q}}\omega]\}^{-1}\ , \tag{12}$$

where $\vec{p}_i$ and $\vec{p}_f$ are the initial- and final-neutron momenta,

$$\vec{k}=\vec{p}_f-\vec{p}_i\ , \tag{13}$$

and $\vec{k}$ and $\vec{q}$ are related via Eq. (4). The λth component of the important quantity $\vec{g}^{\,j}(\vec{k})$ is

$$g_\lambda^{r\mu\gamma}(\vec{k})=\sum_n \bar{a}_n e^{-i\vec{k}\cdot\vec{\rho}_n}\,\xi^{\vec{q}r\mu\gamma}(\vec{\rho}_n)\ , \tag{14}$$

where

$$\bar{a}_n=a_n[M(n)]^{-1/2}\times(\text{Debye–Waller factor}). \tag{15}$$

The above is fairly standard but is included for reference in Sec. III as well as here. At this point ET introduced two essential ideas. *First*, they considered the "structure function" $F^{(r)}(\vec{k})$ discussed in the Introduction,

$$F^{(r)}(\vec{k})=\sum_\gamma\sum_{\mu=1}^{l_r}|\vec{k}\cdot\vec{g}^{\,j}(\vec{k})|^2\ . \tag{16}$$

Comparison of Eqs. (11) and (16) together with the positivity of the summands shows that the vanishing of $F^{(r)}(\vec{k})$ implies the vanishing of $d\sigma(\vec{k}r\gamma)/d\Omega$ for all γ (provided $\bar{\rho}$ is finite). Therefore, since $F^{(r)}(\vec{k})$ is *model independent*, it can be used to make general predictions concerning $d\sigma/d\Omega$ at fixed r and $\vec{k}$ for *all* γ [barring an accidental vanishing of $d\sigma/d\Omega$ for some particular γ when $F^{(r)}(\vec{k})$ is finite]. Utilizing the completeness relation,

$$\sum_j \xi_{\lambda_1}^{\vec{q}j}(\vec{\rho}_{n_1})\xi_{\lambda_2}^{\vec{q}j*}(\vec{\rho}_{n_2})=\delta_{n_1n_2}\delta_{\lambda_1\lambda_2}\ , \tag{17}$$

they derived the sum rule

$$\sum_r F^{(r)}(\vec{k})=(\vec{k}^2)\sum_n|\bar{a}_n|^2\ . \tag{18}$$

Their *second* basic idea is as follows: One would like to use the completeness relation (17) to decide whether or not $F^{(r)}(\vec{k})$ vanishes using Eqs. (11), (14), and (16). However, of the sum on r, μ, and γ implied by the sum on j in Eq. (17), the sum on r is missing in Eq. (16). Therefore they artificially introduced a sum on r_1 by invoking a projection operator $P^{(\vec{q}r)}$. Thus, for the quantity $\xi_\lambda^{\vec{q}r\mu\gamma}(\vec{\rho}_n)$ appearing in Eq. (14) we may write[7]

$$\xi_\lambda^{\vec{q}r\mu\gamma}(\vec{\rho}_n)=\sum_{r_1}P^{(\vec{q}r)}\xi_\lambda^{\vec{q}r_1\mu\gamma}(\vec{\rho}_n) \tag{19}$$

and then employ the completeness relations. Omitting all details, we give the results

$$F^{(r)}(\vec{k})=\sum_{\lambda_1\lambda_2}k_{\lambda_1}B_{\lambda_1\lambda_2}(\vec{k},r)k_{\lambda_2}\ , \tag{20}$$

where the matrix $B(\vec{k},r)$ is defined by the expression

$$B(\vec{k},r)=\sum_n A(n,\vec{k},r)A^\dagger(n,\vec{k},r)\ . \tag{21}$$

In the *zone interior* the matrix $A(n,\vec{k},r)$ is given by the relation

$$A(n,\vec{k},r)=\frac{l_r}{h_0}\sum_\alpha\chi_d^{(r)*}(\alpha)\,e^{-i\vec{k}\cdot(\alpha\vec{\rho}_n+\vec{v}_\alpha)}\,\bar{a}_n\alpha\ , \tag{22}$$

where the sum extends over all matrices α in $G_0^{\vec{q}}$, h_0 is the order of $G_0^{\vec{q}}$, and $\chi_d^{(r)}=\text{tr}\,[d^{(r)}(\alpha)]$. At the *zone boundary*

