

2. SYMMETRY ASPECTS OF EXCITATIONS

to its mechanical polarization, as given by the mode eigenvectors $\mathbf{e}_\kappa(\mathbf{q}, j)$.

In some cases, the optic modes carrying a nonzero effective charge \mathbf{Z}_j (so-called *polar optic* modes) may be classified as *transverse* (TO) or *longitudinal* (LO). Whenever applicable, this classification should be understood in the correct sense, *i.e.* according to the orientation of the associated *electric* polarization $\mathbf{P}_j(\mathbf{q}) = \mathbf{Z}_j(\mathbf{q})Q_j(\mathbf{q})$ relative to the wavevector \mathbf{q} .

2.3.3.1. First-order scattering cross section and Raman spectral line shapes

In the *first-order* scattering by a single excitation of the normal mode (\mathbf{q}, j) of frequency ω_j and wavevector \mathbf{q}_j , the energy and wavevector conservation conditions give

$$\begin{aligned}\omega &= \pm\omega_j \\ \mathbf{q} &= \pm\mathbf{q}_j,\end{aligned}$$

with the + sign corresponding to a *Stokes* process (one excitation quantum is created) and the – sign to an *anti-Stokes* process (one quantum is annihilated).

Let us explicitly consider the Stokes component, described by the term linear in the normal coordinate Q_j of the excitation. Inserting the plane-wave expressions for the quantities into the first term of the expansion (2.3.2.5) for $\delta\chi$ and comparing the terms with common time dependence, we get for the Stokes polarization due to the normal mode (\mathbf{q}, j)

$$\mathbf{P}(\mathbf{k}_S) = \varepsilon_0 \chi^{(j)}(\mathbf{q}, \omega_I, -\omega) Q_j^*(\mathbf{q}, \omega) \mathbf{E}_I(\mathbf{k}_I),$$

which corresponds to a plane wave at a frequency of $\omega_S = \omega_I - \omega$.

Since, in the harmonic approximation, the normal modes (\mathbf{q}, j) are *dynamically independent*, *i.e.* uncorrelated, the cross section for the Stokes component of the first-order scattering by phonons can be written as a sum over contributions from individual excitations. A summation convention over repeated Cartesian indices is understood throughout this chapter:

$$\begin{aligned}\frac{d^2\sigma}{d\Omega d\omega_S} &= \frac{\omega_S^3 \omega_I V^2 n_S}{(4\pi)^2 c^4 n_I} \sum_j \left| e_{I\alpha} \chi_{\alpha\beta}^{(j)}(\mathbf{q}, \omega_I, -\omega) e_{S\beta} \right|^2 \left| \langle Q_j(\mathbf{q}) Q_j^*(\mathbf{q}) \rangle_\omega \right|^2.\end{aligned}\quad (2.3.3.5)$$

Let us first briefly review the last term in this expression, which – together with the universal frequency-dependent first factor – essentially determines the shape of the scattered light spectrum, *i.e.* the frequency and temperature dependence of the spectral differential cross section. It depends exclusively on the fluctuation properties of the excitations participating in the scattering process.

The power spectrum of the fluctuations can be calculated using the linear response theory. The normal coordinates, *i.e.* excitation amplitudes of the normal modes, satisfy the decoupled equations of motion (with phenomenological damping constant $\gamma_{j,\mathbf{q}}$ added to take into account the finite lifetime of excitations in real crystals within the quasi-harmonic approximation):

$$\ddot{Q}_j(\mathbf{q}) + \gamma_{j,\mathbf{q}} \dot{Q}_j(\mathbf{q}) + \omega_j^2 Q_j(\mathbf{q}) = 0.$$

If a fictitious generalized force $F(t)$ with Fourier components $F(\omega)$ is applied to the system, the average of the Fourier components of the excitation amplitude and the force are proportional,

$$\bar{Q}_j(\mathbf{q}, \omega) = T_j(\mathbf{q}, \omega) F(\omega),$$

where the proportionality coefficient $T_j(\mathbf{q}, \omega)$ is called a *linear response function*.

