

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

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

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

2.3.3.5. Noncentrosymmetric crystals

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

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

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

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

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

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

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

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.

2. SYMMETRY ASPECTS OF EXCITATIONS

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

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

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 A₁(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 ($\mathbf{q} \approx 0$) A₁ 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 A₁ phonons are longitudinal (LO_{||}) and both E modes (2TO_⊥) are transverse, remaining degenerate, whereas at $\mathbf{q} \parallel \mathbf{x}$ or $\mathbf{q} \parallel \mathbf{y}$, the A₁ phonons become transverse (TO_⊥) and the E phonons split into a pair of (TO_⊥, LO_⊥) 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 (LO)	—	—	A ₁ (TO)
E(2TO _⊥)	—	—	E _x (LO _⊥)
			E _y (TO _⊥)

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 A₁ 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_⊥) 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