

2.3. RAMAN SCATTERING

The symbol $\langle \dots \rangle_\omega$ stands for the power spectrum (correlation function) of the transition susceptibility fluctuations. The spectral differential cross section is the quantity that can be directly measured in a Raman scattering experiment by analysing the frequency spectrum of the light scattered into a certain direction. By integrating over frequencies ω_s for a particular Raman band and, in addition, over the solid angle, one obtains, respectively, the *differential cross section* ($d\sigma/d\Omega$) and the *total cross section* (σ_{tot}):

$$\frac{d\sigma}{d\Omega} = \int \left(\frac{d^2\sigma}{d\Omega d\omega_s} \right) d\omega_s, \quad \sigma_{\text{tot}} = \int \left(\frac{d\sigma}{d\Omega} \right) d\Omega.$$

These quantities are useful in comparing the integrated scattered intensity by different excitations.

2.3.2.3. Experimental aspects

In a scattering experiment on crystals, the choice of the scattering geometry implies setting the propagation directions \mathbf{k}_I and \mathbf{k}_S and the polarization of the incident and scattered light with respect to the crystallographic axes and defining thus the direction of the scattering wavevector \mathbf{q} as well as the particular component (or a combination of components) of the transition susceptibility tensor $\delta\chi$. In practice, the incident radiation is almost exclusively produced by a suitable laser source, which yields a monochromatic, polarized narrow beam, with a well defined wavevector \mathbf{k}_I . The light scattered in the direction of \mathbf{k}_S is collected over a certain finite solid angle $\Delta\Omega$. Its polarization is analysed with a suitable polarization analyser, and the scattered intensity as a function of frequency ω_s (or Raman shift ω) is analysed using a spectrometer.

To characterize the Raman scattering geometry in a particular experimental arrangement, standard notation for the scattering geometry is often used, giving the orientation of the wavevectors and polarization vectors with respect to a reference Cartesian coordinate system, namely: $\mathbf{k}_I(\mathbf{e}_I, \mathbf{e}_S)\mathbf{k}_S$. Thus, for example, the symbol $x(z,y)z$ means that right-angle scattering geometry is used, where the incident beam polarized in the $z = [001]$ direction propagates along the $x = [100]$ axis, while the scattered beam is collected in the z direction and the polarization analyser is set parallel with the $y = [010]$ direction. The measured intensity, being proportional to $|\chi_{zy}|^2$, gives information on this particular component of the transition susceptibility tensor. By virtue of the momentum conservation, the scattering wavevector \mathbf{q} in this case is oriented along the $[101]$ direction.

In a typical Raman experiment with visible light ($\omega \ll \omega_I \approx \omega_S$), the magnitudes of the wavevectors $k_I \approx k_S = k$ are of the order of 10^5 cm^{-1} , much lower than those of the reciprocal-lattice vectors K ($\approx 10^8 \text{ cm}^{-1}$). Consequently, the range of the magnitudes of the scattering wavevectors q accessible by varying the scattering geometry from $\varphi = 0^\circ$ (forward scattering) to $\varphi = 180^\circ$ (back scattering) is $0 \leq q \leq 2k$, *i.e.* by about three orders of magnitude lower than the usual dimensions of the Brillouin zone. The use of back-scattering geometry is imperative in the case of opaque samples, which show stronger absorption for the exciting (or scattered) light.

It should be noted that the general formula for the spectral differential cross section (2.3.2.5) applies to the situation *inside* the crystal. Since in real experiments the observer is always *outside* the crystal, several corrections have to be taken into account. These are in particular due to refraction, reflection and transmission of the incident and scattered light at the interfaces, as well as absorption of light in the crystal. Attention must be paid in the case of anisotropic or gyrotropic crystals, where birefringence or rotation of the polarization direction of both incident and scattered light may occur on their paths through the crystal, between the interfaces and the scattering volume.

We conclude this section by remarking that, owing to the obvious difficulties in taking all the properties of the experimental setup and the corrections into consideration, measurements of absolute Raman intensities tend to be extremely rare. There exist, however, several crystals for which absolute determination of the cross section for particular excitations has been made with reasonable reliability and which may serve as secondary standards.

2.3.3. First-order scattering by phonons

In what follows, we shall be more specific and by underlying excitations we shall explicitly understand lattice vibrations – *phonons* – although the treatment is also applicable to other types of collective excitations in a crystal.

Let us recall (see Chapter 2.1) that atomic displacements in the crystal lattice can be expressed as linear combinations of the *normal modes of vibrations* – eigenvectors of the dynamical matrix.

$$\mathbf{u}_{\kappa\mathbf{l}} = \sum_{\mathbf{q}} \sum_j \mathbf{u}_{\kappa\mathbf{l}}(\mathbf{q}, j) = \frac{1}{\sqrt{Nm_\kappa}} \sum_{\mathbf{q}} \sum_j Q_j(\mathbf{q}) \mathbf{e}_\kappa(\mathbf{q}, j) \exp(i\mathbf{q}\mathbf{r}_\mathbf{l}), \quad (2.3.3.1)$$

