

## 2.3. Raman scattering

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### 2.3.1. Introduction

The term Raman scattering, traditionally used for light scattering by molecular vibrations or optical lattice vibrations in crystals, is often applied in a general sense to a vast variety of phenomena of inelastic scattering of photons by various excitations in molecules, solids or liquids. In crystals these excitations may be collective (phonons, plasmons, polaritons, magnons) or single-particle (electrons, electron–hole pairs, vibrational and electronic excitation of impurities). Raman scattering provides an important tool for the study of the properties of these excitations. In the present chapter, we shall briefly review the general features of Raman scattering in perfect crystals on a phenomenological basis, paying special attention to the consequences of the crystal symmetry. Our focus will be mainly on Raman scattering by vibrational excitations of the crystal lattice – *phonons*. Nevertheless, most of the conclusions have general validity and may be (with possible minor modifications) transferred also to inelastic scattering by other excitations.

### 2.3.2. Inelastic light scattering in crystals – basic notions

Although quantum concepts must be used in any complete theory of inelastic scattering, basic insight into the problem may be obtained from a semiclassical treatment. In classical terms, the origin of inelastically scattered light in solids should be seen in the modulation of the dielectric susceptibility of a solid by elementary excitations. The exciting light polarizes the solid and the polarization induced *via* the modulated part of the susceptibility is re-radiated at differently shifted frequencies. Thus inelastic scattering of light by the temporal and spatial fluctuations of the dielectric susceptibility that are induced by elementary excitations provides information about the symmetry and wavevector-dependent frequencies of the excitations themselves as well as about their interaction with electromagnetic waves.

#### 2.3.2.1. Kinematics

Let us consider the incident electromagnetic radiation, the scattered electromagnetic radiation and the elementary excitation to be described by plane waves. The incident radiation is characterized by frequency  $\omega_I$ , wavevector  $\mathbf{k}_I$  and polarization vector  $\mathbf{e}_I$ . Likewise, the scattered radiation is characterized by  $\omega_S$ ,  $\mathbf{k}_S$  and  $\mathbf{e}_S$ :

$$\mathbf{E}_{I,S}(\mathbf{r}, t) = E_{I,S} \mathbf{e}_{I,S} \exp(i\mathbf{k}_{I,S} \cdot \mathbf{r} - \omega t). \quad (2.3.2.1)$$

The scattering process involves the annihilation of the incident photon, the emission or annihilation of one or more quanta of elementary excitations and the emission of a scattered photon. The scattering is characterised by a *scattering frequency*  $\omega$  (also termed the *Raman shift*) corresponding to the energy transfer  $\hbar\omega$  from the radiation field to the crystal, and by a *scattering wavevector*  $\mathbf{q}$  corresponding to the respective momentum transfer  $\hbar\mathbf{q}$ . Since the energy and momentum must be conserved in the scattering process, we have the conditions

$$\begin{aligned} \omega_I - \omega_S &= \omega, \\ \mathbf{k}_I - \mathbf{k}_S &= \mathbf{q}. \end{aligned} \quad (2.3.2.2)$$

Strictly speaking, the momentum conservation condition is valid only for sufficiently large, perfectly periodic crystals. It is further assumed that there is no significant absorption of the incident and

scattered light beams, so that the wavevectors may be considered real quantities.

Since the photon wavevectors ( $\mathbf{k}_I$ ,  $\mathbf{k}_S$ ) and frequencies ( $\omega_I$ ,  $\omega_S$ ) are related by the dispersion relation  $\omega = ck/n$ , where  $c$  is the speed of light in free space and  $n$  is the refractive index of the medium at the respective frequency, the energy and wavevector conservation conditions imply for the magnitude of the scattering wavevector  $q$

$$c^2 q^2 = n_I^2 \omega_I^2 + n_S^2 (\omega_I - \omega)^2 - 2n_I n_S \omega_I (\omega_I - \omega) \cos \varphi, \quad (2.3.2.3)$$

where  $\varphi$  is the *scattering angle* (the angle between  $\mathbf{k}_I$  and  $\mathbf{k}_S$ ). This relation defines in the  $(\omega, q)$  plane the region of wavevectors and frequencies accessible to the scattering. This relation is particularly important for scattering by excitations whose frequencies depend markedly on the scattering wavevector (*e.g.* acoustic phonons, polaritons *etc.*).

#### 2.3.2.2. Cross section

In the absence of any excitations, the incident field  $\mathbf{E}_I$  at frequency  $\omega_I$  induces in the crystal the polarization  $\mathbf{P}$ , related to the field by the *linear* dielectric susceptibility tensor  $\chi$  ( $\varepsilon_0$  is the permittivity of free space):

$$\mathbf{P} = \varepsilon_0 \chi(\omega_I) \mathbf{E}_I. \quad (2.3.2.4)$$

The linear susceptibility  $\chi(\omega_I)$  is understood to be independent of position, depending on the crystal characteristics and on the frequency of the radiation field only. In the realm of nonlinear optics, additional terms of higher order in the fields may be considered; they are expressed through the respective *nonlinear* susceptibilities.

The effect of the excitations is to modulate the wavefunctions and the energy levels of the medium, and can be represented macroscopically as an additional contribution to the linear susceptibility. Treating this modulation as a perturbation, the resulting contribution to the susceptibility tensor, the so-called *transition susceptibility*  $\delta\chi$  can be expressed as a Taylor expansion in terms of *normal coordinates*  $Q_j$  of the excitations:

$$\chi \rightarrow \chi + \delta\chi, \quad \text{where } \delta\chi = \sum_j \chi^{(j)} Q_j + \sum_{j,j'} \chi^{(j,j')} Q_j Q_{j'} + \dots \quad (2.3.2.5)$$

The tensorial coefficients  $\chi^{(j)}$ ,  $\chi^{(j,j')}$ , ... in this expansion are, in a sense, *higher-order susceptibilities* and are often referred to as *Raman tensors* (of the first, second and higher orders). They are obviously related to *susceptibility derivatives* with respect to the normal coordinates of the excitations. The time-dependent polarization induced by  $\delta\chi$  *via* time dependence of the normal coordinates can be regarded as the source of the inelastically scattered radiation.

The central quantity in the description of Raman scattering is the *spectral differential cross section*, defined as the relative rate of energy loss from the incident beam (frequency  $\omega_I$ , polarization  $\mathbf{e}_I$ ) as a result of its scattering (frequency  $\omega_S$ , polarization  $\mathbf{e}_S$ ) in volume  $V$  into a unit solid angle and unit frequency interval. The corresponding formula may be concisely written as (see *e.g.* Hayes & Loudon, 1978)

$$\frac{d^2\sigma}{d\Omega d\omega_S} = \frac{\omega_S^3 \omega_I V^2 n_S}{(4\pi)^2 c^4 n_I} \left| \mathbf{e}_I \delta\chi \mathbf{e}_S \right|_{\omega}^2. \quad (2.3.2.6)$$

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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  $\omega_s$  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* ( $\sigma_{\text{tot}}$ ):

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

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  $\omega_s$  (or Raman shift  $\omega$ ) 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  $10^5 \text{ cm}^{-1}$ , 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,  $\kappa$  ( $\kappa = 1, \dots, s$ ) is the index of the atom (mass  $m_\kappa$ ) 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  $\kappa$ th atom in the unit cell. Owing to dynamic contributions of ionic deformability, it is not a scalar but rather a  $(3 \times 3)$  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  $\omega_j$  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  $\alpha, \beta$ . 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  $\omega$  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  $\omega_I$  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*  $\Gamma_{\text{PV}}$  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 ( $T_\alpha$ ). 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  $\Phi$  (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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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 <sub>g</sub>	B B(z) B <sub>g</sub>	E(x, y) E(x, -y) E <sub>g</sub>	
	$\begin{pmatrix} . & c & . \\ -c & . & . \\ . & . & . \end{pmatrix}$		$\begin{pmatrix} . & . & g \\ . & . & i \\ -g & -i & . \end{pmatrix}$	$\begin{pmatrix} . & . & -i \\ . & . & g \\ i & -g & . \end{pmatrix}$

