Scattering tensors and Clebsch-Gordan coefficients in crystals*

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This paper is concerned with the relationship between the scattering tensors for the Raman (inelastic) scattering of light by phonons, or other excitations in a crystal, and the crystal-space-group Clebsch-Gordan coefficients. It is proven that the elements of the first-order scattering tensors are a prescribed linear combination of Clebsch-Gordan coefficients; the elements of the second-order scattering tensors are a prescribed bilinear combination of Clebsch-Gordan coefficients.

I. INTRODUCTION

In the analysis of the elastic or inelastic scattering of light by quasiparticles in solids it is useful to introduce a scattering tensor[1] which relates the Cartesian components of the scattered radiation field to those of the incident field. If the unit polarization vector of the incident radiation is denoted $\hat{\epsilon}_1$ with Cartesian components $\epsilon_{1\beta}$ ($\beta = 1, 2, 3$) and the unit polarization vector of the scattered radiation is denoted $\hat{\epsilon}_2$ with Cartesian components $\epsilon_{2\alpha}$ ($\alpha = 1, 2, 3$) then the intensity of scattered light polarized in the direction α for incident light polarized in the direction β is given as

$$I = C\left|\epsilon_{2\alpha} P_{\alpha\beta}\, \epsilon_{1\beta}\right|^2 . \tag{1.1}$$

In Eq. (1.1), $P_{\alpha\beta}$ is the scattering tensor, and C is a coefficient.

Depending upon the physical process under consideration the tensor $P_{\alpha\beta}$ can be further specified by giving the individual contributions from various subchannels, each of which contributes to the total scattering. For example, in an inelastic first-order (one-excitation) process the intensity of scattering can be written as proportional to

$$C'\left|\epsilon_{2\alpha} P^{(1)}_{\alpha\beta}(j\sigma)\epsilon_{1\beta}\right|^2 , \tag{1.2}$$

where the indices $j\sigma$ specify the symmetry of the excitation produced. For a second-order (two-excitation) process the expression becomes

$$C''\left|\epsilon_{2\alpha} P^{(2)}_{\alpha\beta}(j\sigma; j'\sigma')\epsilon_{1\beta}\right|^2 . \tag{1.3}$$

The excitations involved may be phonons, magnons,[2] etc.

It will be shown here that the elements of the first-order (one-excitation) scattering tensor $P^{(1)}_{\alpha\beta}(j\sigma)$ are precisely certain Clebsch-Gordan coefficients or prescribed linear combinations; the elements $P^{(2)}_{\alpha\beta}(j\sigma; j'\sigma')$ of the second-order tensor are a particular sum of products of Clebsch-Gordan coefficients. To the best of our knowledge this result has not previously been given despite the fact that many scattering-tensor elements have been calculated for particular processes in crystals of different symmetry.

II. SCATTERING TENSOR

A review of some familiar material may be helpful in preparation for the new results. It is simplest to analyze the situation for phonon Raman scattering, although magnon, etc., scattering can be similarly treated. Let the incident and scattered electric fields of the photon be denoted

$$E_j(r, t) = E_{j0}\,\hat{\epsilon}_j e^{i\vec{k}_j\cdot\vec{r} - i\omega_j t} , \tag{2.1}$$

where $j = 1$ and 2 for incident and scattered wave, $\hat{\epsilon}_j$ is the unit polarization vector which is transverse to $\vec{k}_j$ (the propagation vector), and ω_j is the photon frequency. The total intensity of scattering is given by

$$I = C\left|\sum_{\alpha\beta} \epsilon_{2\alpha} P_{\alpha\beta}\, \epsilon_{1\beta}\right|^2 , \tag{2.2}$$

where $P_{\alpha\beta}$ is the scattering tensor, $\alpha\beta = 1, 2, 3$ refer to Cartesian components, and C is a constant. This is a purely macroscopic statement which can be variously related to microscopic theories.