where \mathbf{l} denotes the *primitive* unit cell, κ ($\kappa = 1, \dots, s$) is the index of the atom (mass m_κ) in the unit cell and N is the number of unit cells in the crystal. The *eigenvectors* $\mathbf{e}_\kappa(\mathbf{q}, j)$, also called *polarization vectors*, are normalized vectors describing the displacement pattern of atoms in the reference unit cell in a j th normal mode of vibration ($j = 1, 2, 3, \dots, 3s$) with a wavevector \mathbf{q} . The normal modes can be classified according to irreducible representations of the crystal space group and labelled correspondingly. In the case of degeneracy, the branch index j stands, in fact, for two indices: one for the irreducible representation, and the other distinguishing the degenerate partners of the same frequency. The coefficients $Q_j(\mathbf{q})$ are called *normal coordinates* and represent the time-dependent amplitudes of the normal modes, vibrating with frequencies $\omega_j(\mathbf{q})$. The reality of the displacements and the hermiticity of the dynamical matrix impose the following conditions:

$$\mathbf{e}_\kappa(\mathbf{q}, j) = \mathbf{e}_\kappa^*(-\mathbf{q}, j), \quad \omega_j(\mathbf{q}) = \omega_j(-\mathbf{q}), \quad Q_j(\mathbf{q}) = Q_j^*(-\mathbf{q}). \quad (2.3.3.2)$$

In the limit of $\mathbf{q} \rightarrow 0$, three of the vibrational branches correspond to homogeneous displacements of the crystal with vanishing frequency along three independent directions. These branches are termed *acoustic*. The remaining $3s - 3$ branches (provided that $s > 1$) are called *optic*; they correspond to relative displacement of sublattices with nonzero frequency.

For completeness, we note that in a phenomenological treatment the amplitude of the polarization set up by atomic displacements of the normal modes with wavevector \mathbf{q} can be expressed as

$$P_\alpha(\mathbf{q}) = \sum_j Z_{j\alpha}(\mathbf{q}) Q_j(\mathbf{q}), \quad (2.3.3.3)$$

introducing the $(3s \times 3)$ *effective charge* matrix of the j th normal mode of vibration (per unit cell of volume V_c),

$$Z_{j\alpha}(\mathbf{q}) = \left(\frac{\partial P_\alpha(\mathbf{q})}{\partial Q_j(\mathbf{q})} \right) = \frac{1}{V_c} \sum_{\kappa} z_{\alpha\beta}^{(\kappa)} \frac{e_{\kappa\beta}(\mathbf{q}, j)}{\sqrt{Nm_\kappa}}. \quad (2.3.3.4)$$

The quantity $z_{\alpha\beta}^{(\kappa)}$ represents the *microscopic* effective charge of the κ th atom in the unit cell. Owing to dynamic contributions of ionic deformability, it is not a scalar but rather a (3×3) tensor in general. Hence, in general, the direction of the contribution of a mode to the electrical polarization (2.3.3.3) need not correspond

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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:

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

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:

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

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

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

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

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

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:

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

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.

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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.

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For each normal mode (j) allowed in the scattering, the number of independent components of its Raman tensor is given by the multiplicity coefficients $c^{(j)}$ of the irreducible representation $\Gamma(j)$ in the decomposition

$$\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}} = c^{(1)}\Gamma(1) \oplus c^{(2)}\Gamma(2) \oplus \dots, \quad (2.3.3.14)$$

where the multiplicity coefficient $c^{(j)}$ corresponds to the number of times the given irreducible representation $\Gamma(j)$ enters the decomposition. If the representation $\Gamma(j)$ is two- or three-dimensional, then for each occurrence of $\Gamma(j)$ in (2.3.3.14) there are two or three degenerate partners (of the same frequency) whose Raman tensors are symmetry-related.

The matrix form of the Raman tensor corresponding to a given irreducible representation – *i.e.* *symmetry species* – $\Gamma(j)$ can be readily constructed by finding the appropriate bilinear basis functions that transform according to the corresponding irreducible representation $\Gamma(j)$. The required number of such independent bases is given by the multiplicity coefficient $c^{(j)}$. Alternatively, one may construct invariant polynomials (transforming as scalars) of order *four*, *i.e.* of the same order as the product $E_{I\alpha}E_{S\beta}Q_j$.

Making allowance for possible *antisymmetric* scattering, we have not explicitly supposed that the Raman tensor is symmetric. We recall that the derivative (2.3.3.13) is not necessarily symmetric in the α and β indices as long as the fields $E_{I\alpha}$ and $E_{S\beta}$ correspond to different frequencies (inelastic scattering). However, each second-rank polar tensor $T_{\alpha\beta}$ (nine components), transforming according to $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}$, can be decomposed into a symmetric part $T'_{\alpha\beta} = T'_{\beta\alpha}$ (six components), transforming like a symmetric polar tensor $[\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_S$, and an antisymmetric part $T''_{\alpha\beta} = -T''_{\beta\alpha}$ (three components), transforming like an axial vector (for the definition of axial tensors, see Section 1.1.4.5.3) according to $\Gamma_{\text{AV}} = [\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_A$.

The symmetry-restricted forms of the (3×3) Raman tensors corresponding to all Raman-active symmetry species are summarized in Table 2.3.3.1 (see *e.g.* Hayes & Loudon, 1978) for each of the 32 crystal symmetry classes. Spectroscopic notation is used for the irreducible representations of the point groups. The symbols (x , y or z) for some Raman-active symmetry species in the noncentrosymmetric classes indicate that the respective components of polar vectors also transform according to these irreducible representations. Hence the normal coordinates of the phonons of these *polar* symmetry species (polar phonons) transform in the same way and, consequently, the corresponding component of the effective charge tensor $Z_{j\alpha}(\mathbf{q} = 0)$, see (2.3.3.4), is not required by symmetry to vanish. Polar phonons thus may carry a nonzero dipole moment and contribute to the polarization in the crystal, which manifests itself in *infrared activity* and also in the Raman scattering cross section (see Section 2.3.3.5).

