

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:

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

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.