A useful approach, when neither ω_1 nor ω_2 are at resonance, is to work in a generalized adiabatic framework.[3] Then, $\chi_{n\nu}(R)$ and $\chi_{n'\nu'}(R)$ are initial and final eigenstates of the crystal with n and n' representing *all* vibrational quantum numbers and with ν and ν' representing the electronic quantum numbers, and R is the set of all instantaneous ion positions. In the harmonic approximation $\chi_{n\nu}$ and $\chi_{n'\nu'}$ are symmetrized products of single-oscillator eigenfunctions. In the case of phonon Raman scattering, a polarizibility operator $P_{\alpha\beta}(-\vec{k}_2\vec{k}_1\vec{R})$ can be defined so that the scattering matrix is

$$P_{\alpha\beta}(-\vec{k}_2\vec{k}_1) = \int \chi^*_{n'\nu}(\vec{R})\, P_{\alpha\beta}(-\vec{k}_2\vec{k}_1\vec{R})\, \chi_{n\nu}(\vec{R})\, d\vec{R} . \tag{2.3}$$

The operator $P_{\alpha\beta}(-\vec{k}_2\vec{k}_1\vec{R})$ depends *inter alia* upon initial and final wave vectors, and upon the ion positions. In the work of this paper we shall not be concerned with wave-vector dependence so we suppress $\vec{k}_2\vec{k}_1$ below. Wave-vector dependence will be discussed elsewhere.[4]

The operator $P_{\alpha\beta}(\vec{R})$ can be expanded in a Taylor series in the ion displacements from equilibrium: $\vec{R}=\vec{R}^0+\vec{u}$, where $\vec{u}$ is usual displacement vector. Instead of the individual $\vec{u}$ for each ion, the normal coordinates of the lattice, here denoted Q^j_σ, can be used:

$$P_{\alpha\beta}(\vec{R})=P^{(0)}_{\alpha\beta}(\vec{R}^0)+\sum_{j\sigma}P^{(1)}_{\alpha\beta}(\vec{R}^0;j\sigma)Q^j_\sigma + \sum_{jj'}\sum_{\sigma\sigma'}P^{(2)}_{\alpha\beta}(\vec{R}^0;j\sigma;j'\sigma')Q^j_\sigma Q^{j'}_{\sigma'}+\cdots \quad (2.4)$$

Clearly terms linear in Q^j_σ produce one-phonon scattering, bilinear $Q^j_\sigma Q^{j'}_{\sigma'}$ produce two-phonon scattering, etc.; this is consistent with (1.2) and (1.3). The indices $j\sigma$ will be used to specify the symmetry species of the phonon (*vide infra*).

III. EFFECT OF SYMMETRY

Let S be a symmetry element in the crystal symmetry group $\mathfrak{G}$. In general $S=(\phi_s|\vec{t}_s)$, where ϕ_s is a proper or improper rotation and $\vec{t}_s$ is a lattice plus fractional translation vector. Where there is no risk of confusion we write the Cartesian matrix elements of ϕ_s:

$$(\phi_s)_{\mu\lambda}\equiv S_{\mu\lambda} , \quad (3.1)$$

where $S^{-1}_{\lambda\mu}=S_{\mu\lambda}$ since ϕ is an orthogonal matrix. Under transformation by ϕ_s a polar vector is transformed as

$$\vec{r}\xrightarrow{S}\vec{r}'_s=\phi_s\vec{r}_s \quad (3.2)$$

or

$$r'_\mu=\sum_\lambda S_{\mu\lambda}r_\lambda . \quad (3.3)$$

Clearly the polarization vectors $\hat{\epsilon}_j$ transform as $\vec{r}$. The components $P_{\alpha\beta}$ of (1.1) transform as a second-rank crystal Cartesian tensor

$$P_{\alpha\beta}\xrightarrow{S}P'_{\alpha\beta}=\sum_{\lambda\mu}S_{\alpha\lambda}S_{\beta\mu}P_{\lambda\mu} . \quad (3.4)$$

Owing to the crystal symmetry, $P_{\alpha\beta}=P'_{\alpha\beta}$ so

$$P_{\alpha\beta}=\sum_{\lambda\mu}S_{\alpha\lambda}S_{\beta\mu}P_{\lambda\mu} . \quad (3.5)$$

Microscopic theory[5] indicates that usually for ω_j away from resonance, the scattering tensor for phonons is symmetric $P_{\alpha\beta}=P_{\beta\alpha}$, so that (3.5) should be replaced by

$$P_{\alpha\beta}=\sum_{\lambda\mu}(S_{\alpha\lambda}S_{\beta\mu}+S_{\alpha\mu}S_{\beta\lambda})P_{\lambda\mu} . \quad (3.6)$$

Under transformation by S, the normal coordinates can be taken to transform as

$$Q^j_\sigma\xrightarrow{S}Q^{j\prime}_\sigma=\sum_\tau D^{(j)}(S)_{\tau\sigma}Q^j_\tau \quad (3.7)$$

Thus j epitomizes the irreducible representation and σ is the row by which Q^j_σ transforms. In a crystal the full designation would be $j\to{}^\star\vec{k}j$, where ${}^\star\vec{k}$ is the star of the wave vector and j is an allowable irreducible representation of $\mathfrak{G}(\vec{k})$.