For convenience, the Raman tensors are explicitly split into a symmetric and possible antisymmetric part (upper and lower row of each part of the table, respectively, in each case). The conventional *symmetric* Raman tensors are *appropriate for most cases of practical interest*. Besides the resonant conditions mentioned above, there are other exceptions. For instance, there are optical phonons that transform like *axial vectors*, such as in the case of A_2 (or A_{2g} , A'_2) modes in some uniaxial crystal classes, where the Raman tensor is *purely antisymmetric*. Antisymmetric scattering by these modes may become allowed at finite wave-vector \mathbf{q} . Antisymmetric Raman tensors are also needed for analysing the symmetry of scattering in magnetic materials (scattering by spin waves – *magnons*), or non-magnetic materials under a magnetic field, where the susceptibility itself is essentially nonsymmetric.

We note that the matrix form of the Raman tensors depends on the setting of the Cartesian axes with respect to the crystallographic axes. To avoid ambiguities and apparent disagreement with other sources, we give the results for alternative orientations

Table 2.3.3.1. *Symmetry of Raman tensors in the 32 crystal classes*

The symbols a, b, c, d, e, f, g, h and i in the matrices stand for arbitrary parameters denoting possible independent nonzero components (in general complex) of the Raman tensors. Upper row: conventional symmetric Raman tensors; lower row: antisymmetric part. Alternative orientations of the point group are distinguished by subscripts at 2 or m in the class symbol indicating the direction of the twofold axis or of the normal to the mirror plane.

Triclinic

$\frac{1}{\bar{1}}$	$\begin{pmatrix} a & d & f \\ d & b & h \\ f & h & c \end{pmatrix}$
	$\begin{matrix} A(x, y, z) \\ A_g \end{matrix}$
	$\begin{pmatrix} \cdot & e & g \\ -e & \cdot & i \\ -g & -i & \cdot \end{pmatrix}$

Monoclinic, unique axis z

$\begin{matrix} 2_z \\ m_z \\ 2_z/m \end{matrix}$	$\begin{pmatrix} a & d & \cdot \\ d & b & \cdot \\ \cdot & \cdot & c \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & f \\ \cdot & \cdot & h \\ f & h & \cdot \end{pmatrix}$
	$\begin{matrix} A(z) \\ A'(x, y) \\ A_g \end{matrix}$	$\begin{matrix} B(x, y) \\ A''(z) \\ B_g \end{matrix}$
	$\begin{pmatrix} \cdot & e & \cdot \\ -e & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & g \\ \cdot & \cdot & i \\ -g & -i & \cdot \end{pmatrix}$

Monoclinic, unique axis y

$\begin{matrix} 2_y \\ m_y \\ 2_y/m \end{matrix}$	$\begin{pmatrix} a & \cdot & d \\ \cdot & b & \cdot \\ d & \cdot & c \end{pmatrix}$	$\begin{pmatrix} \cdot & f & \cdot \\ f & \cdot & h \\ \cdot & h & \cdot \end{pmatrix}$
	$\begin{matrix} A(y) \\ A'(x, z) \\ A_g \end{matrix}$	$\begin{matrix} B(x, z) \\ A''(y) \\ B_g \end{matrix}$
	$\begin{pmatrix} \cdot & \cdot & e \\ \cdot & \cdot & \cdot \\ -e & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & g & \cdot \\ -g & \cdot & i \\ \cdot & -i & \cdot \end{pmatrix}$

Orthorhombic

$\begin{matrix} 222 \\ mm2 \\ mmm \end{matrix}$	$\begin{pmatrix} a & \cdot & \cdot \\ \cdot & b & \cdot \\ \cdot & \cdot & c \end{pmatrix}$	$\begin{pmatrix} \cdot & d & \cdot \\ d & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & f \\ \cdot & \cdot & \cdot \\ f & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & h \\ \cdot & h & \cdot \end{pmatrix}$
	$\begin{matrix} A \\ A_1(z) \\ A_g \end{matrix}$	$\begin{matrix} B_1(z) \\ A_2 \\ B_{1g} \end{matrix}$	$\begin{matrix} B_2(y) \\ B_1(x) \\ B_{2g} \end{matrix}$	$\begin{matrix} B_3(x) \\ B_2(y) \\ B_{3g} \end{matrix}$
	$\begin{pmatrix} \cdot & \cdot & e \\ -e & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & g \\ \cdot & \cdot & \cdot \\ -g & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & i \\ \cdot & -i & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & -i & \cdot \end{pmatrix}$

of the point groups in several cases where different settings of the twofold axes or mirror planes with respect to the Cartesian axes are commonly used. This concerns all monoclinic classes (unique

2.3. RAMAN SCATTERING

Table 2.3.3.1 (cont.)