The fluctuation–dissipation theorem (or, more exactly, its quantum version) relates the power spectrum $\langle \dots \rangle_\omega$ of a fluctuating quantity to the imaginary part of the corresponding response function. The results for the Stokes and anti-Stokes components of the scattering are, respectively:

$$\begin{aligned}\langle Q_j(\mathbf{q}) Q_j^*(\mathbf{q}) \rangle_\omega &= (\hbar/\pi) [n(\omega) + 1] \text{Im} T_j(\mathbf{q}, \omega) \text{ and} \\ \langle Q_j^*(\mathbf{q}) Q_j(\mathbf{q}) \rangle_\omega &= (\hbar/\pi) n(\omega) \text{Im} T_j(\mathbf{q}, \omega),\end{aligned}\quad (2.3.3.6)$$

where $n(\omega)$ is the Bose–Einstein statistical factor

$$n(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}, \quad (2.3.3.7)$$

which gives the occupation number of phonon states.

The linear response function of the normal coordinates is readily obtained from the equation of motion (N being the number of primitive cells in the crystal):

$$\begin{aligned}T_j(\mathbf{q}, \omega) &= \frac{1}{N} \frac{1}{\omega_j^2(\mathbf{q}) - \omega^2 - i\omega\gamma_{j,\mathbf{q}}}, \text{ hence} \\ \text{Im} T_j(\mathbf{q}, \omega) &= \frac{1}{N} \frac{\omega \gamma_{j,\mathbf{q}}}{[\omega_j^2(\mathbf{q}) - \omega^2]^2 + \omega^2 \gamma_{j,\mathbf{q}}^2}.\end{aligned}$$

If the damping parameter $\gamma_{j,\mathbf{q}}$ of the excitations is much smaller than the frequency $\omega_j(\mathbf{q})$, as is usually the case for phonons in perfect crystals, this function is closely approximated by a Lorentzian centred at $\omega_j(\mathbf{q})$, with a full width $\gamma_{j,\mathbf{q}}$ at half maximum. Hence, introducing a suitably normalized *lineshape function* $L_j(\omega)$,

$$\int_{-\infty}^{\infty} L_j(\omega) d\omega = 1,$$

we can write for the power spectra (2.3.3.5) of the j th normal mode in the spectral differential cross section

$$\begin{aligned}\langle Q_j(\mathbf{q}) Q_j^*(\mathbf{q}) \rangle_\omega &= \frac{\hbar}{2N\omega_j(\mathbf{q})} \{n[\omega_j(\mathbf{q})] + 1\} L_j(\omega) \text{ and} \\ \langle Q_j^*(\mathbf{q}) Q_j(\mathbf{q}) \rangle_\omega &= \frac{\hbar}{2N\omega_j(\mathbf{q})} n[\omega_j(\mathbf{q})] L_j(\omega)\end{aligned}\quad (2.3.3.8)$$

for the Stokes and anti-Stokes case, respectively.

Note that at low temperatures the differential cross section of the anti-Stokes component in the spectrum becomes vanishingly small, because the mean number of thermally excited phonons vanishes at $T = 0$.

Information about the interaction of photons with individual excitations is contained in the central term in the expression for the cross section (2.3.3.5), *i.e.* in the nonlinear susceptibility $\chi_{\alpha\beta}^{(j)}(\mathbf{q}, \omega_I, -\omega)$.

2.3.3.2. Symmetry properties of the scattering cross section

The quantity that controls the symmetry properties of the scattering cross section due to excitation $Q_j(\mathbf{q})$ is the squared modulus of the corresponding second-order susceptibility (second-rank tensor), contracted with the two polarization vectors of the incident and scattered light:

$$\left| \mathbf{e}_S \chi^{(j)}(\mathbf{q}, \omega_I, -\omega) \mathbf{e}_I \right|^2 \equiv \left| e_{S\alpha} \chi_{\alpha\beta}^{(j)}(\mathbf{q}, \omega_I, -\omega) e_{I\beta} \right|^2. \quad (2.3.3.9)$$

The nonlinear susceptibility tensor $\chi^{(j)}(\mathbf{q}, \omega_I, -\omega)$ is usually referred to as the first-order *Raman tensor* (defined in the literature to within a factor). Before discussing the consequences of the crystal symmetry on the form of the Raman tensor, let us mention two important approximations on which conventional analysis of its symmetry properties is based.