The polarizibility operator $P_{\alpha\beta}(\vec{R})$ can be subjected to transformation by S and so

$$P_{\alpha\beta}(\vec{R})\xrightarrow{S}P'_{\alpha\beta}(\vec{R})=\sum_{\lambda\mu}S_{\alpha\lambda}S_{\beta\mu}P_{\lambda\mu}(S^{-1}\vec{R}) . \quad (3.8)$$

The operator $P_{\alpha\beta}(\vec{R})$ transforms as a second-rank crystal Cartesian tensor field. Owing to crystal symmetry, $P_{\alpha\beta}(\vec{R})=P'_{\alpha\beta}(\vec{R})$ so

$$P_{\alpha\beta}(\vec{R})=\sum_{\lambda\mu}S_{\alpha\lambda}S_{\beta\mu}P_{\lambda\mu}(S^{-1}\vec{R}) . \quad (3.9)$$

At this point one could expand $P_{\lambda\mu}(S^{-1}\vec{R})$ in a Taylor-series expansion about the transformed lattice positions $\{S^{-1}\vec{R}\}$, and then equate term by term in such an expansion with corresponding terms in the expansion (2.4). An equivalent procedure is to consider the set of quantities $\{P^{(1)}_{\alpha\beta}(\vec{R}^0;j\sigma)\}$ to be the basis for $D^{(j)}$, so that (suppressing $\vec{R}^0$) the transformation (3.9) can be written

$$P^{(1)}_{\alpha\beta}(j\sigma)=\sum_{\lambda\mu}S_{\alpha\lambda}S_{\beta\mu}\sum_\tau D^{(j)}(S^{-1})_{\tau\sigma}P^{(1)}_{\lambda\mu}(j\tau)$$

$$=\sum_{\lambda\mu}\sum_\tau S_{\alpha\mu}S_{\beta\mu}D^{(j)}(S)^*_{\sigma\tau}P^{(1)}_{\lambda\mu}(j\tau) , \quad (3.10)$$

since $D^{(j)}$ is unitary. Similarly in second order,

$$P^{(2)}_{\alpha\beta}(j\sigma;j'\sigma')=\sum_{\lambda\mu}\sum_{\tau\tau'}S_{\alpha\lambda}S_{\beta\mu}D^{(j)}(S)^*_{\sigma\tau}D^{(j)}(S)^*_{\sigma'\tau'}\times P^{(2)}_{\lambda\mu}(j\tau;j'\tau') . \quad (3.11)$$

These equations are, of course, well known and are the basis of the conventional method[1] for obtaining the elements of the scattering tensor. In the usual procedure, elements $S, T, \ldots$ of $\mathfrak{G}$ are substituted one at a time into Eqs. (3.10) and (3.11) and compatibility of left-hand and right-hand sides result in only certain elements being nonzero.

IV. RELATION TO CLEBSCH-GORDAN COEFFICIENTS

A second-rank Cartesian tensor transforms, *per definitionem*, according to the representation by which the set of products of Cartesian components $\{r_\alpha r_\beta\}$ transforms. If $D^{(v)}$ is the representation by which the set $\{r_\alpha\}$ transforms [as in Eq. (3.3)], then the Kronecker square matrix $D^{(v)}_2$ is

$$[D^{(v)}(S)_2]_{\alpha\beta\lambda\mu}\equiv S_{\alpha\lambda}S_{\beta\mu} . \quad (4.1)$$

Under circumstances where $P_{\alpha\beta}$ is symmetric in (α,β) and (3.7) applies, the relevant matrix representation is the symmetrized Kronecker square, denoted $D^{(v)}_{(2)}$, and

$$[D^{(v)}(S)_{(2)}]_{\alpha\beta\lambda\mu}\equiv(S_{\alpha\lambda}S_{\beta\mu}+S_{\alpha\mu}S_{\beta\lambda}) . \quad (4.2)$$