$$A(n,\vec{k},r)=\frac{l_r}{h_0}\sum_\alpha \chi_\tau^{(r)*}(\alpha)$$

$$\times\exp[-i\vec{K}\cdot(\alpha\vec{\rho}_n+\vec{v}_\alpha)-i\vec{K}(\vec{q},\alpha)\cdot\vec{\rho}_n]\bar{a}_n\alpha\ , \quad (23)$$

where $\chi_\tau^{(r)}(\alpha)=\mathrm{tr}[\tau^{(r)}(\alpha)]$ and the principal lattice vector $\vec{K}(\vec{q},\alpha)$ is defined by the relation

$$\alpha^{-1}\vec{q}=\vec{q}+\vec{K}(\vec{q},\alpha)\ , \quad \alpha \text{ in } G_0^{\vec{q}}\ . \quad (24)$$

In the *zone interior* $\vec{K}(\vec{q},\alpha)=0$, $\tau^{(r)}(\alpha)$ reduces to $d^{(r)}(\alpha)$ [cf. Eqs. (5) and (6)] and Eq. (23) reduces to Eq. (22), as it must.

As discussed in Ref. 7, the treatment of the projection operators in our Eq. (19) differs from that of ET.[1] Nevertheless, their results are in agreement with our Eqs. (20)–(23). Moreover, their two basic ideas, discussed above, will be carried over in our extension to the rigid-molecule model in Sec. III.

III. RIGID-MOLECULE MODEL

Our discussion here centers in three areas, (A) the dynamics, (B) transformation properties of the weighted coordinates, and (C) application of the projection operators to obtain an expression for $F^{(r)}(\vec{k})$.

A. Dynamics

The Lagrangian $\mathfrak{L}=T-V$ is expressed in terms of the displacements $X_{Ln\lambda}$ of the c.m. and rotations $\theta_{Ln\lambda}$ about the c.m. of the nth molecule in the cell at $\vec{L}$. With regard to X, the component index λ refers to an arbitrary Cartesian coordinate frame fixed with respect to the crystal axes, whereas with respect to θ, λ refers to a component along the equilibrium principal axes of inertia of the nth molecule. The kinetic energy T is

$$T=\sum_{Ln\lambda}[\tfrac{1}{2}M(n)\dot{X}_{Ln\lambda}^2+\tfrac{1}{2}I(n,\lambda)\dot{\theta}_{Ln\lambda}^2]\ , \quad (25)$$

where $I(n,\lambda)$ is the λth principal moment of inertia of molecule n. The expression for the potential energy V can be simplified considerably by introducing the dichotomous variable χ, where $\chi=R$ or θ, and the composite symbol Λ:

$$\Lambda=(n,\chi,\lambda)\ , \quad \chi=R \text{ or } \theta\ . \quad (26)$$

The general coordinate $X_{L\Lambda}$ satisfies

$$X_{L\Lambda}=\begin{cases}X_{Ln\lambda}\ , & \chi=R\\ \theta_{Ln\lambda}\ , & \chi=\theta\end{cases}\ . \quad (27)$$

In terms of the force constants $\bar{C}_{\Lambda\Lambda'}(L,L')$,

$$V=\tfrac{1}{2}\sum_{LL'}\sum_{\Lambda\Lambda'}X_{L\Lambda}\bar{C}_{\Lambda\Lambda'}(\vec{L}-\vec{L}')X_{L'\Lambda'}\ . \quad (28)$$

Letting

$$B(\Lambda)=\begin{cases}M(n)\ , & \chi=R\\ I(n,\lambda)\ , & \chi=\theta\end{cases} \quad (29)$$

we may write

$$T=\tfrac{1}{2}\sum_{L\Lambda}B(\Lambda)\dot{X}_{L\Lambda}^2\ . \quad (30)$$

Introducing weighted coordinates

$$Y_{L\Lambda}=[B(\Lambda)]^{1/2}X_{L\Lambda} \quad (31)$$

and force constants

$$C_{\Lambda\Lambda'}(\vec{L}-\vec{L}')=[B(\Lambda)B(\Lambda')]^{-1/2}\bar{C}_{\Lambda\Lambda'}(\vec{L}-\vec{L}')\ , \quad (32)$$

we have

$$T=\tfrac{1}{2}\sum_{L\Lambda}\dot{Y}_{L\Lambda}^2 \quad (33)$$

and

$$V=\tfrac{1}{2}\sum_{LL'}\sum_{\Lambda\Lambda'}Y_{L\Lambda}C_{\Lambda\Lambda'}(\vec{L}-\vec{L}')Y_{L'\Lambda'}\ . \quad (34)$$