Tetragonal

4 4 4/m	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$	$\begin{pmatrix} d & e & . \\ e & -d & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & f \\ . & . & h \\ f & h & . \end{pmatrix}$	$\begin{pmatrix} . & . & -h \\ . & . & f \\ -h & f & . \end{pmatrix}$
	A(z) A A _g	B B(z) B _g	E(x, y) E(x, -y) E _g	
	$\begin{pmatrix} . & c & . \\ -c & . & . \\ . & . & . \end{pmatrix}$		$\begin{pmatrix} . & . & g \\ . & . & i \\ -g & -i & . \end{pmatrix}$	$\begin{pmatrix} . & . & -i \\ . & . & g \\ i & -g & . \end{pmatrix}$

422 4mm 4̄2 _x m _{xy} 4m _x 2 _{xy} 4/mmm	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$		$\begin{pmatrix} d & . & . \\ . & -d & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & e & . \\ e & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & f \\ . & . & . \\ f & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & f \\ . & f & . \end{pmatrix}$
	A ₁ A ₁ (z)	A ₂ (z) A ₂	B ₁ B ₁	B ₂ B ₂	E(-y, x) E(x, y)	
	A ₁ A ₁	A ₂ A ₂	B ₁ B ₁	B ₂ (z) B ₂ (z)	E(y, x) E(-x, y)	
	A _{1g}	A _{2g}	B _{1g}	B _{2g}	E _g	
		$\begin{pmatrix} . & c & . \\ -c & . & . \\ . & . & . \end{pmatrix}$			$\begin{pmatrix} . & . & g \\ . & . & i \\ -g & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & g \\ . & -g & . \end{pmatrix}$

Trigonal

3 3	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$	$\begin{pmatrix} c & f & e \\ f & -c & d \\ e & d & . \end{pmatrix}$	$\begin{pmatrix} f & -c & -d \\ -c & -f & e \\ -d & e & . \end{pmatrix}$
	A(z) A _g	E(x, y) E _g	
	$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & i \\ . & . & g \\ -i & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & i \\ g & -i & . \end{pmatrix}$

32 _x 3m _x 3̄m _x	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$		$\begin{pmatrix} f & . & . \\ . & -f & d \\ . & d & . \end{pmatrix}$	$\begin{pmatrix} . & -f & -d \\ -f & . & . \\ -d & . & . \end{pmatrix}$
	A ₁ A ₁ (z)	A ₂ (z) A ₂	E(x, y) E(y, -x)	
	A _{1g}	A _{2g}	E _g	
		$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & g \\ . & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & . \\ g & . & . \end{pmatrix}$

32 _y 3m _y 3̄m _y	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$		$\begin{pmatrix} . & f & . \\ f & . & d \\ . & d & . \end{pmatrix}$	$\begin{pmatrix} f & . & -d \\ . & -f & . \\ -d & . & . \end{pmatrix}$
	A ₁ A ₁ (z)	A ₂ (z) A ₂	E(x, y) E(y, -x)	
	A _{1g}	A _{2g}	E _g	
		$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & g \\ . & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & . \\ g & . & . \end{pmatrix}$

direction parallel to **y** or **z**), tetragonal class 4̄2m, trigonal classes 32, 3m and 3̄m, as well as hexagonal class 6̄2m.

1̄, 2/m, mmm, 4/m, 4/mmm, 3̄, 3̄m, 6/m, 6/mmm, m3, m3m,

2.3.3.4. Centrosymmetric crystals

In those point groups that contain the inversion operation, *i.e.* in the eleven centrosymmetric (*nonpolar*) crystal classes

the irreducible representations are divided into two groups, odd and even, according to the parity. Since second-rank polar tensors must transform according to the *even* parity representations only, whereas polar vectors transform according to *odd* parity representations, the selection rules for electric dipole absorption

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Table 2.3.3.1 (cont.)

Hexagonal

$\begin{matrix} 6 \\ \bar{6} \\ 6/m \end{matrix}$	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$	$\begin{pmatrix} . & . & e \\ . & . & d \\ e & d & . \end{pmatrix}$	$\begin{pmatrix} . & . & -d \\ . & . & e \\ -d & e & . \end{pmatrix}$	$\begin{pmatrix} c & f & . \\ f & -c & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} f & -c & . \\ -c & -f & . \\ . & . & . \end{pmatrix}$	
	$\begin{matrix} A(z) \\ A' \\ A_g \end{matrix}$	$\begin{matrix} E_1(x, y) \\ E'' \\ E_{1g} \end{matrix}$	$\begin{matrix} E_2 \\ E'(x, y) \\ E_{2g} \end{matrix}$			
	$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & i \\ . & . & g \\ -i & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & i \\ g & -i & . \end{pmatrix}$			

$\begin{matrix} 622 \\ \bar{6}mm \\ \bar{6}m, 2_y \\ \bar{6}2_x m_y \\ 6/mmm \end{matrix}$	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$		$\begin{pmatrix} . & . & . \\ . & . & d \\ . & d & . \end{pmatrix}$	$\begin{pmatrix} . & . & -d \\ . & . & . \\ -d & . & . \end{pmatrix}$	$\begin{pmatrix} . & f & . \\ f & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} f & . & . \\ . & -f & . \\ . & . & . \end{pmatrix}$	
	$\begin{matrix} A_1 \\ A_1(z) \\ A_1' \\ A_1' \\ A_{1g} \end{matrix}$	$\begin{matrix} A_2(z) \\ A_2 \\ A_2' \\ A_2' \\ A_{2g} \end{matrix}$	$\begin{matrix} E_1(x, y) \\ E_1(y, -x) \\ E'' \\ E'' \\ E_{1g} \end{matrix}$	$\begin{matrix} E_2 \\ E_2 \\ E'(x, y) \\ E'(y, -x) \\ E_{2g} \end{matrix}$			
		$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & g \\ . & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & . \\ g & . & . \end{pmatrix}$			