Our analysis is not affected by which of the two [Eq. (4.1) or (4.2)] is relevant, but since (4.2) is the conventional nonresonant situation we shall assume it applies [i.e., (3.6) describes the transformation of the scattering tensor]. Let U be the unitary matrix which brings $D^{(v)}_{(2)}$ to the fully reduced form

$$U^{-1} D^{(v)}_{(2)} U = \overline{\Delta} , \tag{4.3}$$

where

$$\overline{\Delta}_{l n l' n'} = \delta_{l l'} D^{(l)}_{n n'} . \tag{4.4}$$

We assume that $D^{(v)}$ is irreducible and, for the moment, that each $D^{(l)}$ occurs only once in the reduced $\overline{\Delta}$. Then, from (4.3) and (4.4),

$$(D^{(v)}(S)_{(2)})_{\alpha\beta\lambda\mu} = \sum_{l n n'} U_{\alpha\beta l n} D^{(l)}(S)_{n n'} U^{-1}_{l n' \lambda\mu} . \tag{4.5}$$

Rewriting (3.10) we have

$$P^{(1)}_{\alpha\beta}(j\sigma) = \sum_{\lambda\mu} \sum_{\tau} [D^{(v)}(S)_{(2)}]_{\alpha\beta\lambda\mu} D^{(j)} \times (S)^*_{\sigma\tau} P^{(1)}_{\lambda\mu}(j\tau) ; \tag{4.6}$$

then using (4.5),

$$P^{(1)}_{\alpha\beta}(j\sigma) = \sum_{\lambda\mu} \sum_{\tau} \sum_{l n n'} U_{\alpha\beta l n} D^{(l)}(S)_{n n'} \times U^{-1}_{l n' \lambda\mu} D^{(j)}(S)^*_{\sigma\tau} P^{(1)}_{\lambda\mu}(j\tau) . \tag{4.7}$$

Now we sum both left-hand and right-hand sides of (4.7) over all elements of the group $\mathfrak{G}$ and use the orthonormality relation for irreducible representations to obtain

$$P^{(1)}_{\alpha\beta}(j\sigma) = \sum_{\lambda\mu\tau} U_{\alpha\beta j\sigma} U^{-1}_{j\tau\lambda\mu} P^{(1)}_{\lambda\mu}(j\tau) \frac{1}{l_j} , \tag{4.8}$$

where l_j is the dimension of the irreducible representation $D^{(j)}$. To solve this equation take

$$P^{(1)}_{\lambda\mu}(j\tau) = c(j) U_{\lambda\mu j\tau} . \tag{4.9}$$

On substituting this expression back into (4.9) it is seen that it is consistent. The quantity $c(j)$ depends on the irreducible representation j. This proves that the elements of the first-order scattering tensor are precisely Clebsch-Gordan coefficients multiplied by a constant $c(j)$ for the reduction of the symmetrized square into irreducible components, in this case. (See Appendix A.)

Now we turn to the second-order scattering tensor. Assuming that the second-order tensor also is symmetric in $(\alpha\beta)$, Eq. (3.11) can be rewritten

$$P^{(2)}_{\alpha\beta}(j\sigma; j'\sigma') = \sum_{\lambda\mu} \sum_{\tau\tau'} (D^{(v)}(S)_{(2)})_{\alpha\beta\lambda\mu} D^{(j)}_{\sigma\tau}(S)^* \times D^{(j')}(S)^*_{\sigma'\tau'} P^{(2)}_{\lambda\mu}(j\tau; j'\tau') . \tag{4.10}$$

Let V be the unitary matrix which brings $D^{(j)} \otimes D^{(j')}$ to fully reduced form

$$V^{-1} D^{(j)} \otimes D^{(j')} V = \overline{\overline{\Delta}} , \tag{4.11}$$

where

$$\overline{\overline{\Delta}}_{k m k' m'} = \delta_{k k'} D^{(k)}_{m m'} . \tag{4.12}$$

Hence,

$$D^{(j)}(S)^*_{\sigma\tau} D^{(j')}(S)^*_{\sigma'\tau'} = \sum_{k m m'} V^*_{\sigma\sigma' k m} D^{(k)}(S)^*_{m m'} (V^{-1}_{k m' \tau\tau'})^* . \tag{4.13}$$