Proceeding now in standard fashion, the coordinates $Y_{L\Lambda}$ can be expanded in terms of quantized normal modes

$$Y_{L\Lambda}=\sum_{\vec{q}j}(2\omega_{\vec{q}j})^{-1/2}(a_{\vec{q}j}\Phi_{L\Lambda}^{\vec{q}j}+a_{\vec{q}j}^\dagger\Phi_{L\Lambda}^{\vec{q}j*})\ , \quad (35)$$

where

$$\Phi_{L\Lambda}^{\vec{q}j}=N^{-1/2}e^{i\vec{q}\cdot\vec{L}}\xi_\Lambda^{\vec{q}j}\ . \quad (36)$$

The normal modes $\Phi_{L\Lambda}^{\vec{q}j}$ and polarization "vectors" $\xi_\Lambda^{\vec{q}j}$ satisfy

$$\sum_{L'\Lambda'}C_{\Lambda\Lambda'}(\vec{L}-\vec{L}')\Phi_{L'\Lambda'}^{\vec{q}j}=\omega_{\vec{q}j}^2\Phi_{L\Lambda}^{\vec{q}j} \quad (37)$$

and

$$\sum_{\Lambda'}C_{\Lambda\Lambda'}(\vec{q})\xi_{\Lambda'}^{\vec{q}j}=\omega_{\vec{q}j}^2\xi_\Lambda^{\vec{q}j}\ , \quad (38)$$

where

$$C_{\Lambda\Lambda'}(\vec{q})=\sum_{L'}C_{\Lambda\Lambda'}(\vec{L}-\vec{L}')e^{-i\vec{q}\cdot(\vec{L}-\vec{L}')}\ . \quad (39)$$

The matrix $C(\vec{q})$ is Hermitian, $\xi^{\vec{q}j*}=\xi^{-\vec{q}j}$, and the following normalization and completeness relations are satisfied:

$$\sum_{L\Lambda}\Phi_{L\Lambda}^{\vec{q}j*}\Phi_{L\Lambda}^{\vec{q}'j'}=\delta_{\vec{q}\vec{q}'}\sum_\Lambda\xi_\Lambda^{\vec{q}j*}\xi_\Lambda^{\vec{q}j'}=\delta_{\vec{q}\vec{q}'}\delta_{jj'}\ , \quad (40a)$$

$$\sum_{\vec{q}j}\Phi_{L\Lambda}^{\vec{q}j}\Phi_{L'\Lambda'}^{\vec{q}j*}=\delta_{\vec{L}\vec{L}'}\sum_j\xi_\Lambda^{\vec{q}j}\xi_{\Lambda'}^{\vec{q}j*}=\delta_{\vec{L}\vec{L}'}\delta_{\Lambda\Lambda'}\ . \quad (40b)$$

B. Transformation Properties

Looking ahead, the displacements $\vec{u}_{Lni}$ from equilibrium of each atomic nucleus will have to be expressed in terms of the generalized displacements $Y_{L\Lambda}$ since, by Eq. (35), the $Y_{L\Lambda}$ contain the annihilation and creation operators $a_{\vec{q}j}$ and $a_{\vec{q}j}^\dagger$ which contribute to the neutron-phonon scattering matrix. As in Sec. II, we shall want to apply projection operators to the $\xi_\Lambda^{\vec{q}j}$, whence its transformation properties must be determined. However, as remarked in the Introduction, for $\chi=\theta$, the transformation properties of $X_{L\Lambda}$, i.e., of $\theta_{Ln\lambda}$, are *not simple*, owing to the fact that these angular dis-

placements are *by definition* associated with a special set of axes, namely, the principal axes of the inertial ellipsoid.[8] We introduce in place of $X_{L\Lambda}$ or $Y_{L\Lambda}$ yet another set of displacements, $W_{L\Lambda}$, which transform as simple-vector and axial-vector fields for $\chi = R$ and θ, respectively. Then, working through the sequence

$$W \to X \to Y \to \Phi^{\vec{q}j} \to \xi^{\vec{q}j} , \tag{41}$$

we ultimately deduce the requisite transformation properties of the $\xi^{\vec{q}j}_{\Lambda}$.