422 4mm 4̄2 <sub>x</sub> m <sub>xy</sub> 4m <sub>x</sub> 2 <sub>xy</sub> 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 <sub>1</sub> A <sub>1</sub> (z)	A <sub>2</sub> (z) A <sub>2</sub>	B <sub>1</sub> B <sub>1</sub>	B <sub>2</sub> B <sub>2</sub>	E(-y, x) E(x, y)	
	A <sub>1</sub> A <sub>1</sub>	A <sub>2</sub> A <sub>2</sub>	B <sub>1</sub> B <sub>1</sub>	B <sub>2</sub> (z) B <sub>2</sub> (z)	E(y, x) E(-x, y)	
	A <sub>1g</sub>	A <sub>2g</sub>	B <sub>1g</sub>	B <sub>2g</sub>	E <sub>g</sub>	
		$\begin{pmatrix} . & c & . \\ -c & . & . \\ . & . & . \end{pmatrix}$			$\begin{pmatrix} . & . & g \\ . & . & i \\ -g & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & g \\ . & -g & . \end{pmatrix}$

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 <sub>g</sub>	E(x, y) E <sub>g</sub>	
	$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & i \\ . & . & g \\ -i & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & i \\ g & -i & . \end{pmatrix}$

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

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

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

## 2. SYMMETRY ASPECTS OF EXCITATIONS

Table 2.3.3.1 (cont.)

Hexagonal

	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$	$\begin{pmatrix} . & . & e \\ . & . & d \\ e & d & . \end{pmatrix}$	$\begin{pmatrix} . & . & -d \\ . & . & e \\ -d & e & . \end{pmatrix}$	$\begin{pmatrix} c & f & . \\ f & -c & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} f & -c & . \\ -c & -f & . \\ . & . & . \end{pmatrix}$
6 6 6/m	A(z) A' A <sub>g</sub>	E <sub>1</sub> (x, y) E'' E <sub>1g</sub>		E <sub>2</sub> E'(x, y) E <sub>2g</sub>	
	$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & i \\ . & . & g \\ -i & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & i \\ g & -i & . \end{pmatrix}$		

	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$		$\begin{pmatrix} . & . & . \\ . & . & d \\ . & d & . \end{pmatrix}$	$\begin{pmatrix} . & . & -d \\ . & . & . \\ -d & . & . \end{pmatrix}$	$\begin{pmatrix} . & f & . \\ f & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} f & . & . \\ . & -f & . \\ . & . & . \end{pmatrix}$
622 6mm 6m, 2y 62x, my 6/mmm	A <sub>1</sub> A <sub>1</sub> (z) A <sub>1</sub> ' A <sub>1</sub> ' A <sub>1g</sub>	A <sub>2</sub> (z) A <sub>2</sub> A <sub>2</sub> ' A <sub>2</sub> ' A <sub>2g</sub>	E <sub>1</sub> (x, y) E <sub>1</sub> (y, -x) E'' E'' E <sub>1g</sub>		E <sub>2</sub> E <sub>2</sub> E'(x, y) E'(y, -x) E <sub>2g</sub>	
		$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & g \\ . & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & . \\ g & . & . \end{pmatrix}$		

Cubic

	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & a \end{pmatrix}$	$\begin{pmatrix} b & . & . \\ . & b & . \\ . & . & -2b \end{pmatrix}$	$\begin{pmatrix} -\sqrt{3}b & . & . \\ . & \sqrt{3}b & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & c \\ . & c & . \end{pmatrix}$	$\begin{pmatrix} . & . & c \\ . & . & . \\ c & . & . \end{pmatrix}$	$\begin{pmatrix} . & c & . \\ c & . & . \\ . & . & . \end{pmatrix}$
23 m3	A A <sub>g</sub>	E E <sub>g</sub>		F(x, y, z) F <sub>g</sub>		
				$\begin{pmatrix} . & . & . \\ . & . & d \\ . & -d & . \end{pmatrix}$	$\begin{pmatrix} . & . & d \\ . & . & . \\ -d & . & . \end{pmatrix}$	$\begin{pmatrix} . & d & . \\ . & . & . \\ . & . & . \end{pmatrix}$

	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & a \end{pmatrix}$	$\begin{pmatrix} b & . & . \\ . & b & . \\ . & . & -2b \end{pmatrix}$	$\begin{pmatrix} -\sqrt{3}b & . & . \\ . & \sqrt{3}b & . \\ . & . & . \end{pmatrix}$		$\begin{pmatrix} . & . & . \\ . & . & c \\ . & c & . \end{pmatrix}$	$\begin{pmatrix} . & . & c \\ . & . & . \\ c & . & . \end{pmatrix}$	$\begin{pmatrix} . & c & . \\ c & . & . \\ . & . & . \end{pmatrix}$
432 43m m3m	A <sub>1</sub> A <sub>1</sub> A <sub>1g</sub>	E E E <sub>g</sub>	F <sub>1</sub> (x, y, z) F <sub>1</sub> F <sub>1g</sub>		F <sub>2</sub> F <sub>2</sub> (x, y, z) F <sub>2g</sub>		
			$\begin{pmatrix} . & . & . \\ . & . & d \\ . & -d & . \end{pmatrix}$	$\begin{pmatrix} . & . & d \\ . & . & . \\ -d & . & . \end{pmatrix}$	$\begin{pmatrix} . & d & . \\ . & . & . \\ . & . & . \end{pmatrix}$		

(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<sub>1g</sub>, B<sub>1g</sub>, B<sub>2g</sub> and E<sub>g</sub>. (the A<sub>2g</sub> 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:

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

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

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

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

## 2.3. RAMAN SCATTERING

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 <sub>1g</sub>	B <sub>1g</sub>	B <sub>2g</sub>	E <sub>g</sub>
$\bar{z}(xz)z, \bar{z}(yy)z$	$y(xx)z, x(yy)z$	$\sim  a ^2$	$\sim  d ^2$	—	—
$\bar{x}(zz)x, \bar{y}(zz)y$	$x(zz)y$	$\sim  b ^2$	—	—	—
$\bar{z}(xy)z$	$y(xy)x, z(xy)x$	—	—	$\sim  e ^2$	—
$\bar{y}(xz)y, \bar{x}(yz)x$	$y(xz)x, x(yz)y$	—	—	—	$\sim  f ^2$
$\bar{z}(x'x')z$	$y'(x'x')z$	$\sim  a ^2$	—	$\sim  e ^2$	—
$\bar{z}(x'y')z$	$y'(x'y')z$	—	$\sim  d ^2$	—	—

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<sub>2g</sub> 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<sub>2g</sub> 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

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

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  $\mathbf{F}$ :

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

$$\text{where } \mathbf{R}^j(\mathbf{F}) = \mathbf{R}^j_0 + \mathbf{R}^{jF}\mathbf{F} + \frac{1}{2}\mathbf{R}^{jFF}\mathbf{F}\mathbf{F} + \dots$$

$$(2.3.4.1)$$

Here,  $\mathbf{R}^j_0 = \chi^{(j)}(0) = (\partial\chi_{\alpha\beta}/\partial Q_j)$  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  $|\mathbf{e}_s(\mathbf{R}^j_0 + \mathbf{R}^{jF}\mathbf{F} + \frac{1}{2}\mathbf{R}^{jFF}\mathbf{F}\mathbf{F} + \dots)\mathbf{e}_l|^2$ , which, in general, may modify the polarization selection rules. If, for example, the mode is *intrinsically* Raman inactive, *i.e.*  $\mathbf{R}^j_0 = 0$  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

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representation is contained in the reducible representation of the  $n$ th-order Raman tensor.