Cubic

$\begin{matrix} 23 \\ m\bar{3} \end{matrix}$	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & a \end{pmatrix}$	$\begin{pmatrix} b & . & . \\ . & b & . \\ . & . & -2b \end{pmatrix}$	$\begin{pmatrix} -\sqrt{3}b & . & . \\ . & \sqrt{3}b & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & c \\ . & c & . \end{pmatrix}$	$\begin{pmatrix} . & . & c \\ . & . & . \\ c & . & . \end{pmatrix}$	$\begin{pmatrix} . & c & . \\ c & . & . \\ . & . & . \end{pmatrix}$	
	$\begin{matrix} A \\ A_g \end{matrix}$	$\begin{matrix} E \\ E_g \end{matrix}$		$\begin{matrix} F(x, y, z) \\ F_g \end{matrix}$			
					$\begin{pmatrix} . & . & . \\ . & . & d \\ . & -d & . \end{pmatrix}$	$\begin{pmatrix} . & . & d \\ . & . & . \\ -d & . & . \end{pmatrix}$	$\begin{pmatrix} . & d & . \\ . & . & . \\ . & . & . \end{pmatrix}$

$\begin{matrix} 432 \\ \bar{4}3m \\ m\bar{3}m \end{matrix}$	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & a \end{pmatrix}$	$\begin{pmatrix} b & . & . \\ . & b & . \\ . & . & -2b \end{pmatrix}$	$\begin{pmatrix} -\sqrt{3}b & . & . \\ . & \sqrt{3}b & . \\ . & . & . \end{pmatrix}$		$\begin{pmatrix} . & . & . \\ . & . & c \\ . & c & . \end{pmatrix}$	$\begin{pmatrix} . & . & c \\ . & . & . \\ c & . & . \end{pmatrix}$	$\begin{pmatrix} . & c & . \\ c & . & . \\ . & . & . \end{pmatrix}$
	$\begin{matrix} A_1 \\ A_1 \\ A_{1g} \end{matrix}$	$\begin{matrix} E \\ E \\ E_g \end{matrix}$		$\begin{matrix} F_1(x, y, z) \\ F_1 \\ F_{1g} \end{matrix}$	$\begin{matrix} F_2 \\ F_2(x, y, z) \\ F_{2g} \end{matrix}$		
					$\begin{pmatrix} . & . & . \\ . & . & d \\ . & -d & . \end{pmatrix}$	$\begin{pmatrix} . & . & d \\ . & . & . \\ -d & . & . \end{pmatrix}$	$\begin{pmatrix} . & d & . \\ . & . & . \\ . & . & . \end{pmatrix}$

(infrared activity) and for Raman scattering are incompatible. This is often expressed as the *mutual exclusion rule* or *complementarity principle*: The excitations in a crystal belonging to a centrosymmetric class cannot be simultaneously active in infrared absorption and in Raman scattering. Let us note, however, that even-parity excitations are not necessarily all Raman active, and that odd-parity excitations are not necessarily infrared active.

In the remaining noncentrosymmetric crystal classes, the excitations have no defined parity with respect to inversion and can be, in principle, both Raman and infrared active.

Example: Consider a Raman scattering experiment on a crystal of tetragonal symmetry, class $4/mmm$. Raman-active phonons, allowed in conventional symmetric scattering, are of the symmetry species A_{1g} , B_{1g} , B_{2g} and E_g . (the A_{2g} species admits purely antisymmetric scattering only). Straightforward application of Table 2.3.3.1 makes it possible to determine the polar-

ization selection rules, *i.e.* to determine which symmetry species will contribute to the scattering cross section in various experimental configurations. Choosing the Cartesian axes $x \equiv [100]$, $y \equiv [010]$, $z \equiv [001]$ consistent with the standard setting of the $4/mmm$ point group, *i.e.* the fourfold rotation axis $4 \parallel \mathbf{z}$, let us further introduce the notation $x' \equiv [110]$, $y' \equiv [\bar{1}10]$. Then the contributions to the cross section for different symmetry species can be distinguished by their dependence on the polarization vectors \mathbf{e}_I and \mathbf{e}_S of the incident and scattered light:

$$A_{1g} : |(e_{Ix}e_{Sx} + e_{Iy}e_{Sy})a + e_{Iz}e_{Sz}b|^2$$

$$B_{1g} : |(e_{Ix}e_{Sx} - e_{Iy}e_{Sy})d|^2$$

$$B_{2g} : |(e_{Ix}e_{Sy} + e_{Iy}e_{Sx})e|^2$$

$$E_g : [(e_{Ix}e_{Sz} + e_{Iz}e_{Sx})^2 + (e_{Iy}e_{Sz} + e_{Iz}e_{Sy})^2]|f|^2.$$

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Table 2.3.3.2. Raman selection rules in crystals of the 4/mmm class

Scattering configuration		Cross section for symmetry species			
Back scattering	Right-angle scattering	A _{1g}	B _{1g}	B _{2g}	E _g
$\bar{z}(xz)z, \bar{z}(yy)z$	$y(xx)z, x(yy)z$	$\sim a ^2$	$\sim d ^2$	—	—
$\bar{x}(zz)x, \bar{y}(zz)y$	$x(zz)y$	$\sim b ^2$	—	—	—
$\bar{z}(xy)z$	$y(xy)x, z(xy)x$	—	—	$\sim e ^2$	—
$\bar{y}(xz)y, \bar{x}(yz)x$	$y(xz)x, x(yz)y$	—	—	—	$\sim f ^2$
$\bar{z}(x'x')z$	$y'(x'x')z$	$\sim a ^2$	—	$\sim e ^2$	—
$\bar{z}(x'y')z$	$y'(x'y')z$	—	$\sim d ^2$	—	—

Examples of some special scattering geometries that permit the separation of the contributions of different symmetry species are shown in Table 2.3.3.2 (five distinct configurations are sufficient to determine the five independent parameters a, b, d, e, f of the symmetric Raman tensors).