The coordinates $W_{L\Lambda}$ are defined as follows:

$$W_{L\Lambda} = \begin{cases} X_{Ln\lambda} = X_{L\Lambda} , & \chi = R \\ \Theta_{Ln\lambda} , & \chi = \theta . \end{cases} \tag{42}$$

Thus, for $\chi = R$, $W_{L\Lambda} = X_{L\Lambda}$. However, for $\chi = \theta$, they are different in that $\vec{\Theta}_{Ln}$ describes the rotation of the molecule about its c.m. with respect to an *arbitrary* set of axes (which we select as coincident with that describing $\vec{X}_{Ln}$). Hence, unlike $\theta_{Ln\lambda}$, the components $\Theta_{Ln\lambda}$, i.e., $\Theta_\lambda(\vec{x}_{Ln})$, transform *simply* as *axial-vector fields* just as the components $X_{Ln\lambda}$, i.e., $X_\lambda(\vec{x}_{Ln})$, transform as vector fields.

The kinetic energy becomes

$$T = \tfrac{1}{2}\sum_{Ln} M(n)\dot{X}_\lambda(\vec{x}_A)\dot{X}_\lambda(\vec{x}_A) + \tfrac{1}{2}\sum_{Ln} \dot{\Theta}_\rho(\vec{x}_A) I_{\rho\nu}(n)\dot{\Theta}_\nu(\vec{x}_A) , \tag{43}$$

where in place of the composite $\Lambda = (n, \chi, \lambda)$ we have introduced a new composite $A = (L, n)$, and we invoke the *Einstein summation convention* with respect to *repeated Cartesian subscripts only*. Rewriting Eq. (25) in this notation,

$$T = \tfrac{1}{2}\sum_{Ln} M(n)\dot{X}_\lambda(\vec{x}_A)\dot{X}_\lambda(\vec{x}_A) + \tfrac{1}{2}\sum_{Ln} I(n, \lambda)\dot{\theta}_\lambda(\vec{x}_A)\dot{\theta}_\lambda(\vec{x}_A) , \tag{25'}$$

and comparing with Eq. (43) we obtain the desired relationship between Θ_λ and θ_λ:

$$\Theta_\rho(\vec{x}_A) = R_{\rho\lambda}(n)\theta_\lambda(\vec{x}_A) , \tag{44}$$

where

$$R_{\rho\lambda}(n) I_{\rho\nu}(n) R_{\nu\omega}(n) = I(n, \lambda)\delta_{\lambda\omega} . \tag{45}$$

We see that $\Theta_\rho(\vec{x}_A)$ and $\theta_\lambda(\vec{x}_A)$ are related by the matrix $R(n)$ which diagonalizes the moment-of-inertia tensor $I_{\rho\nu}(n)$.

We turn now to a consideration of the explicit transformation properties of the fields $W_\lambda(\vec{x}_A \mid \chi)$, $X_\lambda(\vec{x}_A \mid \chi)$, and $Y_\lambda(\vec{x}_A \mid \chi)$ under the Wigner operators $O_{(\alpha \mid \vec{a})}$:

$$O_{(\alpha \mid \vec{a})} X_\lambda(\vec{x}_A) = X'_\lambda(\vec{x}_A) = \alpha_{\lambda\nu} X_\nu(\vec{x}''_A) , \tag{46a}$$

$$O_{(\alpha \mid \vec{a})} \Theta_\lambda(\vec{x}_A) = \Theta'_\lambda(\vec{x}_A) = \alpha^P_{\lambda\nu} \Theta_\nu(\vec{x}''_A) , \tag{46b}$$

where the superscript P denotes *proper* rotation and

$$\vec{x}''_A = (\alpha^{-1}\vec{x}_A - \alpha^{-1}\vec{a}) . \tag{47}$$

$\vec{\Theta}(\vec{x}_A)$ is the appropriate angular displacement in terms of which to express the individual atomic displacements $\vec{u}_{Lni} = \vec{u}(\vec{x}_{Ai})$. That is,

$$\vec{u}(\vec{x}_{Ai}) = \vec{X}(\vec{x}_A) + \vec{\Theta}(\vec{x}_A) \times \vec{b}(n, i) . \tag{48}$$

To compute $O_{(\alpha \mid \vec{a})}\theta_\lambda(\vec{x}_A)$ we invoke Eqs. (44) and (46b) to write

$$\Theta'_\lambda(\vec{x}_A) = \alpha^P_{\lambda\nu} R_{\nu\mu}(n'')\theta_\mu(\vec{x}''_A) , \tag{49}$$

when n'' is defined by Eq. (47) and the relations

$$\vec{x}_A = \vec{L} + \vec{\rho}_n , \tag{50a}$$

$$\vec{x}''_A = \vec{L}'' + \vec{\rho}_{n''} = \vec{x}_{A''} . \tag{50b}$$

But the new functions of the old variables, $\Theta'_\lambda(\vec{x}_A)$ and $\theta'_\lambda(\vec{x}_A)$, must also satisfy Eq. (44), i.e.,

$$\Theta'_\lambda(\vec{x}_A) = R_{\lambda\omega}(n)\theta'_\omega(\vec{x}_A) . \tag{44'}$$