2.3. RAMAN SCATTERING

In a general case, the second-order susceptibilities are not necessarily symmetric. However, they fulfil a general symmetry property which follows from the symmetry of the scattering with respect to time inversion. Since the anti-Stokes process can be regarded as a time-inverted Stokes process (exchanging the role of the incident and scattered photons), it can be shown that in non-magnetic materials the susceptibilities obey the relation

$$\chi_{\beta\alpha}^{(j)}(-\mathbf{q}, \omega_S, \omega) = \chi_{\alpha\beta}^{(j)}(\mathbf{q}, \omega_I, -\omega). \quad (2.3.3.10)$$

In the *quasi-static* limit, *i.e.* if the scattering frequency is negligibly small compared with the incident photon frequency ($0 \approx \omega \ll \omega_I \approx \omega_S$), it follows that the susceptibilities of non-magnetic materials become *symmetric* in the Cartesian indices α, β . This symmetry is very well fulfilled in a great majority of cases. Appreciable antisymmetric contributions are known to occur, *e.g.* under *resonant conditions*, where the quasi-static approximation breaks down as the energy of the incident (or scattered) photon approaches those of electronic transitions.

Thus, in the first approximation, we set ω equal to zero and remove the time dependence in the phonon amplitudes, treating the normal coordinates as *static*. Then the nonlinear susceptibilities correspond to susceptibility derivatives,

$$\chi_{\alpha\beta}^{(j)}(\mathbf{q}, \omega_I, -\omega) \rightarrow \mathbf{R}_{\alpha\beta}^j(\mathbf{q}) \equiv \chi_{\alpha\beta}^{(j)}(\mathbf{q}, \omega_I) = \frac{\partial \chi_{\alpha\beta}(\omega_I)}{\partial Q_j^*(\mathbf{q})}, \quad (2.3.3.11)$$

where we suppressed the explicit dependence on ω_I and introduced a simplified notation for the Raman tensor $\mathbf{R}^j(\mathbf{q})$, still keeping the dependence on the scattering wavevector.

In deriving the symmetry properties of the Raman tensor $\mathbf{R}^j(\mathbf{q})$ that follow from the crystal lattice symmetry, the main point is thus to determine its transformation properties under the symmetry operation of the crystal *space group*.

Since the magnitude of the scattering vector $q \equiv |\mathbf{q}|$ is very small compared with the Brillouin-zone dimensions, another conventional approximation is to neglect the \mathbf{q} dependence of the susceptibilities. Setting $\mathbf{q} \rightarrow 0$ enables us to analyse the symmetry of the Raman tensor in terms of the *factor group* G_0 , which is isomorphous to the point group of the crystal lattice. This approach is, again, appropriate for the vast majority of cases. An important exception is, for instance, the scattering by acoustic modes (*Brillouin scattering*) or scattering by longitudinal plasma waves in semiconductors (*plasmons*): in these cases the Raman tensor vanishes for $\mathbf{q} = 0$, since this limit corresponds to a homogeneous displacement of the system. Possible \mathbf{q} -dependent effects can be treated by expanding the Raman tensor in powers of \mathbf{q} and using compatibility relations between the symmetries at $\mathbf{q} = 0$ and at the full symmetries applicable in the $\mathbf{q} \neq 0$ case.

Let us mention that another notation is sometimes used in the literature for the Raman tensor. Since the square modulus of a second-rank tensor contracted with two vectors can be written as a fourth-rank tensor contracted with four vectors, one can introduce a fourth-rank tensor $\mathbf{I}^{(j)}$,

$$I_{\alpha\beta\mu\nu}^{(j)} = \frac{\partial \chi_{\alpha\beta}^*}{\partial Q_j} \frac{\partial \chi_{\mu\nu}}{\partial Q_j^*},$$

so that the scattering cross section of the j th mode is

$$\frac{d\sigma^{(j)}}{d\Omega d\omega_S} \approx e_{I\alpha} e_{I\mu} e_{S\beta} e_{S\nu} I_{\alpha\beta\mu\nu}^{(j)}.$$

If there are no antisymmetric components in the susceptibility derivatives, it can be shown that the fourth-rank tensor $\mathbf{I} = (I_{\alpha\beta\mu\nu})$ has at most 21 independent components, as for the elastic constants tensor.