An equivalent formulation is that the  $n$ th-order tensor-like coefficients in the corresponding force-induced Raman tensor, *i.e.*

$$R_{\alpha\beta\mu\dots\nu}^{jF\dots F} = \left( \frac{\partial^{1+n} \chi_{\alpha\beta}}{\partial Q_j \partial F_\mu \dots \partial F_\nu} \right) \text{ in the term } \mathbf{R}^{jF\dots F} \mathbf{F} \dots \mathbf{F},$$

vanish identically for symmetry reasons unless  $[\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}] \otimes [\Gamma(\mathbf{F})]_S^n \supset \Gamma(j)$ . Here  $[\Gamma(\mathbf{F})]_S^n = [\Gamma(\mathbf{F}) \otimes \Gamma(\mathbf{F}) \otimes \dots \otimes \Gamma(\mathbf{F})]_S$  is the *symmetrized  $n$ th power* of the representation  $\Gamma(\mathbf{F})$  according to which the generalized force  $\mathbf{F}$  transforms under the operation of the point group. The requirement for the symmetrized part is dictated by the interchangeability of the higher-order derivatives with respect to the components of the force. We recall that the first factor representing the susceptibility,  $[\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]$ , need not be symmetric in general. However, for most purposes (non-resonant conditions, non-magnetic crystals in the absence of a magnetic field) it can be replaced by its symmetrized part  $[\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_S$ .

Standard group-theoretical methods can be used to determine the force-induced Raman activity in a given order of the field and to derive the matrix form of the corresponding Raman tensors. Before treating several important cases of morphic effects in more detail in the following sections, let us make a few comments.

Beside the force-induced effects on the scattering tensors, there are also the direct morphic effects of the forces on the excitations themselves (possible frequency shifts, lifting of mode degeneracies *etc.*), which can be investigated by an analogous perturbation treatment, *i.e.* by expanding the dynamical matrix in powers of  $\mathbf{F}$  and determining the corresponding force-induced corrections in the respective orders.

The lifting of degeneracies is a typical sign of the fact that the symmetry of the problem is reduced. The extended system *crystal + applied force* corresponds to a new symmetry group resulting from those symmetry operations that leave the extended system invariant. Consequently, the new normal modes (in the long-wavelength limit) can be formally classified according to the new point group appropriate for the extended system, which qualitatively accounts for the new reduced symmetries and degeneracies.

The force-induced Raman tensors referring to the original crystal symmetry should thus be equivalent to the Raman tensors of the corresponding modes in the new point group *via* the compatibility relations. The new point-group symmetry of the extended system is often used to investigate Raman-induced activity. It should be noted, however, that this approach generally fails to predict to what order in the force the induced changes in the Raman tensors appear. Such information is usually of prime importance for the scattering experiment, where appropriate

setup and detection techniques can be applied to search for a force-induced effect of a particular order. Thus the perturbation method is usually preferable (Anastassakis, 1980).

In the following sections, we shall briefly treat the most important cases in the conventional limit  $\mathbf{q} \rightarrow 0$  (neglecting for the moment the spatial dispersion).

#### 2.3.4.2. Electric-field-induced scattering

Expanding the linear dielectric susceptibility into a Taylor series in the field, we write

$$\chi_{\alpha\beta}(\mathbf{E}) = \chi_{\alpha\beta}(0) + \frac{\partial \chi_{\alpha\beta}}{\partial E_\gamma} E_\gamma + \frac{\partial^2 \chi_{\alpha\beta}}{\partial E_\gamma \partial E_\delta} E_\gamma E_\delta + \dots \quad (2.3.4.3)$$

The coefficients of the field-dependent terms in this expansion are, respectively, third-, fourth- and higher-rank polar tensors; they describe linear, quadratic and higher-order *electro-optic effects*. The corresponding expansion of the Raman tensor of the  $j$ th optic mode is written as  $\mathbf{R}^j(\mathbf{E}) = \mathbf{R}^{j0} + \mathbf{R}^{jE} \mathbf{E} + \frac{1}{2} \mathbf{R}^{jEE} \mathbf{E} \mathbf{E} + \dots$

Since the representation  $\Gamma(\mathbf{E}) = \Gamma_{\text{PV}}$ , the coefficients of the linear term in the expansion for  $\chi$ , *i.e.* the third-rank tensor  $b_{\alpha\beta\gamma} = (\partial \chi_{\alpha\beta} / \partial E_\gamma)$ , transform according to the reducible representation given by the direct product:

$$[\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_S \otimes \Gamma_{\text{PV}}.$$

First-order field-induced Raman activity (conventional symmetric scattering) is thus obtained by reducing this representation into irreducible components  $\Gamma(j)$ . Higher-order contributions are treated analogously.

It is clear that in centrosymmetric crystals the reduction of a third-rank polar tensor cannot contain even-parity representations; consequently, electric-field-induced scattering by even-parity modes is forbidden in the first order (and in all odd orders) in the field. The lowest non-vanishing contributions to the field-induced Raman tensors of even-parity modes in these crystals are thus quadratic in  $\mathbf{E}$ ; their form is obtained by reducing the representation of a fourth-rank symmetric polar tensor  $[\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_S \otimes [\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_S$  into irreducible components  $\Gamma(j)$ . On the other hand, since the electric field removes the centre of inversion, scattering by odd-parity modes becomes allowed in first order in the field but remains forbidden in all even orders. In noncentrosymmetric crystals, parity considerations do not apply.

For completeness, we note that, besides the direct electro-optic contribution to the Raman tensor due to field-induced distortion of the electronic states of the atoms in the unit cell, there are two additional mechanisms contributing to the total first-order change of the dielectric susceptibility in an external electric field  $\mathbf{E}$ . They come, respectively, from field-induced relative displacements of atoms due to field-induced excitation of polar optical phonons  $Q_p(\mathbf{E}) \sim \mathbf{E}$  and from field-induced elastic deformation  $\mathbf{S}(\mathbf{E}) = \mathbf{d}\mathbf{E}$  (*piezoelectric effect*,  $\mathbf{d}$  being the piezoelectric tensor).

Table 2.3.4.1. Symmetrized (*s*) and antisymmetrized (*a*) sets of trilinear basis functions corresponding to symmetry species of the  $4mm$  class

Species	Basis functions	Symmetry
A <sub>1</sub>	$(x_1 x_2 + y_1 y_2) z_3; z_1 z_2 z_3; (x_1 z_2 + z_1 x_2) x_3 + (y_1 z_2 + z_1 y_2) y_3$	(s)
	$(x_1 z_2 - z_1 x_2) x_3 + (y_1 z_2 - z_1 y_2) y_3$	(a)
A <sub>2</sub>	$(x_1 z_2 + z_1 x_2) y_3 - (y_1 z_2 + z_1 y_2) x_3$	(s)
	$(x_1 y_2 - y_1 x_2) z_3; (x_1 z_2 - z_1 x_2) y_3 - (y_1 z_2 - z_1 y_2) x_3$	(a)
B <sub>1</sub>	$(x_1 x_2 - y_1 y_2) z_3; (x_1 z_2 + z_1 x_2) x_3 - (y_1 z_2 + z_1 y_2) y_3$	(s)
	$(x_1 z_2 - z_1 x_2) x_3 - (y_1 z_2 - z_1 y_2) y_3$	(a)
B <sub>2</sub>	$(x_1 y_2 + y_1 x_2) z_3; (x_1 z_2 + z_1 x_2) y_3 + (y_1 z_2 + z_1 y_2) x_3$	(s)
	$(x_1 z_2 - z_1 x_2) y_3 + (y_1 z_2 - z_1 y_2) x_3$	(a)
E	$[(x_1 x_2 + y_1 y_2) x_3, (x_1 x_2 + y_1 y_2) y_3]; [z_1 z_2 x_3, z_1 z_2 y_3]; [(x_1 z_2 + z_1 x_2) z_3, (y_1 z_2 + z_1 y_2) z_3]; [(x_1 x_2 - y_1 y_2) x_3, -(x_1 x_2 - y_1 y_2) y_3]; [(x_1 y_2 + y_1 x_2) y_3, (x_1 y_2 + y_1 x_2) x_3]$	(s)
	$[(x_1 z_2 - z_1 x_2) z_3, (y_1 z_2 - z_1 y_2) z_3]; [(x_1 y_2 - y_1 x_2) y_3, -(x_1 y_2 - y_1 x_2) x_3]$	(a)