Now substitute (4.5) and (4.13) into (4.10) to obtain

$$P^{(2)}_{\alpha\beta}(j\sigma; j'\sigma') = \sum_{\lambda\mu} \sum_{\tau\tau'} \sum_{l n n'} \sum_{k m m'} U_{\alpha\beta l n} D^{(l)}(S)_{n n'} U^{-1}_{l n' \lambda\mu} \times V^*_{\sigma\sigma' k m} D^{(k)}(S)^*_{m m'} V^{-1*}_{k m' \tau\tau'} P^{(2)}_{\lambda\mu}(j\tau; j'\tau') . \tag{4.14}$$

Again, sum left-hand and right-hand sides over all group elements S in $\mathfrak{G}$ and use the orthonormality rule to obtain

$$P^{(2)}_{\alpha\beta}(j\sigma; j'\sigma') = \sum_{\lambda\mu} \sum_{\tau\tau'} \sum_{l n n'} U_{\alpha\beta l n} U^{-1}_{l n' \lambda\mu} V^*_{\sigma\sigma' l n} \times (V^{-1}_{l n' \tau\tau'})^* P^{(2)}_{\lambda\mu}(j\tau; j'\tau') \frac{1}{l} . \tag{4.15}$$

In (4.15), l is the dimension of $D^{(l)}$. Now to solve (4.15), let

$$P^{(2)}_{\lambda\mu}(j\tau; j'\tau') = \sum_{\xi\eta\xi'\eta'} U_{\lambda\mu\xi\eta} C_{\xi\eta\xi'\eta'} V_{\tau\tau'\xi'\eta'} . \tag{4.16}$$

This form is chosen since it is the most general bilinear in the components of the matrices U and V. Substituting (4.16) into (4.15) we obtain

$$P^{(2)}_{\alpha\beta}(j\sigma; j'\sigma') = \sum_{l n} U_{\alpha\beta l n} V^*_{\sigma\sigma' l n} \left[\frac{1}{l} \sum_{n'} C_{l n' l n'} \right] . \tag{4.17}$$

Call

$$K(l) \equiv \frac{1}{l} \sum_{n'} C_{l n' l n'} \tag{4.18}$$

Then,

$$P^{(2)}_{\alpha\beta}(j\sigma; j'\sigma') = \sum_{l n} U_{\alpha\beta l n} V^*_{\sigma\sigma' l n} K(l) \tag{4.19}$$

is a consistent solution. In (4.19), $K(l)$ depends on the index l of the irreducible representation. [Note that the irreducible representation $D^{(l)}$ is common to the reduction of $D^{(v)}_{(2)}$ and $D^{(j)} \otimes D^{(j')}$, i.e., must appear in both $\overline{\Delta}$ and $\overline{\overline{\Delta}}$, or else $K(l) = 0$.] This proves that the elements of the second-order scattering tensor are bilinear sums of Clebsch-Gordan coefficients, in this case.

In Sec. V we continue with the assumptions that $D^{(v)}$ is irreducible and that each irreducible $D^{(l)}$ occurs only once in $\overline{\Delta}$ since this permits us to discuss the physics with minimal notational complexity. In the Appendix we generalize by removing these restrictions.

V. TOTAL SCATTERING INTENSITY

The total scattering intensity is the incoherent superposition of scattering from individual (partial) subchannels. Each order of scattering may be treated separately, and within each order the incoherent superposition is assumed.

The total first-order scattering intensity is

$$I^{(1)}=\sum_{j\sigma}\left|\sum_{\alpha\beta}\epsilon_{2\alpha}P^{(1)}_{\alpha\beta}(j\sigma)\epsilon_{1\beta}\right|^2 \qquad (5.1)$$

or

$$I^{(1)}=\sum_{j\sigma}\left(\sum_{\alpha\beta}\epsilon_{2\alpha}C(j)U_{\alpha\beta j\sigma}\epsilon_{1\beta}\right)\times\left(\sum_{\alpha'\beta'}\epsilon_{2\alpha'}C^*(j)U^*_{\alpha'\beta'j\sigma}\epsilon_{1\beta'}\right)$$

$$=\sum_{j\sigma}\left(\sum_{\alpha\beta\alpha'\beta'}\epsilon_{2\alpha}\epsilon_{2\alpha'}|C(j)|^2\times U_{\alpha\beta j\sigma}U^*_{\alpha'\beta'j\sigma}\epsilon_{1\beta}\epsilon_{1\beta'}\right). \qquad (5.2)$$