2.3.3.3. Raman tensor and selection rules at $\mathbf{q} \approx 0$

The scattering cross section, being a scalar quantity, must be invariant with respect to all symmetry elements of the space group of the crystal. This invariance has two important consequences: it determines which normal modes (j) can contribute to the scattering (*Raman activity* of the modes) and it also gives the restrictions on the number of independent components of the Raman tensor (*polarization selection rules*).

At $\mathbf{q} \approx 0$, the transformation properties of the incident and scattered light are described by the three-dimensional *polar vector representation* Γ_{PV} of the appropriate point group of the crystal, since the quantities that characterize the light ($\mathbf{E}_I, \mathbf{E}_S, \mathbf{P} \dots$) are all *polar vectors*, *i.e.* first-rank polar tensors (T_α). The transformation properties of a normal mode j must correspond to an irreducible matrix representation $\Gamma(j)$ of the crystal point group. We recall that in cases of two- or three-dimensional representations (degeneracy), the index j represents two indices.

In order that a particular normal mode j in a given crystal be Raman active, *i.e.* *symmetry-allowed* to contribute to the (first-order) scattering cross section, the necessary condition is that the corresponding irreducible representation $\Gamma(j)$ must be contained in the decomposition of the direct Kronecker product representation $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}$ at least once:

$$\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}} \supset \Gamma(j). \quad (2.3.3.12)$$

In this case, the Kronecker product $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}} \otimes \Gamma(j)$ contains the identity representation at least once, so the cross section remains invariant under the transformation of the crystal point group. In the phenomenological formulation, the susceptibility derivatives correspond to third derivatives of a particular potential energy Φ (interaction Hamiltonian),

$$R_{\alpha\beta}^j = \left(\frac{\partial \chi_{\alpha\beta}}{\partial Q_j^*} \right) \sim \left(\frac{\partial^3 \Phi}{\partial E_{I\alpha} \partial E_{S\beta}^* \partial Q_j^*} \right), \quad (2.3.3.13)$$

such that the product $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}} \otimes \Gamma(j)$ is the reducible representation of the Raman tensor. If condition (2.3.3.12) holds, then the Raman tensor \mathbf{R}^j does not vanish identically and may have at least one independent nonzero component. As the representation $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}$ is that of a second-rank polar tensor, equivalent formulation of the Raman activity of a normal mode j is that the corresponding normal coordinate Q_j must transform like one or more components of a polar tensor. The transition susceptibility $\delta\chi^{(j)}$ transforms accordingly. The task of determining whether a given normal mode j is Raman active or not thus consists of simply decomposing the representation $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}$ and identifying the irreducible components $\Gamma(j)$.

The second consequence of the invariance condition is the imposition of restrictions on the Cartesian components of the Raman tensor for modes allowed to participate in the scattering. By virtue of the properties of the irreducible representations $\Gamma(j)$, some components of the corresponding Raman tensor are required to vanish whereas others may have related values. This fact results in anisotropies in the observed cross section depending on the polarization directions of the incident and scattered light, and is usually referred to as *polarization selection rules*. As the scattering cross section of the excitation (j) is proportional to the scalar quantity

$$|\mathbf{e}_S \mathbf{R}^j \mathbf{e}_I|^2 \equiv \left| e_{S\alpha} R_{\alpha\beta}^j e_{I\beta} \right|^2,$$

one can generally ‘isolate’ a given component of the Raman tensor by suitably arranging the scattering geometry in the experiment, *i.e.* by choosing the orientation of the wavevectors \mathbf{k}_I and \mathbf{k}_S and the polarization vectors \mathbf{e}_I and \mathbf{e}_S with respect to crystallographic axes.