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In order to separate these contributions, we write formally  $\chi(\mathbf{E}) = \chi(\mathbf{E}, Q_p(\mathbf{E}), \mathbf{S}(\mathbf{E}))$  and get, to first order in the field,

$$\begin{aligned} \delta\chi(\mathbf{E}) &= (\partial\chi/\partial\mathbf{E})\mathbf{E} + \sum_p (\partial\chi/\partial Q_p)Q_p(\mathbf{E}) + (\partial\chi/\partial\mathbf{S})\mathbf{S}(\mathbf{E}) \\ &= \sum_j \mathbf{R}^{jE}\mathbf{E}Q_j, \text{ where we define} \\ \mathbf{R}^{jE} &= (\partial\mathbf{R}^j/\partial\mathbf{E}) + \sum_p (\partial\mathbf{R}^j/\partial Q_p)(dQ_p/d\mathbf{E}) + (\partial\mathbf{R}^j/\partial\mathbf{S})\mathbf{d}. \end{aligned} \quad (2.3.4.4)$$

The first term in these equations involves the susceptibility derivative  $\mathbf{b} = (\partial\chi/\partial\mathbf{E})$  at constant  $Q_p$  and  $\mathbf{S}$ . The second term involves the second-order susceptibility derivatives with respect to the normal coordinates:  $\chi^{(j,p)} = (\partial^2\chi/\partial Q_j\partial Q_p) = (\partial\mathbf{R}_{\alpha\beta}^j/\partial Q_p)$ . Since  $Q_p(\mathbf{E}) \sim Z_{pv}E_v$ , where the quantity  $\mathbf{Z}_p = (Z_{pv})$  is the effective charge tensor (2.3.3.4) of the normal mode  $p$ , its nonzero contributions are possible only if there are infrared-active optical phonons (for which, in principle,  $\mathbf{Z}_p \neq 0$ ) in the crystal. The third term is proportional to the field-induced elastic strain  $\mathbf{S}(\mathbf{E}) = d\mathbf{E}$  via the elasto-optic tensor  $\mathbf{p} = (\partial\chi/\partial\mathbf{S})$  and can occur only in piezoelectric crystals.

*Example:* As an illustration, we derive the matrix form of linear electric-field-induced Raman tensors (including possible antisymmetric part) in a tetragonal crystal of the  $4mm$  class. The corresponding representation  $[\Gamma_{PV} \otimes \Gamma_{PV}] \otimes \Gamma_{PV}$  in this class reduces as follows:

$$\begin{aligned} [\Gamma_{PV} \otimes \Gamma_{PV}]_S \otimes \Gamma_{PV} &= 3A_1 \oplus A_2 \oplus 2B_1 \oplus 2B_2 \oplus 5E, \\ [\Gamma_{PV} \otimes \Gamma_{PV}]_A \otimes \Gamma_{PV} &= A_1 \oplus 2A_2 \oplus B_1 \oplus B_2 \oplus 2E. \end{aligned}$$

Suitable sets of symmetrized ( $s$ ) and antisymmetrized ( $a$ ) basis functions (third-order polynomials) for the representations of the  $4mm$  point group can be easily derived by inspection or using projection operators. The results are given in Table 2.3.4.1. Using these basis functions, one can readily construct the Cartesian form of the linear contributions to the electric-field-induced Raman tensors  $\mathbf{R}^i(\mathbf{E}) = \mathbf{R}^{iE}\mathbf{E}$  for all symmetry species of the  $4mm$ -class crystals. The tensors are split into symmetric (conventional allowed scattering) and antisymmetric part.

Symmetric	Antisymmetric
$A_1 : \begin{pmatrix} a_1 E_z & \cdot & a_2 E_x \\ \cdot & a_1 E_z & a_2 E_y \\ a_2 E_x & a_2 E_y & b_1 E_z \end{pmatrix}$	$+ \begin{pmatrix} \cdot & \cdot & a_3 E_x \\ \cdot & \cdot & a_3 E_y \\ -a_3 E_x & -a_3 E_y & \cdot \end{pmatrix}$
$A_2 : \begin{pmatrix} \cdot & \cdot & c_2 E_y \\ \cdot & \cdot & -c_2 E_x \\ c_2 E_y & -c_2 E_x & \cdot \end{pmatrix}$	$+ \begin{pmatrix} \cdot & c_1 E_z & c_3 E_y \\ -c_1 E_z & \cdot & -c_3 E_x \\ -c_3 E_y & c_3 E_x & \cdot \end{pmatrix}$
$B_1 : \begin{pmatrix} d_1 E_z & \cdot & d_2 E_x \\ \cdot & -d_1 E_z & -d_2 E_y \\ d_2 E_x & -d_2 E_y & \cdot \end{pmatrix}$	$+ \begin{pmatrix} \cdot & \cdot & d_3 E_x \\ \cdot & \cdot & -d_3 E_y \\ -d_3 E_x & d_3 E_y & \cdot \end{pmatrix}$
$B_2 : \begin{pmatrix} \cdot & e_1 E_z & e_2 E_y \\ e_1 E_z & \cdot & e_2 E_x \\ e_2 E_y & e_2 E_x & \cdot \end{pmatrix}$	$+ \begin{pmatrix} \cdot & \cdot & e_3 E_y \\ \cdot & \cdot & e_3 E_x \\ -e_3 E_y & -e_3 E_x & \cdot \end{pmatrix}$
$E : \begin{pmatrix} (f_1 + f_2)E_x & f_4 E_y & f_5 E_z \\ f_4 E_y & (f_1 - f_2)E_x & \cdot \\ f_5 E_z & \cdot & f_3 E_x \end{pmatrix}$	$+ \begin{pmatrix} \cdot & g_4 E_y & g_5 E_z \\ -g_4 E_y & \cdot & \cdot \\ -g_5 E_z & \cdot & \cdot \end{pmatrix}$
$\begin{pmatrix} (f_1 - f_2)E_y & f_4 E_x & \cdot \\ f_4 E_x & (f_1 + f_2)E_y & f_3 E_z \\ \cdot & f_3 E_z & f_3 E_y \end{pmatrix}$	$+ \begin{pmatrix} \cdot & -g_4 E_x & \cdot \\ g_4 E_x & \cdot & g_5 E_z \\ \cdot & -g_5 E_z & \cdot \end{pmatrix}$

### 2.3.4.3. Raman scattering in a magnetic field

In a magnetic field, the dielectric susceptibility tensor of a crystal is known to obey the general relation (Onsager reciprocity theorem for generalized kinetic coefficients)

$$\chi_{\alpha\beta}(\mathbf{H}) = \chi_{\beta\alpha}(-\mathbf{H}). \quad (2.3.4.5)$$

Further, in the absence of absorption, the susceptibility must be Hermitian, *i.e.*

$$\chi_{\alpha\beta}(\mathbf{H}) = \chi_{\beta\alpha}^*(\mathbf{H}). \quad (2.3.4.6)$$

Hence,  $\chi(\mathbf{H})$  is neither symmetric nor real. Expanding  $\chi(\mathbf{H})$  in the powers of the field,

$$\chi_{\alpha\beta}(\mathbf{H}) = \chi_{\alpha\beta}(0) + \frac{\partial\chi_{\alpha\beta}}{\partial H_\mu} H_\mu + \frac{\partial^2\chi_{\alpha\beta}}{\partial H_\mu\partial H_\nu} H_\mu H_\nu + \dots, \quad (2.3.4.7)$$

it follows that all terms of the magnetic-field-induced Raman tensor that are of odd powers in  $\mathbf{H}$  are purely imaginary and antisymmetric in  $\alpha$  and  $\beta$ , whereas all terms of even powers in  $\mathbf{H}$  are real and symmetric.