The first-order scattering from mode j is then given as

$$I^{(1)}(j)=\sum_{\alpha\alpha'\beta\beta'}\epsilon_{2\alpha}\epsilon_{2\alpha'}I^{(1)}_{\alpha\alpha'\beta\beta'}(j)\epsilon_{1\beta}\epsilon_{1\beta'}\ , \qquad (5.3)$$

where

$$I^{(1)}_{\alpha\alpha'\beta\beta'}(j)\equiv|C(j)|^2\sum_{\sigma}U_{\alpha\beta j\sigma}U^*_{\alpha'\beta'j\sigma}\ . \qquad (5.4)$$

Obviously this is independent of σ since all partners σ are degenerate. The microscopic dynamics is contained in $C(j)$ which is the quantity not prescribed by symmetry. Since each set of degenerate modes $j\sigma$ has a fixed common energy, in this approximation the first-order scattering is simply a superposition of scattering from individual modes.

The total second-order scattering intensity in which any two modes are created is

$$I^{(2)}=\sum_{j\sigma}\sum_{j'\sigma'}\left|\sum_{\alpha\beta}\epsilon_{2\alpha}P^{(2)}_{\alpha\beta}(j\sigma\,;j'\sigma')\epsilon_{1\beta}\right|^2$$

$$=\sum_{jj'}\sum_{\sigma\sigma'}\left|\sum_{\alpha\beta}\epsilon_{2\alpha}\sum_{ln}U_{\alpha\beta ln}V^*_{\sigma\sigma' ln}K(l)\epsilon_{1\beta}\right|^2$$

$$=\sum_{jj'}\sum_{\sigma\sigma'}\left(\sum_{\alpha\beta}\sum_{ln}\epsilon_{2\alpha}U_{\alpha\beta ln}V^*_{\sigma\sigma' ln}K(l)\epsilon_{1\beta}\right)\times\left(\sum_{\alpha'\beta'}\sum_{l'n'}\epsilon_{2\alpha'}U^*_{\alpha'\beta'l'n'}V_{\sigma\sigma'l'n'}K(l')^*\epsilon_{1\beta'}\right). \qquad (5.5)$$

Recall that V is unitary, so

$$V^*_{\sigma\sigma'l'n'}=V^{-1}_{l'n'\sigma\sigma'}\ . \qquad (5.6)$$

Then, the sum on $\sigma\sigma'$ can be easily carried out to obtain

$$I^{(2)}=\sum_{jj'}\left(\sum_{\alpha\beta}\sum_{\alpha'\beta'}\sum_{ln}\epsilon_{2\alpha}\epsilon_{2\alpha'}U_{\alpha\beta ln}\times U^*_{\alpha'\beta'ln}|K(l)|^2\epsilon_{1\beta}\epsilon_{1\beta'}\right). \qquad (5.7)$$

It then follows that the second-order scattering from all excitations j and j' (summed over $\sigma\sigma'$) which combine to produce particular allowed representations $D^{(l)}$ contained in $D^{(\nu)}_{(2)}$ depends only on the coefficient $|K(l)|^2$. Explicitly it is given as

$$I^{(2)}_{\alpha\alpha'\beta\beta'}(jj'|l)=|K(l)|^2\sum_n U_{\alpha\beta ln}U^*_{\alpha'\beta'ln}\ . \qquad (5.8)$$

Interestingly it is independent of the coupling coefficient matrix V, but only depends upon the indicated combinations of the coefficients from the matrix U, and an effective "reduced matrix element" $|K(l)|$. The microscopic dynamics is contained in $K(l)$. For a *given* jj' the partial scattering intensity in all allowed channels $D^{(l)}$ is

$$I^{(2)}_{jj'}=\sum_{\alpha\beta}\sum_{\alpha'\beta'}\epsilon_{2\alpha}\epsilon_{2\alpha'}\times I^{(2)}(jj')_{\alpha\alpha'\beta\beta'}\epsilon_{1\beta}\epsilon_{1\beta'}\ , \qquad (5.9)$$

where

$$I^{(2)}_{\alpha\alpha'\beta\beta'}(jj')\equiv\sum_{ln}|K(l)|^2U_{\alpha\beta ln}U^*_{\alpha'\beta'ln}\ . \qquad (5.10)$$

The matrices $I^{(2)}_{\alpha\alpha'\beta\beta'}(jj'|l)$ or $I^{(2)}_{\alpha\alpha'\beta\beta'}(jj')$, when averaged over a small frequency interval, correspond to the second-order scattering matrices introduced by Born and Bradburn,[6] which have been widely used in phonon Raman scattering; analogous matrices were also introduced for magnon scattering.[2]

VI. SUMMARY

The close relationship between scattering matrices and Clebsch-Gordan coefficients has been demonstrated explicitly in this paper. Although the work emphasized the case of phonon scattering it can easily be extended to magnon scattering by using correpresentation theory and using the appropriate generalized Clebsch-Gordan coefficients. Also extensions to higher-order processes can be given. In a separate paper an application to the calculation of the scattering tensors for multipole-dipole-resonance Raman scattering in Cu_2O will be given.