Combining Eq. (49) with Eq. (44'), we obtain

$$O_{(\alpha \mid \vec{a})}\theta_\eta(\vec{x}_A) = \theta'_\eta(\vec{x}_A) = R^{-1}_{\eta\lambda}(n)\alpha^P_{\lambda\nu}R_{\nu\mu}(n'')\theta_\mu(\vec{x}_{A''}) , \tag{51}$$

where

$$R^{-1}_{\eta\lambda}(n) = R_{\lambda\eta}(n) . \tag{52}$$

Equations (46a) and (51) exhibit the transformation properties of the X variables in the sequence (41). From the defining relations (29) and (31), we may proceed down the chain, obtaining in similar fashion

$$O_{(\alpha \mid \vec{a})} Y_\lambda(\vec{x}_A \mid R) = Y'_\lambda(\vec{x}_A \mid R) = \alpha_{\lambda\omega} Y_\omega(\vec{x}_{A''} \mid R) \tag{53}$$

and

$$Y'_\lambda(\vec{x}_A \mid \theta) = \Gamma_{\lambda\omega}(n, \alpha) Y_\omega(\vec{x}_{A''} \mid \theta) , \tag{54}$$

where

$$\Gamma_{\lambda\omega}(n, \alpha) = \left(\frac{I(n, \lambda)}{I(n'', \omega)}\right)^{1/2} R^{-1}_{\lambda\eta}(n)\alpha^P_{\eta\nu}R_{\nu\omega}(n'') . \tag{55}$$

The next link is trivial since the normal modes $\Phi^{\vec{q}j}_\lambda(\vec{x}_A \mid \chi)$ transform identically with the $Y_\lambda(\vec{x}_A \mid \chi)$ as may be seen from the expansion (35) reinterpreted in the new notation.

Finally, using the defining relation (36) and noting that in the zeroth cell

$$\vec{\rho}_n = \vec{x}_A , \quad \vec{L} = 0 , \tag{56}$$

we obtain the transformation properties of the polarization "vectors" $\xi_\lambda(\vec{\rho}_n \mid \chi)$. The results are

$$O_{(\alpha \mid \vec{a})}\xi^{\vec{q}j}_\lambda(\vec{\rho}_n \mid R) = \xi'^{\vec{q}j}_\lambda(\vec{\rho}_n \mid R) = e^{i\vec{q}\cdot\vec{L}''}\alpha_{\lambda\omega}\xi^{\vec{q}j}_\omega(\vec{\rho}_{n''} \mid R) \tag{57}$$

and

$$O_{(\alpha \mid \vec{a})}\xi^{\vec{q}j}_\xi(\vec{\rho}_n \mid \theta) = \xi'^{\vec{q}j}_\xi(\vec{\rho}_n \mid \theta) = e^{i\vec{q}\cdot\vec{L}''}\Gamma_{\xi s}(n, \alpha)\xi^{\vec{q}j}_s(\vec{\rho}_{n''} \mid \theta) , \tag{58}$$

where

$$\alpha^{-1}\vec{\rho}_n - \alpha^{-1}\vec{a} = \vec{L}'' + \vec{\rho}_{n''} \ . \tag{59}$$

We also have

$$O_{(\alpha|\vec{a})}\Phi_\lambda^{\vec{q}r\mu\gamma}(\vec{x}_A|\chi) = \sum_{\mu'} D_{\mu'\mu}^{(\vec{q}r)}[(\alpha|\vec{a})]\,\Phi_\lambda^{\vec{q}r\mu'\gamma} \ , \tag{60}$$

where, as noted earlier, $D^{(\vec{q}r)}$ is an IR of $G^{\vec{q}}$. Furthermore, setting $\vec{L}=0$ in Eq. (36),

$$\Phi_\lambda^{\vec{q}j}(\vec{x}_A|\chi) = N^{-1/2}\,\xi_\lambda^{\vec{q}j}(\vec{\rho}_n|\chi) \ , \quad \vec{L}=0 \ . \tag{61}$$