Let us discuss in more detail the symmetry properties of the first-order term, which can be written as

$$\Delta\chi_{\alpha\beta}(\mathbf{H}) = if_{\alpha\beta\mu}H_\mu, \quad (2.3.4.8)$$

where the tensor  $\mathbf{f}$ , referred to as the *magneto-optic tensor*, is real and purely antisymmetric in the first two indices:

$$f_{\alpha\beta\nu} \equiv -i(\partial\chi_{\alpha\beta}/\partial H_\nu) = -f_{\beta\alpha\nu}.$$

The representation  $\Gamma(\mathbf{f})$  of the magneto-optic tensor  $\mathbf{f}$  may thus be symbolically written as

$$\begin{aligned} \Gamma(\mathbf{f}) &= [\Gamma_{PV} \otimes \Gamma_{PV}]_A \otimes \Gamma_{AV} = \Gamma_{AV} \otimes \Gamma_{AV} = \Gamma_{PV} \otimes \Gamma_{PV} \\ &= \Gamma(T_\alpha T_\beta), \end{aligned} \quad (2.3.4.9)$$

since the antisymmetric part of the product of two polar vectors transforms like an axial vector, and the product of two axial vectors transforms exactly like the product of two polar vectors. Hence, the representation  $\Gamma(\mathbf{f})$  is equivalent to the representation of a general nonsymmetric second-rank tensor and reduces in exactly the same way (2.3.3.14).

$$\Gamma(\mathbf{f}) = \Gamma_{PV} \otimes \Gamma_{PV} = c^{(1)}\Gamma(1) \oplus c^{(2)}\Gamma(2) \oplus \dots$$

We arrive thus at the important conclusion that, to first order in the field, only the modes that normally show intrinsic Raman activity (either symmetric and antisymmetric) can take part in magnetic-field-induced scattering. Moreover, the magnetic-field-induced Raman tensors for these symmetry species must have the same number of components as the general nonsymmetric Raman tensors at zero field.

In order to determine the symmetry-restricted matrix form of the corresponding field-induced Raman tensors (linear in  $\mathbf{H}$ ) in Cartesian coordinates, one can use the general method and construct the tensors from the respective (antisymmetric) basis functions. In this case, however, a simpler method can be adopted, which makes use of the transformation properties of the magneto-optic tensor as follows.

From the definition of the tensor  $\mathbf{f}$ , it is clear that its Cartesian components  $f_{\alpha\beta\nu}$  must have the same symmetry properties as the product  $[E_\alpha E_\beta]_A H_\nu$ . The antisymmetric factor  $[E_\alpha E_\beta]_A$  transforms, however, as  $\varepsilon_{\alpha\beta\mu}H_\mu$ , where  $\varepsilon_{\alpha\beta\mu}$  is the fully antisymmetric third-rank pseudotensor (*Levi-Civita tensor*). Consequently,  $f_{\alpha\beta\nu}$  must transform in the same way as  $\varepsilon_{\alpha\beta\mu}H_\mu H_\nu$ , which in turn transforms identically to  $\varepsilon_{\alpha\beta\mu}E_\mu E_\nu$ . Therefore, comparison of the matrices corresponding to the irreducible components  $\Gamma(j)$  provides a simple mapping between the components of the Cartesian forms of the linear field-induced Raman tensors  $\mathbf{R}^i(\mathbf{H}) = \mathbf{R}^{iH}\mathbf{H}$  and the intrinsic Raman tensors  $\mathbf{R}^j$ . Explicitly, this mapping is given by

$$R_{\alpha\beta\nu}^{iH} \equiv \frac{\partial^2\chi_{\alpha\beta}}{\partial Q_j\partial H_\nu} = if_{\alpha\beta\nu}^{(j)} \leftarrow i\varepsilon_{\alpha\beta\mu}R_{\mu\nu}^j. \quad (2.3.4.10)$$

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For any given symmetry species, this relation can be used to deduce the matrix form of the first-order field-induced Raman tensors from the tensors given in Table 2.3.3.1.

*Example:* We consider again the  $4mm$  class crystal. The representation  $\Gamma(\mathbf{f})$  of the magneto-optic tensor  $\mathbf{f}$  in the  $4mm$  class reduces as follows:

$$\Gamma(\mathbf{f}) = \Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}} = 2A_1 \oplus A_2 \oplus B_1 \oplus B_2 \oplus 2E.$$

Straightforward application of the mapping mentioned above then gives the following symmetry-restricted matrix forms of contributions to the magnetic-field-induced Raman tensors  $\mathbf{R}^{jH}$  for all symmetry species of the  $4mm$ -class crystals. The number of independent parameters for each species is the same as in the intrinsic nonsymmetric zero-field Raman tensors:

$$\begin{aligned} A_1 : & \begin{pmatrix} \cdot & ib'H_z & -ia'H_y \\ -ib'H_z & \cdot & ia'H_x \\ ia'H_y & -ia'H_x & \cdot \end{pmatrix} \\ A_2 : & \begin{pmatrix} \cdot & \cdot & ic'H_x \\ \cdot & \cdot & ic'H_y \\ -ic'H_x & -ic'H_y & \cdot \end{pmatrix} \\ B_1 : & \begin{pmatrix} \cdot & \cdot & id'H_y \\ \cdot & \cdot & id'H_x \\ -id'H_y & -id'H_x & \cdot \end{pmatrix} \\ B_2 : & \begin{pmatrix} \cdot & \cdot & -ie'H_x \\ \cdot & \cdot & ie'H_y \\ ie'H_x & -ie'H_y & \cdot \end{pmatrix} \\ E : & \begin{pmatrix} \cdot & ig'H_x & \cdot \\ -ig'H_x & \cdot & if'H_z \\ \cdot & -if'H_z & \cdot \\ \cdot & ig'H_y & -if'H_z \\ -ig'H_y & \cdot & \cdot \\ if'H_z & \cdot & \cdot \end{pmatrix}. \end{aligned}$$

Let us note that the conclusions mentioned above apply, strictly speaking, to non-magnetic crystals. In magnetic materials in the presence of spontaneous ordering (*ferro-* or *antiferromagnetic* crystals) the analysis has to be based on magnetic point groups.

#### 2.3.4.4. Stress- (strain-) induced Raman scattering

Stress-induced Raman scattering is an example of the case when the external 'force' is a higher-rank tensor. In the case of stress, we deal with a symmetric second-rank tensor. Since symmetric stress ( $\mathbf{T}$ ) and strain ( $\mathbf{S}$ ) tensors have the same symmetry and are uniquely related *via* the fourth-rank *elastic stiffness tensor* ( $\mathbf{c}$ ),

$$T_{\alpha\beta} = c_{\alpha\beta\mu\nu} S_{\mu\nu},$$

it is immaterial for symmetry purposes whether stress- or strain-induced effects are considered. The linear strain-induced contribution to the susceptibility can be written as

$$\Delta\chi_{\alpha\beta}(\mathbf{S}) = \left( \frac{\partial\chi_{\alpha\beta}}{\partial S_{\mu\nu}} \right) S_{\mu\nu}$$

so that the respective strain coefficients (conventional symmetric scattering) transform evidently as

$$[\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_{\text{S}} \otimes [\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_{\text{S}},$$

*i.e.* they have the same symmetry as the *piezo-optic* or *elasto-optic* tensor. Reducing this representation into irreducible components  $\Gamma(j)$ , we obtain the symmetry-restricted form of the linear strain-induced Raman tensors. Evidently, their matrix form is the same as for quadratic electric-field-induced Raman tensors. In centrosymmetric crystals, strain-induced Raman scattering (in any order in the strain) is thus allowed for even-parity modes only.

#### 2.3.5. Spatial-dispersion effects

For  $\mathbf{q} = 0$ , the normal modes correspond to a homogeneous phonon displacement pattern (all cells vibrate in phase). Phenomenologically, the  $\mathbf{q}$ -dependence of Raman tensors can be understood as a kind of morphic effect due to the gradients of the displacement field. Developing the contribution of the long-wavelength  $j$ th normal mode to the susceptibility in Cartesian components of the displacement of atoms in the primitive cell and their gradients, we obtain

$$\delta\chi_{\alpha\beta}^{(j)}(\mathbf{q}) = \sum_{\kappa} \left( \frac{\partial\chi_{\alpha\beta}}{\partial u_{\kappa,\gamma}^{(j)}} \right)_0 u_{\kappa,\gamma}^{(j)}(\mathbf{q}) + i \sum_{\kappa} \left( \frac{\partial\chi_{\alpha\beta}}{\partial(\nabla u_{\kappa,\gamma}^{(j)})_{\delta}} \right)_0 q_{\delta} u_{\kappa,\gamma}^{(j)}(\mathbf{q}), \quad (2.3.5.1)$$

where the derivatives are taken at  $\mathbf{q} = 0$ , and we use the obvious relation  $\nabla u_{\kappa,\gamma}^{(j)} = i\mathbf{q}u_{\kappa,\gamma}^{(j)}$ .