Despite the many explicit calculations of the first-order scattering matrices and several calculations of second-order scattering matrices, we believe that Eq. (4.9) and (4.19) pointing out the explicit connections with Clebsch-Gordan coefficients are new, and to the best of our knowledge has not previously appeared in the literature.

From a mathematical point of view, the present work is an example of extension of the Wigner-

Eckart theorem for the matrix element of an operator which transforms as a row of a Kronecker product representation under the operations of the group. Koster[7] discussed the case of an operator which transforms irreducibly under the group operations but did not give the particular application to the scattering matrices.

The factorization of a physical quantity (matrix element, scattering tensor element, etc.) in a generalized fashion into a Clebsch-Gordan coefficient, $U_{\lambda\mu j\tau}$, and a "reduced matrix element" $c(j)$ epitomized by Eq. (4.9) or Eq. (4.19) represents a maximum realization of the simplifications due to the symmetry of a problem. The Clebsch-Gordan coefficients for groups of interest (crystal point groups, crystal space groups, rotation group, etc.) are more and more becoming available and being used. In addition to the results given here, Clebsch-Gordan coefficients will be shown to arise in an analogous fashion (making necessary changes) in the following physical situations: (i) Brillouin scattering tensor, (ii) scattering tensors for morphic effects, (iii) higher-order moment expansions in infrared absorption, (iv) two-photon absorption matrix elements, and (v) diagonalization of the dynamical matrix. The theory for these phenomena as well as extensions to co-representation theory will be published elsewhere.

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APPENDIX: GENERALIZATION INCLUDING MULTIPLICITY AND TIME REVERSAL

In the analysis in Secs. IV and V it was assumed that $D^{(v)}$ is an irreducible representation and that $D^{(l)}$ occurs only once in $\overline{\Delta}$ and $\overline{\overline{\Delta}}$. We can deal with the most general case by removing these restrictions.

A. Multiplicity

If the vector representation $D^{(v)}$ is a sum of irreducible representations $D^{(i)}$ in $\mathfrak{G}$, it is convenient to use double indices and write

$$D^{(v)}_{i\alpha i'\beta} = \delta_{ii'} D^{(i)}_{\alpha\beta} \quad . \tag{A1}$$

Then the scattering tensor also has double indices and equations (4.8) and (5.15) for the first- and second-order scattering tensors become

$$P^{(1)}_{i\alpha i'\beta}(j\sigma) = \sum_{k\lambda k'\mu}\sum_{\tau}\sum_{lnn'} U_{i\alpha i'\beta ln} D^{(l)}(S)_{nn'}\, U^{-1}_{ln'k\lambda k'\mu}\, D^{(j)}(S)^*_{\sigma\tau} P^{(1)}_{k\lambda k'\mu}(j\tau) \tag{A2}$$

and

$$P^{(2)}_{i\alpha i'\beta}(j\sigma\,;j'\sigma') = \sum_{k\lambda k'\mu}\sum_{\tau\tau'}\sum_{lnn'}\sum_{kmm'} U_{i\alpha i'\beta ln} D^{(l)}(S)_{nn'}\, U^{-1}_{ln'k\lambda k'\mu} \times V^*_{\sigma\sigma' km} D^{(k)}(S)^*_{mm'}\, V^{-1*}_{km'\tau\tau'} P^{(2)}_{k\lambda k'\mu}(j\tau\,;j'\tau')\ . \tag{A3}$$

Now sum on S and use the orthonormality relation as before, then the solutions, (4.9) and (4.19), become

$$P^{(1)}_{k\lambda k'\mu}(j\tau) = C(kk'j)\, U_{k\lambda k'\mu j\tau} \tag{A4}$$

and

$$P^{(2)}_{k\lambda k'\mu}(j\tau\,;j'\tau') = \sum_{ln} K(kk'l)\, U_{k\lambda k'\mu ln} V^*_{\tau\tau' ln}\ . \tag{A5}$$

The indices $k\lambda$ and $k'\mu$ refer to rows of the irreducible representations $D^{(k)}$ and $D^{(k')}$, respectively, and $D^{(k)}$ and $D^{(k')}$ are contained in $D^{(v)}$. These indices correspond to the usual Cartesian indices since the basis functions belonging to row λ of $D^{(k)}$ and row μ of $D^{(k')}$ are either (x, y, z) or are related to (x, y, z) by a unitary transformation.