If, for some reason, antisymmetric scattering is allowed, possible contribution of the A_{2g} modes should be considered as well. The contribution to cross section from these modes is proportional to $|(e_{Ix}e_{Sy} - e_{Iy}e_{Sx})c|^2$, hence it can be distinguished from the contribution of the B_{2g} symmetry species by a suitable choice of the scattering geometry.

2.3.3.5. Noncentrosymmetric crystals

Special care is required in treating the scattering by those optical phonons in the 21 noncentrosymmetric (*polar*) crystal classes (1, 2, m , 222, $mm2$, 4, $\bar{4}$, 422, $4mm$, $\bar{4}2m$, 3, 32, 3m, 6, $\bar{6}$, 622, $6mm$, $6m2$, 23, 432, $43m$) that are simultaneously infrared-active. Since these polar modes carry a nonzero macroscopic effective charge (2.3.3.4), they contribute to the total polarization in the crystal, hence also to the macroscopic electric field, which in turn leads to a coupling between these modes. The polarization being a *polar vector*, the modes that contribute have the same symmetry character, *i.e.* they must also transform like the components of polar vectors.

An important consequence of the macroscopic field associated with polar modes in the crystal is the partial lifting of the degeneracies of the long-wavelength ($\mathbf{q} \approx 0$) mode frequencies (so-called TO–LO splitting). Since the macroscopic field in the crystal is longitudinal, it must be proportional to the longitudinal component of the polarization. Hence, the equations of motion for all polar modes carrying a nonzero longitudinal polarization (*i.e.* $\mathbf{P}_j \cdot \mathbf{q} \neq 0$) become coupled by the field and, consequently, their frequencies depend on the direction of \mathbf{q} . This phenomenon is called *directional dispersion* and is connected with the fact that in the electrostatic approximation the dynamical matrix with long-range Coulomb forces shows non-analytic behaviour for $\mathbf{q} \rightarrow 0$. In lattice dynamics, the limit can be treated correctly by taking into account the retardation effects in the range where cq becomes comparable to $\omega_j(\mathbf{q})$, *i.e.* in the crossing region of free photon and optical phonon dispersion curves. As a result, one finds that for small \mathbf{q} the true eigenmodes of the system – *polaritons* – have a mixed phonon–photon character and their frequencies show strong dispersion in the very close vicinity of $\mathbf{q} = 0$. Experimentally, this *polariton* region is partially accessible only in near-forward Raman scattering [see (2.3.2.3)]. For larger scattering wavevectors in the usual right-angle or back-scattering geometries, the electrostatic approximation, $cq \gg \omega$, is well applicable and the excitations behave like phonons. Owing to the coupling *via* the longitudinal macroscopic electric field, however, the directional dispersion of these phonon branches remains.

Detailed analysis is complicated in the general case of a low-symmetry crystal with more polar modes (see *e.g.* Claus *et al.*, 1975). In crystals with at least orthorhombic symmetry, the principal axes of the susceptibility tensor are fixed by symmetry

and for the wavevectors oriented along these principal axes the polar optic modes have purely transverse (TO) or longitudinal (LO) character with respect to the associated polarization. The character of a mode is usually mixed for a general direction of the wavevector.

Strictly speaking, conventional symmetry analysis in terms of irreducible representations of the factor group (point group) of the crystal, though giving a true description of polaritons at $\mathbf{q} = 0$, cannot account for the lifting of degeneracies and for the directional dispersion of polar modes. A correct picture of the symmetries and degeneracies is, however, obtained by taking into account the finiteness of the wavevector \mathbf{q} and classifying the vibrations according to the irreducible (*multiplier*) corepresentations of the *point group of the wavevector* $G_0(\mathbf{q})$, which is a subgroup of the factor group. Compatibility relations of the representations at $\mathbf{q} \rightarrow 0$ can then be used to establish a correspondence between the two approaches.