Transforming to normal coordinates, using (2.3.3.1), we identify the  $\mathbf{q} = 0$  intrinsic Raman tensor  $\mathbf{R}^{j0}$  of the  $j$ th normal mode, explicitly expressed *via* Cartesian displacements of atoms,

$$R_{\alpha\beta}^{j0} \equiv \chi_{\alpha\beta}^{(j)}(0) \equiv \left( \frac{\partial\chi_{\alpha\beta}}{\partial Q_j} \right) = \sum_{\kappa} \left( \frac{\partial\chi_{\alpha\beta}}{\partial u_{\kappa,\mu}} \right) \frac{e_{\kappa,\mu}(0, j)}{\sqrt{Nm_{\kappa}}}, \quad (2.3.5.2)$$

and introduce the first-order  $\mathbf{q}$ -induced atomic displacement Raman tensor coefficients  $\mathbf{R}^{jq}$ :

$$\begin{aligned} R_{\alpha\beta\gamma}^{jq} & \equiv -i \left( \frac{\partial\chi_{\alpha\beta}}{\partial q_{\gamma}} \right) = -i \left( \frac{\partial^2\chi_{\alpha\beta}}{\partial Q_j \partial q_{\gamma}} \right) \\ & = \sum_{\kappa} \left( \frac{\partial\chi_{\alpha\beta}}{\partial(\nabla u_{\kappa,\mu})_{\gamma}} \right) \frac{e_{\kappa,\mu}(0, j)}{\sqrt{Nm_{\kappa}}}. \end{aligned} \quad (2.3.5.3)$$

Hence, to the lowest order in  $\mathbf{q}$ , the transition susceptibility is expressed as

$$\delta\chi_{\alpha\beta}^{(j)}(\mathbf{q}) \cong \left( R_{\alpha\beta}^{j0} + iR_{\alpha\beta\gamma}^{jq} q_{\gamma} \right) Q_j(0). \quad (2.3.5.4)$$

In a more general case, spatial dispersion should be considered together with the electro-optic contributions due to the internal macroscopic field  $\mathbf{E}$  and its gradients. Assuming the linear susceptibility to be modulated by the atomic displacements  $Q_j$  and the macroscopic electric field  $\mathbf{E}$  as well as by their gradients  $\nabla Q_j$  and  $\nabla \mathbf{E}$ , we can expand the transition susceptibility of the  $j$ th phonon mode  $Q_j(\mathbf{q})$  to terms linear in  $\mathbf{q}$  and formally separate the atomic displacement and electro-optic parts of the Raman tensor [see (2.3.3.15)]:

$$\begin{aligned} \delta\chi^{(j)}(\mathbf{q}) & = (\partial\chi/\partial Q_j) Q_j(\mathbf{q}) + i(\partial\chi/\partial \nabla Q_j) \mathbf{q} Q_j(\mathbf{q}) \\ & \quad + (\partial\chi/\partial \mathbf{E}) \mathbf{E}^j(\mathbf{q}) + i(\partial\chi/\partial \nabla \mathbf{E}) \mathbf{q} \mathbf{E}^j(\mathbf{q}), \end{aligned}$$

or concisely

$$\delta\chi^{(j)}(\mathbf{q}) = \mathbf{a}^j(\mathbf{q}) Q_j(\mathbf{q}) + \mathbf{b}(\mathbf{q}) \mathbf{E}^j(\mathbf{q}),$$

with

$$\mathbf{a}^j(\mathbf{q}) = (\mathbf{a}^{j0} + i\mathbf{a}^{jq} \mathbf{q}), \quad \mathbf{b}(\mathbf{q}) = (\mathbf{b}^0 + i\mathbf{b}^q \mathbf{q}). \quad (2.3.5.5)$$

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Hence, setting  $\mathbf{E}^j(\mathbf{q}) = (d\mathbf{E}/dQ_j)Q_j(\mathbf{q})$ , we write for the total Raman tensor

$$\mathbf{R}^j(\mathbf{q}) = \mathbf{a}^j(\mathbf{q}) + \mathbf{b}(\mathbf{q})(d\mathbf{E}/dQ_j). \quad (2.3.5.6)$$

The definitions of the tensors  $\mathbf{a}^j$  and  $\mathbf{a}^{jq}$  correspond to (2.3.5.2) and (2.3.5.3). Analogously, the tensors  $\mathbf{b}^0$  and  $\mathbf{b}^q$  are defined by

$$b_{\alpha\beta\gamma}^0 = \left( \frac{\partial \chi_{\alpha\beta}}{\partial E_\gamma} \right), \quad b_{\alpha\beta\gamma\delta}^q = -i \left( \frac{\partial^2 \chi_{\alpha\beta}}{\partial q_\gamma \partial E_\delta} \right) = \left( \frac{\partial \chi_{\alpha\beta}}{\partial (\nabla E_\delta)_\gamma} \right). \quad (2.3.5.7)$$

The  $\mathbf{q}$ -independent part  $\mathbf{a}^{j0}$  of the atomic displacement Raman tensor corresponds to the standard  $\mathbf{q} = 0$  Raman tensors  $\mathbf{R}^{j0}$ , whose symmetry properties and matrix form were discussed in Section 2.3.3.3.

Like  $\mathbf{a}^{j0}$ , the form of the  $\mathbf{q}$ -dependent contribution  $\mathbf{a}^{jq}$  also depends on the symmetry properties of the corresponding normal coordinate  $Q_j(\mathbf{q} \approx 0)$ . Since  $\mathbf{q}$  (or  $\nabla Q_j$ ) and  $\mathbf{E}$  are polar vectors, the symmetry properties of the  $\mathbf{a}^{jq}$  are identical to those of the coefficients  $\mathbf{R}^{jE}$  of the electric-field-induced Raman tensor discussed in Section 2.3.4.2: they transform according to the  $\mathbf{q} = 0$  representation  $[\Gamma_{PV} \otimes \Gamma_{PV}]_S \otimes \Gamma_{PV} \otimes \Gamma(j)$ . Hence, the symmetry-restricted matrix form of the  $\mathbf{q}$ -dependent contribution to the atomic displacement Raman tensor  $\mathbf{a}^{jq}$  is exactly the same as that of the corresponding electric-field-induced Raman tensor  $\mathbf{R}^{jE}$ . In general, these linear terms must vanish for even-parity modes in centrosymmetric crystals (where the lowest-order non-vanishing contributions to the Raman tensor are quadratic). The third-rank tensor  $\mathbf{b}^0$  corresponds to the first-order susceptibility derivative  $\mathbf{b}$  and the fourth-rank tensor  $\mathbf{b}^q$  to its first-order  $\mathbf{q}$ -dependent part.

As mentioned above, the  $\mathbf{q}$ -independent third-rank polar tensor  $\mathbf{b}^0$  is nonzero only in noncentrosymmetric (piezoelectric) crystals, where it contributes to Raman tensors for polar longitudinal optical (LO) phonons. The corresponding electro-optic terms in  $\mathbf{R}^j$ , connected with the accompanying longitudinal electric field  $\mathbf{E}$ , are given by  $\mathbf{b}^0(d\mathbf{E}/dQ_j)$ . Symmetry arguments imply that the  $\mathbf{q}$ -independent part of such terms must have the same form as the atomic displacement Raman tensor for polar LO phonons, since the corresponding normal coordinates transform as components of polar vectors.

The  $\mathbf{q}$ -dependent part of the electro-optic contribution, the polar fourth-rank tensor  $\mathbf{b}^q = (b_{\alpha\beta\gamma\delta}^q)$ , transforms as  $[\Gamma_{PV} \otimes \Gamma_{PV}]_S^2 \otimes \Gamma_{PV} \otimes \Gamma_{PV}$  and its symmetry properties are similar to those of the quadratic electro-optic tensor (however, as  $\mathbf{q}$  and  $\mathbf{E}$  are not interchangeable, there is no symmetry in the last two indices  $\gamma, \delta$ ). Thus, for finite  $\mathbf{q}$ , the term  $\mathbf{b}^q\mathbf{q}$  has nonzero components in all crystal classes. The corresponding contribution to the Raman tensor, however, is possible only in noncentrosymmetric crystals. Again, because of the  $(d\mathbf{E}/dQ_j)$  factor, the symmetry-restricted matrix form of this contribution for polar LO phonons will be equivalent to that of the  $\mathbf{a}^j\mathbf{q}$  term. As far as symmetry is concerned, the distinction between atomic displacement and electro-optic contributions is therefore immaterial.