It follows that the $\xi_\lambda^{\vec{q}j}(\vec{\rho}_n|\chi)$ also satisfy Eq. (60). That is, it is the $\xi_\lambda^{\vec{q}j}(\vec{\rho}_n|\chi)$ which transform irreducibly under the group operators $O_{(\alpha|\vec{a})}$ and not, as discussed in Ref. 7, the quantities $g_\lambda^j(\vec{k})$. Therefore, in deriving $F^{(r)}(\vec{k})$ for the rigid-molecule model, we shall apply the projection operator $P^{(\vec{q}j)}$ to $\xi_\lambda^{\vec{q}j}(\vec{\rho}_n|\chi)$, obtaining as the generalization of our Eq. (19)

$$\xi_\lambda^{\vec{q}r\mu\gamma}(\vec{\rho}_n|\chi) = \sum_{r_1} P^{(\vec{q}r)}\xi_\lambda^{\vec{q}r_1\mu\gamma}(\vec{\rho}_n|\chi) \ , \tag{62}$$

where the projection operator is given by the expression

$$P^{(\vec{q}r)} = \frac{l_r}{h}\sum_{(\alpha|\vec{a})}\chi_D^{(\vec{q}r)*}[(\alpha|\vec{a})]O_{(\alpha|\vec{a})} \ . \tag{63}$$

Here h is the order of the little group $G^{\vec{q}}$, i.e., $h = Nh_0$, $\chi_D^{(\vec{q}r)} = \mathrm{tr}\,(D^{(\vec{q}r)})$, and the sum extends over all $(\alpha|\vec{a})$ in $G^{\vec{q}}$.

Relations (57)–(59), together with Eq. (55) defining $\Gamma_{\lambda\omega}(n,\alpha)$, are necessary in applying (62) and (63) to obtain $F^{(r)}(\vec{k})$, as we shall now do.

C. Computation of $F^{(r)}(\vec{k})$

Here we employ the results of Secs. III A and III B to generalize the calculation in Sec. II. In place of Eq. (9) we have for the Fermi potential

$$V_F(\vec{x}) = \frac{2\pi}{m}\sum_{Ai} a_{ni}\delta[\vec{x} - (\vec{x}_{Ai} + \vec{u}_{Ai})] \ , \tag{64}$$

where $\vec{u}_{Ai} = \vec{u}(\vec{x}_{Ai})$ and is given by Eq. (48), which we rewrite here in component form in terms of the Levi-Civita symbol $\epsilon_{\lambda\mu\nu}$,

$$u_\lambda(\vec{x}_{Ai}) = X_\lambda(\vec{x}_A) + \epsilon_{\lambda\mu\nu}\Theta_\mu(\vec{x}_A)b_\nu(n,i) \ . \tag{48'}$$

From relations (27), (29), (31), and (44), Eq. (48′) becomes

$$u_\lambda(\vec{x}_{Ai}) = [M(n)]^{-1/2}Y_\lambda(\vec{x}_A|R) + \epsilon_{\lambda\mu\nu}[I(n,\eta)]^{-1/2}R_{\mu\eta}(n)\,Y_\eta(\vec{x}_A|\theta)b_\nu(n,i) \ , \tag{65}$$

where from Eqs. (35) and (36),

$$Y_\lambda(\vec{x}_A|\chi) = \sum_{\vec{q}j}(2N\omega_{\vec{q}j})^{-1/2}[a_{\vec{q}j}e^{i\vec{q}\cdot\vec{L}}\xi_\lambda^{\vec{q}j}(\vec{\rho}_\eta|\chi) + \mathrm{H.c.}] \ . \tag{66}$$

Proceeding now as in Sec. II we find the cross section $d\sigma(\vec{k}, r, \vec{\gamma})/d\Omega$ is given by Eqs. (11), (12), and [in place of Eq. (14)] the following expression for $g_\lambda^j(\vec{k})$:

$$g_\lambda^j(\vec{k}) = \sum_{ni} a_{ni}\,e^{-i\vec{k}\cdot(\vec{\rho}_n + \vec{b}_{ni})}\{[M(n)]^{-1/2}\xi_\lambda^{\vec{q}j}(\vec{\rho}_n|R) + \epsilon_{\lambda\mu\nu}[I(n,\eta)]^{-1/2}R_{\mu\eta}(n)\xi_\eta^{\vec{q}j}(\vec{\rho}_n|\theta)b_\nu(n,i)\} \ . \tag{67}$$

As before, $\vec{k}$ and $\vec{q}$ are given by Eqs. (13) and (4), respectively. $F^{(r)}(\vec{k})$ is expressed in terms of $\vec{g}^j(\vec{k})$ by Eq. (16) and the same relationship between the vanishing of $d\sigma(\vec{k}r\gamma)/d\Omega$ and of $F^{(r)}(\vec{k})$ obtains as occurs in Sec. II. In place of the completeness relation (17) we have from Eq. (40b)

$$\sum_j \xi_{\lambda_1}^{\vec{q}j}(\vec{\rho}_{n_1}|\chi_1)\,\xi_{\lambda_2}^{\vec{q}j*}(\vec{\rho}_{n_2}|\chi_2) = \delta_{n_1n_2}\delta_{\chi_1\chi_2}\delta_{\lambda_1\lambda_2} \ . \tag{68}$$