If $D^{(l)}$ occurs more than once in $\overline{\Delta}$ or $\overline{\overline{\Delta}}$ we must make additional generalizations. Note that in Eq. (4.4) the index l is used to label a row in the matrix U and also a particular representation in the reduced matrix $\overline{\Delta}$, and similarly for index k in Eq. (4.13). It is convenient to introduce a modified Kronecker δ symbol δ_{DlDj} which is unity if representation l is the same as representation j. Hence summing on S in Eqs. (4.8) and (4.15) and using orthonormality with inclusion of multiplicity, we find

$$P^{(1)}_{\lambda\mu}(j\tau) = \sum_{j'} c(j')\, U_{\lambda\mu j'\tau}\, \delta_{DjDj'} \tag{A6}$$

and

$$P^{(2)}_{\lambda\mu}(j\tau\,;j'\tau') = \sum_{ll'n} U_{\lambda\mu ln} K(ll')\, V^*_{\tau\tau' l'n}\, \delta_{DlDl'}\ . \tag{A7}$$

When $D^{(v)}$ is a sum of irreducible representations $D^{(k)}$, and $D^{(j)}$ occurs more than once in the decomposition of $D^{(k)}\otimes D^{(k')}$; then, combining Eqs. (A4) and (A6), the most general form of the first-order scattering tensor is

$$P^{(1)}_{k\lambda k'\mu}(j\tau) = \sum_{j'} c(kk'j')\, U_{k\lambda k'\mu j'\tau}\, \delta_{DjDj'}\ . \tag{A8}$$

Similarly, the most general second-order tensor is

$$P^{(2)}_{k\lambda k'\mu}(j\tau\,;j'\tau') = \sum_{ll'n} U_{k\lambda k'\mu ln} V^{*}_{\tau\tau' l'n} K(kk'll')\delta_{D l D l'} \; . \tag{A9}$$

B. Time reversal

When the representations involved are complex, time-reversal symmetry must be considered. Instead of the symmetry group $\mathfrak{G}$ we then have the antinuitary group $\mathcal{G}$ where, in general $\mathcal{G}$ has the structure

$$\mathcal{G} = \mathfrak{G} + \theta S \mathfrak{G} \; . \tag{A10}$$

θ is the time-reversal operator and S may or may not belong to $\mathfrak{G}$. Then,

$$\theta S P^{(1)}_{\alpha\beta}(j\sigma) = P^{(1)}_{\alpha\beta}(j\sigma) = \sum_{\lambda\mu\tau} S_{\alpha\lambda} S_{\beta\mu}\, D^{(j)}[(\theta S)^{-1}]_{\tau\sigma} P^{(1)*}_{\lambda\mu}(j\tau) \; , \tag{A11}$$

where $D^{(j)}$ is a corepresentation of $\mathcal{G}$.

Equation (A11) may introduce some relationships among elements of the scattering tensor. As an example, consider a group for which S is the identity and for which the inclusion of time reversal causes two one-dimensional representations j_1 and j_2, to form one two-dimensional corepresentation j with rows σ_1 and σ_2. Then from Eq. (A11)

$$P^{(1)}_{\alpha\beta}(j\sigma_1) = P^{(1)*}_{\alpha\beta}(j\sigma_2) \; . \tag{A12}$$

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[1]For phonon scattering see: R. Loudon [Adv. in Phys. 13, 423 (1964)] who gives these tensors and references to earlier work. See also H. Poulet and J. P. Mathieu *Spectres de Vibration et Symmetrie des Cristaux* (Gordon and Breach, New York, 1971), Chap. IX.

[2]For magnon scattering see Y. R. Shen and N. Bloembergen, Phys. Rev. 143, 372 (1966); P. Fleury and R. Loudon, Phys. Rev. 166, 514 (1968); T. Moriya, J. Phys. Soc. Jap. 23, 490 (1967); A. P. Cracknell, J. Phys. C. 2, 500 (1969).

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