The occurrence of  $\mathbf{q}$ -dependent terms leads to polarization selection rules that are generally different from those of intrinsically ( $\mathbf{q} = 0$ ) Raman-active modes. For this reason, this phenomenon is sometimes referred to as *forbidden* scattering. It is often observed under resonance conditions.

We recall that the terms linear in  $\mathbf{q}$ , *i.e.* proportional to displacement gradients and elastic strains, are fundamental for the description of inelastic light scattering by those excitations for which the transition susceptibility identically vanishes in the limit  $\mathbf{q} \rightarrow 0$  regardless of lattice point symmetry. This is the case for scattering by acoustic phonons (*Brillouin scattering*) and also for scattering by plasma waves (plasmons in semiconductors).

We have explicitly considered only the  $\mathbf{q}$ -dependent effects, due to gradients of phonon fields. In general, spatial dispersion

may be also due to the gradients of the electric (or magnetic) field of the incident or scattered photons. The corresponding effects are often referred to as  $\mathbf{k}$ -dependent effects. In view of the wavevector conservation condition (2.3.2.2), the three wavevectors  $\mathbf{q}$ ,  $\mathbf{k}_I$  and  $\mathbf{k}_S$  are always related, which simplifies the symmetry analysis. Without going into details, we note that, microscopically, the  $\mathbf{k}$ -dependent effects come from photon–electron interactions beyond the usual dipole approximation, *i.e.* from multipolar effects. The symmetry-allowed matrix form of the  $\mathbf{k}$ -induced contributions, depending on the nature of the leading microscopic mechanism, can be obtained by standard group-theoretical techniques.

*Example:* As an example we give the symmetry-restricted form for the linear  $\mathbf{q}$ -dependent contribution to the Raman tensors for *Raman-inactive* triply degenerate  $F_{1u}$  modes in the  $m3m$  ( $O_h$ ) class:

$$\mathbf{R}^j = 0; \\ \mathbf{R}^{jq} = \begin{pmatrix} cq_x & bq_y & bq_z \\ bq_y & aq_x & \cdot \\ bq_z & \cdot & aq_x \end{pmatrix}, \begin{pmatrix} aq_y & bq_x & \cdot \\ bq_x & cq_y & bq_z \\ \cdot & bq_z & aq_y \end{pmatrix}, \\ \begin{pmatrix} aq_z & \cdot & bq_x \\ \cdot & aq_z & bq_y \\ bq_x & bq_y & cq_z \end{pmatrix}.$$

The same form of the  $\mathbf{q}$ -dependent contribution holds for Raman-active optic  $F_2$  modes in the  $\bar{4}3m$  ( $T_d$ ) class. The conventional ( $\mathbf{q} = 0$ ) intrinsic Raman tensor of  $F_2$  is nonzero, but has off-diagonal components only. Since these modes are also infrared-active, there is a concomitant splitting of LO and TO frequencies as well as a possible electro-optic contribution to the Raman tensor due to the accompanying longitudinal macroscopic field. If one chooses  $\mathbf{q} \parallel \mathbf{z}$ , for instance, the first two matrices correspond to two degenerate TO modes and the third one to the LO mode. Combining the  $\mathbf{q}$ -independent and  $\mathbf{q}$ -dependent contributions, we get for each triplet of (2TO + LO)  $F_2$  modes

$$\mathbf{R}^{j0} + \mathbf{R}^{jq} = \begin{pmatrix} \cdot & \cdot & bq_z \\ \cdot & \cdot & c_{TO} \\ bq_z & c_{TO} & \cdot \end{pmatrix} \quad j_1 = F_2(\text{TO}_x), \\ \begin{pmatrix} \cdot & \cdot & c_{TO} \\ \cdot & \cdot & bq_z \\ c_{TO} & bq_z & \cdot \end{pmatrix} \quad j_2 = F_2(\text{TO}_y), \\ \begin{pmatrix} aq_z & c_{LO} & \cdot \\ c_{LO} & aq_z & \cdot \\ \cdot & \cdot & dq_z \end{pmatrix} \quad j_3 = F_2(\text{LO}_z).$$

The difference in the parameters  $c_{TO}$  and  $c_{LO}$  is due to the electro-optic contribution to the Raman tensor for the LO mode. In the back-scattering geometry for scattering from the (001) face of the crystal, only the  $\text{LO}_z$  modes can take part. Intrinsic allowed components  $|c_{LO}|^2$  are observable in the crossed ( $xy$ ) polarization geometry, whereas the  $\mathbf{q}$ -dependent terms  $|aq_z|^2$  appear as ‘forbidden’ scattering in parallel ( $xx$ ) or ( $yy$ ) geometries.

### 2.3.6. Higher-order scattering

In higher-order processes, the scattering involves participation of two or more quanta ( $j$  and  $j'$ ) of the elementary excitations. Let us discuss briefly the second-order scattering by phonons, where the energy and wavevector conservation conditions read

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$$\begin{aligned}\omega_I - \omega_S = \omega &= \pm\omega_j \pm \omega_{j'}, \\ \mathbf{k}_I - \mathbf{k}_S = \mathbf{q} &= \pm\mathbf{q}_j \pm \mathbf{q}_{j'}.\end{aligned}\quad (2.3.6.1)$$

The combinations of signs in these equations correspond to four possibilities, in which either both phonons,  $j$  and  $j'$ , are created (Stokes process: ++), both annihilated (anti-Stokes process: --), or one is created and the other annihilated (difference process: +-, -+). If in the Stokes or anti-Stokes case both excitations are of the same type,  $j = j'$ , one speaks of *overtone*s. The corresponding terms in the transition susceptibility are the coefficients of a bilinear combination of normal coordinates in the expansion of  $\delta\chi$ .

In the quasi-static limit, the transition susceptibilities for the second-order scattering correspond, again, to the susceptibility derivatives. Thus, the spectral differential cross section for the second-order scattering (Stokes component) can be formally written as

$$\begin{aligned}\frac{d^2\sigma}{d\omega d\Omega} \approx \sum_{\substack{j,j' \\ \mathbf{q}_j + \mathbf{q}_{j'} = \mathbf{q} \approx 0}} \left| e^{S\alpha} \frac{\partial^2 \chi_{\alpha\beta}}{\partial Q_j^*(\mathbf{q}_j) \partial Q_{j'}^*(\mathbf{q}_{j'})} e^{I\beta} \right|^2 \\ \times \delta[\omega_j(\mathbf{q}_j) + \omega_{j'}(\mathbf{q}_{j'}) - \omega],\end{aligned}$$

with  $\omega = \omega_I - \omega_S > 0$ . In this formula, we have suppressed the universal factors [see (2.3.3.5)] and the explicit expression for the response function (thermal factors). Instead, the *delta* function (response function in the limit of zero damping) expresses the energy-conservation condition.

The wavevector selection rules in the long-wavelength limit, with  $\mathbf{q} = 0$ , imply that  $\mathbf{q}_j = -\mathbf{q}_{j'}$  (the same holds for anti-Stokes components, while  $\mathbf{q}_j = \mathbf{q}_{j'}$  for difference scattering), so the wavevectors themselves need not be small and, in principle, scattering by phonons with all wavevectors from the Brillouin zone can be observed.