Substituting Eq. (67) for $\vec{g}^j(k)$ in Eq. (16), summing on r, and invoking Eq. (68), one obtains [in place of Eq. (18)] the following sum rule:

$$\sum_r F^{(r)}(\vec{k}) = (\vec{k}^2)\sum_n |\bar{a}_n(\vec{k})|^2 + \sum_n |k_\lambda\epsilon_{\lambda\mu\nu}r_{\mu\eta}(n)h_\nu(n,\vec{k})|^2 \ , \tag{69}$$

where $\bar{a}_n(\vec{k})$ and $h_\nu(n,\vec{k})$ are given by Eqs. (2) and (3) with $\bar{a}_{ni} = a_{ni}[M(n)]^{-1/2}\times$ (Debye–Waller factor). Here $r_{\mu\eta}(n)$ is a weighted rotation matrix related to the $R_{\mu\eta}(n)$ defined by Eq. (45) via the expression

$$r_{\mu\eta}(n) = [M(n)/I(n,\eta)]^{1/2}R_{\mu\eta}(n) \ . \tag{70}$$

We see that there are two terms on the right-hand side of the rigid-molecule sum rule (69). The first consists of contributions from translational vibrations of the c.m. of the molecule, the second, from rotational vibrations about the c.m. If one ignores the second, the sum rule (69) reduces to the point-molecule (i.e., atomic) sum rule (18) first obtained by ET, but with the effective atomic scattering length $\bar{a}_n$ replaced by the $\vec{k}$-dependent form factor $\bar{a}_n(\vec{k})$. As anticipated in Sec. I, $F^{(r)}(\vec{k})$ itself will be of similar composition.

We return now to the computation of $F^{(r)}(\vec{k})$. After some algebra, we obtain

$$F^{(r)}(\vec{k}) = \sum_{(\alpha|\vec{a})}\sum_{(\beta|\vec{b})}\sum_n (l_r/h)^2 k_{\lambda_1}k_{\lambda_2}\chi_D^{(\vec{q}r)*}[(\alpha|\vec{a})]\chi_D^{(\vec{q}r)}[(\beta|\vec{b})]\,e^{-i\vec{k}\cdot(\alpha\vec{\rho}_n + \vec{a})}\,e^{+i\vec{k}\cdot(\beta\vec{\rho}_n + \vec{b})}$$

$$\times\{[\bar{a}_n(\alpha^{-1}\vec{k})\bar{a}_n^*(\beta^{-1}\vec{k})\alpha_{\lambda_1\omega}\beta_{\lambda_2\omega}] + [\alpha_{\lambda_1 z_1}\epsilon_{z_1u_1t_1}\beta_{\lambda_2 z_2}\epsilon_{z_2u_2t_2}r_{u_1\omega}(n)r_{u_2\omega}(n)h_{t_1}(n,\alpha^{-1}\vec{k})h_{t_2}^*(n,\beta^{-1}\vec{k})]\} \ . \tag{71}$$

Equation (71) may be reduced to the form given in Eq. (1):

$$F^{(\gamma)}(\vec{k}) = F^{(\gamma)}(\vec{k}|R) + F^{(\gamma)}(\vec{k}|\theta)\,, \tag{1}$$

where $F^{(\gamma)}(\vec{k}|\chi)$, $\chi = R$ or θ, can be written in terms of a matrix $B(\vec{k}, r|\chi)$:

$$F^{(\gamma)}(\vec{k}|\chi) = k_{\lambda_1} B_{\lambda_1\lambda_2}(\vec{k}, r|\chi) k_{\lambda_2}, \quad \chi = R, \theta\,. \tag{72}$$