The oscillating macroscopic field associated with long-wavelength LO polar modes acts as another source of modulation of the susceptibility. In addition to the standard atomic displacement contribution connected with the mechanical displacements of atoms, one also has to consider that the transition susceptibility also contains the electro-optic term arising from the distortion of electron shells of atoms in the accompanying macroscopic field \mathbf{E} . Separating both contributions, we may write

$$\begin{aligned} \delta\chi_{\alpha\beta}^{(j)}(\mathbf{q} \approx 0, \omega_l) &= \frac{d\chi_{\alpha\beta}}{dQ_j} Q_j \\ &= \frac{\partial\chi_{\alpha\beta}}{\partial Q_j} Q_j + \frac{\partial\chi_{\alpha\beta}}{\partial E_\gamma} E_\gamma^j \\ &= \left(\frac{\partial\chi_{\alpha\beta}}{\partial Q_j} + \frac{\partial\chi_{\alpha\beta}}{\partial E_\gamma} \frac{dE_\gamma}{dQ_j} \right) Q_j, \end{aligned} \tag{2.3.3.15}$$

or, in terms of the Raman tensor,

$$\delta\chi = \sum_j \mathbf{R}^j Q_j = \sum_j (\mathbf{a}^j Q_j + \mathbf{b}E^j) = \sum_j [\mathbf{a}^j + \mathbf{b}(d\mathbf{E}/dQ_j)] Q_j,$$

where we introduce the notation \mathbf{a}^j and $\mathbf{b}(d\mathbf{E}/dQ_j)$ for the *atomic displacement* and *electro-optic* contributions to the Raman tensor \mathbf{R}^j . As usual, Q_j stands for the normal coordinate of the j th mode and \mathbf{E} for the total macroscopic electric field resulting from the longitudinal polarization of all optic modes. The modes that contribute to \mathbf{E} are only LO polar modes; they transform as Cartesian components of polar vectors (x, y, z). Hence the electro-optic term contributes to the Raman cross section only if $\mathbf{E}^j = (d\mathbf{E}/dQ_j) \neq 0$, *i.e.* if the mode has at least partially longitudinal character. Hence, not only the frequencies but also the scattering cross sections of the TO and LO components of polar modes belonging to the same symmetry species are, in general, different.

Nevertheless, in view of the fact that the macroscopic electric field associated with LO polar phonons transforms in the same way as its polarization vector, the symmetry properties of both the atomic displacement and the electro-optic contributions to the Raman tensors of polar modes are identical. They correspond to *third-rank polar tensors*, which have nonzero components only in *piezoelectric crystals*. The symmetry-restricted form of these tensors can also be derived from Table 2.3.3.1 by combining the matrices corresponding to the x, y and z components. Note that these may belong to different irreducible representations in lower-symmetry classes (*e.g.* z cannot mix with x, y), and that in some uniaxial classes the z component is missing completely. Finally, in the noncentrosymmetric class 32 of the cubic system, the Raman tensors of the triply degenerate polar modes (F_1) are purely antisymmetric; therefore all components of the piezoelectric tensor also vanish.

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Table 2.3.3.3. Raman selection rules in crystals of the $4mm$ class

Scattering configuration		Cross section for symmetry species	
		A_1	E
$\mathbf{q} \parallel \mathbf{z}$	$z(xx)z, z(yy)z$	$\sim a_{LO} ^2$	—
$\mathbf{q} \perp \mathbf{z}$	$x(zz)x, x(zz)y$	$\sim b_{TO} ^2$	—
	$\bar{y}(xz)y, \bar{x}(yz)x$	—	$\sim f_{TO} ^2$
	$x'(zx')y', x'(y'z)y'$	—	$\frac{1}{2} f_{TO} ^2 + \frac{1}{2} f_{LO} ^2$

Example: To illustrate the salient features of polar-mode scattering let us consider a crystal of the $4mm$ class, where of the Raman-active symmetry species the modes $A_1(z)$ and $E(x, y)$ are polar. According to Table 2.3.3.1, their ($\mathbf{q} = 0$) Raman tensors are identical to those of the A_{1g} and E_g modes in the preceding example of a $4/mmm$ -class crystal. Owing to the macroscopic electric field, however, here one has to expect directional dispersion of the frequencies of the long wavelength ($\mathbf{q} \approx 0$) A_1 and E optic phonon modes according to their longitudinal or transverse character. Consequently, in determining the polarization selection rules, account has to be taken of the direction of the phonon wavevector (*i.e.* the scattering wavevector) \mathbf{q} with respect to the crystallographic axes. Since for a general direction of \mathbf{q} the modes are coupled by the field, a suitable experimental arrangement permitting the efficient separation of their respective contributions should have the scattering wavevector \mathbf{q} oriented along principal directions. At $\mathbf{q} \parallel \mathbf{z}$, the A_1 phonons are longitudinal (LO_{\parallel}) and both E modes ($2TO_{\perp}$) are transverse, remaining degenerate, whereas at $\mathbf{q} \parallel \mathbf{x}$ or $\mathbf{q} \parallel \mathbf{y}$, the A_1 phonons become transverse (TO_{\perp}) and the E phonons split into a pair of (TO_{\perp}, LO_{\perp}) modes of different frequencies. The subscripts \parallel or \perp explicitly indicate the orientation of the electric dipole moment carried by the mode with respect to the fourfold axis ($4 \parallel \mathbf{c} \equiv \mathbf{z}$).

Schematically, the situation (*i.e.* frequency shifts and splittings) at $\mathbf{q} \approx 0$ can be represented by

	$\mathbf{q} \parallel \mathbf{z}$	$\mathbf{q} \parallel \mathbf{x}$	
	—	—	$A_1(TO_{\parallel})$
$A_1(LO_{\parallel})$	—	—	$E_x(LO_{\perp})$
$E(2TO_{\perp})$	—	—	$E_y(TO_{\perp})$

For a general direction of \mathbf{q} , the modes are of a mixed character and their frequencies show directional (angular) dispersion. The overall picture depends on the number of A_1 and E phonons present in the given crystal, as well as on their effective charges and on the ordering of their eigenfrequencies. In fact, only the $E(TO_{\perp})$ modes remain unaffected by the directional dispersion.