Without invoking any symmetry arguments for the Raman activity, such as the restrictions imposed by crystal symmetry on the susceptibility derivatives, it is clear that the intensity of second-order scattering at a frequency  $\omega$  is controlled by the number of those combinations of phonons whose frequencies obey  $\omega = \omega_j(\mathbf{q}) + \omega_{j'}(-\mathbf{q})$ . The quantity determining this number is the combined density of states of phonon pairs, *i.e.*

$$\rho_2(\omega) = \sum_{j,j'} \sum_{\mathbf{q}} \delta[\omega_j(\mathbf{q}) + \omega_{j'}(-\mathbf{q}) - \omega]. \quad (2.3.6.2)$$

This function can be calculated provided the *dispersion curves*  $\omega_j(\mathbf{q})$  of the excitations are known. The density of states is a continuous function and shows features known as the van Hove singularities corresponding to the *critical points*, where one or more components of the gradient  $\nabla_{\mathbf{q}}[\omega_j(\mathbf{q}) + \omega_{j'}(-\mathbf{q})]$  vanish. Most of the critical points occur for wavevectors on the boundary, where the vanishing gradients of the individual dispersion curves are often dictated by the crystal symmetry, but they also occur in those regions of the reciprocal space where both dispersion curves have opposite or equal slopes at the same wavevector  $\mathbf{q}$ . To a first approximation, the second-order spectrum is thus essentially continuous, reflecting the two-phonon density of states, with peaks and sharp features at frequencies close to the positions of the van Hove singularities. This is to be contrasted with the first-order scattering, where (in perfect crystals) only single peaks corresponding to long-wavelength ( $\mathbf{q} \approx 0$ ) phonons occur.

Group-theoretical arguments may again be invoked in deriving the selection rules that determine the Raman activity of a particular combination of excitations (Birman, 1974). The susceptibility derivative again transforms as a tensor. For a given pair of excitations ( $j, \mathbf{q}$ ) and ( $j', -\mathbf{q}$ ) responsible for the modu-

Table 2.3.6.1. *Thermal factors for second-order Raman scattering*

$n(\omega)$  is given by (2.3.3.7).

Factor	Process	Raman shift
$[n(\omega_j) + 1][n(\omega_{j'}) + 1]$	Stokes	$(\omega = \omega_j + \omega_{j'})$
$[n(\omega_j) + 1]n(\omega_{j'})$	Difference	$(\omega = \omega_j - \omega_{j'})$
$n(\omega_j)n(\omega_{j'})$	Anti-Stokes	$(\omega = -\omega_j - \omega_{j'})$

lation, the combined excitation symmetry is obtained by taking the direct product of the irreducible representations of the space group corresponding to the participating excitations,

$$\Gamma(j, j') = D_{j,\mathbf{q}} \otimes D_{j',-\mathbf{q}}. \quad (2.3.6.3)$$

The representation  $\Gamma(j, j')$ , unlike  $D_{j,\mathbf{q}}$ , corresponds to a zero-wavevector representation of the crystal space group and is therefore equivalent to a (reducible) representation of the crystal point group. It can be decomposed into irreducible components. Raman scattering of the pair is allowed if a Raman-active  $\mathbf{q} = 0$  representation is contained in this decomposition of  $\Gamma(j, j')$  or, alternatively, if the product  $[\Gamma_{PV} \otimes \Gamma_{PV}]_S \otimes \Gamma(j, j')$  contains the totally symmetric representation  $\Gamma(1)$ .

The selection rules for the second-order scattering are, in general, far less restrictive than in the first-order case. For example, it can be shown that for a general wavevector  $\mathbf{q}$  in the Brillouin zone there are no selection rules on the participation of phonons in the second-order scattering, since the representations  $\Gamma(j, j')$  contain all Raman-active symmetries. In specific crystal structures, however, restrictions occur for the wavevectors corresponding to special symmetry positions (points, lines or planes) in the Brillouin zone. This implies that the selection rules may suppress some of the van Hove singularities in the second-order spectra.

*Morphic* effects in second-order scattering, due to an applied external force  $\mathbf{F}$  (see Section 2.3.4.1), may be investigated using the same criteria as in first-order scattering, *i.e.* decomposing the  $\mathbf{q} = 0$  representation  $\Gamma(\mathbf{F}) \otimes [\Gamma_{PV} \otimes \Gamma_{PV}]_S \otimes \Gamma(j, j')$  and searching for the matrix form of the corresponding second-order Raman tensors.

Generalization to third- and higher-order processes is obvious.

Concluding this section, we note that in a Raman-scattering experiment, higher-order features in the spectra can in principle be distinguished from first-order features by different behaviour of the differential scattering cross section with temperature. For example, the respective thermal factors entering the expression for the second-order scattering cross section are given in Table 2.3.6.1.

### 2.3.7. Conclusions

In this overview of Raman scattering in crystals, we have almost exclusively based our considerations on a phenomenological, semi-classical viewpoint without going into details of the underlying microscopic theory. This is surely an appropriate approach to a discussion of the fundamental consequences of crystal symmetry on the selection rules governing the varied phenomena of inelastic light scattering and on the symmetry-restricted form of the corresponding tensorial quantities encountered in this vast and fruitful field. We have attempted to treat the most important symmetry aspects of the inelastic scattering of light by collective excitations in perfect crystals, concentrating on scattering by optical phonons – in the traditional sense of Raman scattering studies. Within a limited scope, we tried to give some insight into the nature of the phenomena relevant in connection with this topic. Our coverage is certainly not exhaustive (nor original); we have also deliberately omitted all scattering phenomena connected with purely electronic excitations, although the corresponding symmetry aspects can be analysed on the same footing. The essence of the truth is rather simple: As long as the

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excitations are characterized by *irreducible representations* of the symmetry group of the system, the well proven tools of the theory of representations are at hand to work out the consequences (if common sense does not readily provide the answer).

For an experimental physicist, symmetry analysis is invaluable in designing the experimental arrangement expected to give evidence of some particular phenomenon. The type of answer one may expect from such analysis is characteristic of the group-theoretical predictions. One can learn whether a particular effect is *allowed* or *forbidden*, and – if it is allowed – one can learn *how many* independent coefficients may be needed to describe it. Symmetry analysis alone cannot predict *how large* the effect is, or *why* it occurs, though it may well indicate the way to make it more easily observable. In order to understand or justify its actual magnitude, one has to analyse in greater detail the underlying microphysical mechanisms; however, the analysis must be consistent with restrictions dictated by the symmetry of the problem and, here again, symmetry arguments with powerful group-theoretical tools provide reliable guidance.

For the sake of brevity, citations have been largely suppressed in the present overview. Instead, the relevant sources are included in the list of references.

For detailed information about all the varied aspects of light scattering in solids and recent advances in this vast and fruitful field, the reader is referred to specialized monographs, e.g. Turrell (1972), Hayes & Loudon (1978), and to a comprehensive series edited by Cardona & Güntherodt (1975–).

### 2.3.8. Glossary

$\alpha, \beta, \gamma, \delta, \dots, \mu, \nu$ : Greek indices are used for Cartesian components of vectors and tensors (summation over repeated indices is understood).

<b>a<sub>j</sub></b>	atomic displacement Raman tensor of the <i>j</i> th phonon mode, defined as $\partial\chi/\partial Q_j$
<b>b</b>	susceptibility derivative $\partial\chi/\partial\mathbf{E}$ (closely related to the electro-optic tensor <b>r</b> )
<i>c</i>	velocity of light
<b>c</b>	elastic stiffness tensor
<b>d</b>	piezoelectric tensor
<b>χ</b>	susceptibility tensor
<b>e<sub>I,S</sub></b>	polarization vector of incident and scattered light
<b>e<sub>κ</sub>(<b>q</b>, <i>j</i>)</b>	phonon eigenvector of the <i>j</i> th phonon mode of wavevector <b>q</b>
<b>E</b>	electric field intensity
<b>f</b>	magneto-optic tensor

$\gamma_{j,\mathbf{q}}$	damping constant of mode ( <i>j</i> , <b>q</b> )
<b>H</b>	magnetic field intensity
$\epsilon_0$	permittivity of free space
<b>ε</b>	permittivity tensor
<b>k<sub>I,S</sub></b>	wavevector of incident and scattered light
<i>n<sub>I,S</sub></i>	refractive index for incident and scattered light
<b>P</b>	polarization
<b>q</b>	phonon wavevector
<b>Q<sub>j</sub>(<b>q</b>)</b>	normal coordinate (amplitude of the <i>j</i> th phonon mode of wavevector <b>q</b> )
<b>R<sup>j</sup></b>	Raman tensor of <i>j</i> th phonon mode
<b>S</b>	strain tensor
<b>T</b>	stress tensor
$\sigma$	scattering cross section
$\omega$	angular frequency
<b>Z(<b>q</b>)</b>	effective charge matrix

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