$B(\vec{k}, r)$ can be expressed as a quadratic form in the matrix A,

$$B(\vec{k}, r|\chi) = \sum_n A(n, \vec{k}, r|\chi) A^{\dagger}(n, \vec{k}, r|\chi)\,, \tag{73}$$

where in the zone interior

$$A_{\lambda_1\omega}(n, \vec{k}, r|R) = \frac{l_r}{h_0} \sum_{\alpha} \chi_d^{(\gamma)*}(\alpha)\, e^{-i\vec{R}\cdot(\alpha\vec{\rho}_n + \vec{v}_\alpha)} \times \bar{a}_n(\alpha^{-1}\vec{k})\alpha_{\lambda_1\omega}\,, \tag{74}$$

$$A_{\lambda_1\omega}(n, \vec{k}, r|\theta) = \frac{l_r}{h_0} \sum_{\alpha} \chi_d^{(\gamma)*}(\alpha) e^{-i\vec{R}\cdot(\alpha\vec{\rho}_n + \vec{v}_\alpha)} \times \alpha_{\lambda_1 s}\epsilon_{stu} h_t(n, \alpha^{-1}\vec{k}) r_{u\omega}(n)\,. \tag{75}$$

To obtain the corresponding matrices $A_{\lambda_1\omega}(n, \vec{k}, r|\chi)$, $\chi = R$ or θ, at the zone boundary, replace the quantity $\chi_d^{(\gamma)*}(\alpha)$ appearing in (74) and (75) by a quantity involving the multiplier representations $\tau^{(\gamma)}(\alpha)$, i.e.,

$$\chi_d^{(\gamma)*}(\alpha) \to \chi_\tau^{(\gamma)*}(\alpha)\, e^{-i\vec{R}(\vec{q}, \alpha)\cdot\vec{\rho}_n}\,, \tag{76}$$

where $\vec{K}(\vec{q}, \alpha)$, defined by Eq. (24), is not to be confused with $\vec{K} = \vec{k} - \vec{q}$ which appears in (74) and (75).

The expressions (74) and (75) are generalizations of Eq. (22) of Sec. II. The effect of the substitution (76) on these is two similar relations which constitute the generalization of Eq. (23).

IV. SUMMARY AND OUTLOOK

Our main qualitative conclusions are discussed in Sec. I and are therefore omitted here. For the experimentalist interested in applying our results but not in following the arguments in Sec. III, we recall that when the quantity $F^{(\gamma)}(\vec{k})$ is zero the differential cross sections $d\sigma(\vec{k}, r, \gamma)/d\Omega$ vanish for all values of the principal quantum number γ. Our quantitative results for $F^{(\gamma)}(\vec{k})$ within the rigid-molecule model are contained in the relations (1)–(3), (72)–(76), and the sum rule (69), where repeated subscripts are summed over. Note that our expression (22) for point molecules contains no explicit dependence on the phonon wave vector $\vec{q}$; $\vec{q}$ enters only in defining $G_0^{\vec{q}}$ which limits the sum on α in (22). In contrast, the molecular form factor $\bar{a}_n(\alpha^{-1}\vec{k})$ which appears in Eq. (74) depends directly on $\vec{q}$ as may be seen from Eq. (4) and the defining relation (2).

We believe that our extention of ET's work to the rigid-molecule model class greatly enhances its diagnostic power for crystals containing several complex but relatively tightly bound molecules in unit cell. We hope therefore that our work, together with theirs, will receive wide application in elucidating the phonon modes of such crystals via thermal neutron scattering. We are presently engaged in applying our technique to the sodium nitrate and potassium azide crystals concurrently with extending previous measurements on these crystals.[9] Moreover, we plan to have available a flexible computer program for assisting interested users.[10]

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[6]See, for example, L. Van Hove, N. M. Hugenhoetz, and L. P. Howland, *Quantum Theory of Many Particle Systems* (Benjamin, New York, 1961).

[7]At this point we differ from Elliott and Thorpe in that we apply $P^{(\vec{q}, r)}$ to the polarization vector $\xi_\lambda^{\vec{q}j}(\vec{\rho}_n)$ rather than to the quantity $g_\lambda^j(\vec{k})$, arguing that $\xi_\lambda^{\vec{q}j}(\vec{\rho}_n)$ is an eigenvector of the dynamical matrix, with invariance properties under the symmetry operations. [More precisely it is the quantity $\Phi_\lambda^{\vec{q}j}(\vec{R}_{Ln}) = N^{-1/2} e^{-i\vec{q}\cdot\vec{L}} \xi_\lambda^{\vec{q}j}(\vec{\rho}_n)$, which transforms irreducibly under the Wigner operators $O_{(\alpha|\vec{a})}$ which leave the small-vibration Hamiltonian invariant. Setting $\vec{L} = 0$, $\Phi_\lambda^{\vec{q}j} \propto \xi_\lambda^{\vec{q}j}$. See Sec. III B for further discussion.]

[8]See, for example, G. Venkataraman and V. C. Sahni, Rev. Mod. Phys. 42, 409 (1970).

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