Table 2.3.3.3 gives the corresponding contributions of these modes to the cross section for several representative scattering geometries, where subscripts TO and LO indicate that the components of the total Raman tensor may take on different values for TO and LO modes due to electro-optic contributions in the latter case.

2.3.3.6. \mathbf{q} -dependent terms

So far, we have not explicitly considered the dependence of the Raman tensor on the magnitude of the scattering wavevector, assuming $\mathbf{q} \rightarrow 0$ (the effects of directional dispersion in the case of scattering by polar modes were briefly mentioned in the preceding section). In some cases, however, the Raman tensors vanish in this limit, or \mathbf{q} -dependent corrections to the scattering may appear. Formally, we may expand the susceptibility in a Taylor series in \mathbf{q} . The coefficients in this expansion are higher-order susceptibility derivatives taken at $\mathbf{q} = 0$. The symmetry-restricted form of these tensorial coefficients may be determined in the same way as that of the zero-order term, *i.e.* by decomposing the reducible representation of the third-, fourth- and

higher-order polar Cartesian tensors into irreducible components $\Gamma(j)$. General properties of the \mathbf{q} -dependent terms can be advantageously discussed in connection with the so-called *morphic* effects (see Sections 2.3.4 and 2.3.5).

2.3.4. Morphic effects in Raman scattering

By *morphic* effects we understand the effects that arise from a reduction of the symmetry of a system caused by the application of *external forces*. The relevant consequences of morphic effects for Raman scattering are changes in the selection rules. Applications of external forces may, for instance, render it possible to observe scattering by excitations that are otherwise inactive. Again, group-theoretical arguments may be applied to obtain the symmetry-restricted component form of the Raman tensors under applied forces.

It should be noted that under external forces in this sense various ‘built-in’ fields can be included, *e.g.* electric fields or elastic strains typically occurring near the crystal surfaces. Effects of ‘intrinsic’ macroscopic electric fields associated with long-wavelength LO polar phonons can be treated on the same footing. Spatial-dispersion effects connected with the finiteness of the wavevectors, \mathbf{q} or \mathbf{k} , may also be included among morphic effects, since they may be regarded as being due to the gradients of the fields (displacement or electric) propagating in the crystal.

2.3.4.1. General remarks

Various types of applied forces – in a general sense – can be classified according to symmetry, *i.e.* according to their transformation properties. Thus a force is characterized as a *polar* force if it transforms under the symmetry operation of the crystal like a polar tensor of appropriate rank (rank 1: electric field \mathbf{E} ; rank 2: electric field gradient $\nabla\mathbf{E}$, stress \mathbf{T} or strain \mathbf{S}). It is an *axial* force if it transforms like an axial tensor (rank 1: magnetic field \mathbf{H}). Here we shall deal briefly with the most important cases within the macroscopic approach of the susceptibility derivatives. We shall treat explicitly the first-order scattering only and neglect, for the moment, \mathbf{q} -dependent terms.

In a perturbation approach, the first-order transition susceptibility $\delta\chi$ in the presence of an applied force \mathbf{F} can be expressed in terms of Raman tensors $\mathbf{R}^j(\mathbf{F})$ expanded in powers of \mathbf{F} :

$$\delta\chi(\mathbf{F}) = \sum_j \mathbf{R}^j(\mathbf{F})Q_j,$$

$$\text{where } \mathbf{R}^j(\mathbf{F}) = \mathbf{R}^{j0} + \mathbf{R}^{jF}\mathbf{F} + \frac{1}{2}\mathbf{R}^{jFF}\mathbf{F}\mathbf{F} + \dots$$

(2.3.4.1)

Here, $\mathbf{R}^{j0} = \chi^{(j)}(0) = (\partial\chi_{\alpha\beta}/\partial Q_j)$ is the zero-field *intrinsic* Raman tensor, whereas the tensors

$$\mathbf{R}^{jF}\mathbf{F} = \left(\frac{\partial^2 \chi_{\alpha\beta}}{\partial Q_j \partial F_{\mu}} \right) F_{\mu},$$

$$\mathbf{R}^{jFF}\mathbf{F}\mathbf{F} = \left(\frac{\partial^3 \chi_{\alpha\beta}}{\partial Q_j \partial F_{\mu} \partial F_{\nu}} \right) F_{\mu} F_{\nu} \text{ etc.} \quad (2.3.4.2)$$

are the *force-induced* Raman tensors of the respective order in the field, associated with the j th normal mode. The scattering cross section for the j th mode becomes proportional to $|\mathbf{e}_s(\mathbf{R}^{j0} + \mathbf{R}^{jF}\mathbf{F} + \frac{1}{2}\mathbf{R}^{jFF}\mathbf{F}\mathbf{F} + \dots)\mathbf{e}_l|^2$, which, in general, may modify the polarization selection rules. If, for example, the mode is *intrinsically* Raman inactive, *i.e.* $\mathbf{R}^{j0} = 0$ whereas $\mathbf{R}^{jF} \neq 0$, we deal with purely force-induced Raman scattering; its intensity is proportional to F^2 in the first order. Higher-order terms must be investigated if, for symmetry reasons, the first-order terms vanish.

For force-induced Raman activity, in accordance with general rules, invariance again requires that a particular symmetry species $\Gamma(j)$ can contribute to the first-order transition susceptibility by terms of order n in the force only if the identity