

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
q z	$z(xx)z, z(yy)z$	$\sim a_{LO} ^2$	—
q ⊥ 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 A₁(z) and E(x, y) are polar. According to Table 2.3.3.1, their (**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 (**q** ≈ 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) **q** with respect to the crystallographic axes. Since for a general direction of **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 **q** oriented along principal directions. At **q** || **z**, the A₁ phonons are longitudinal (LO_{||}) and both E modes (2TO_⊥) are transverse, remaining degenerate, whereas at **q** || **x** or **q** || **y**, the A₁ phonons become transverse (TO_⊥) and the E phonons split into a pair of (TO_⊥, LO_⊥) modes of different frequencies. The subscripts || or ⊥ explicitly indicate the orientation of the electric dipole moment carried by the mode with respect to the fourfold axis (4 || **c** ≡ **z**).

Schematically, the situation (*i.e.* frequency shifts and splittings) at **q** ≈ 0 can be represented by

	q z	q x	
	—	—	A ₁ (TO)
A ₁ (LO)	—	—	E _x (LO _⊥)
E(2TO _⊥)	—	—	E _y (TO _⊥)

For a general direction of **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. **q**-dependent terms

So far, we have not explicitly considered the dependence of the Raman tensor on the magnitude of the scattering wavevector, assuming **q** → 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 **q**-dependent corrections to the scattering may appear. Formally, we may expand the susceptibility in a Taylor series in **q**. The coefficients in this expansion are higher-order susceptibility derivatives taken at **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 Γ(*j*). General properties of the **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, **q** or **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 **E**; rank 2: electric field gradient ∇**E**, stress **T** or strain **S**). It is an *axial* force if it transforms like an axial tensor (rank 1: magnetic field **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, **q**-dependent terms.

In a perturbation approach, the first-order transition susceptibility δχ in the presence of an applied force **F** can be expressed in terms of Raman tensors **R**^{*i*}(**F**) expanded in powers of **F**:

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

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

(2.3.4.1)

Here, **R**^{*j*}0 = χ^(*j*)(0) = (∂χ_{αβ}/∂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 |**e**_s(**R**^{*j*}0 + **R**^{*j*}F \mathbf{F} + $\frac{1}{2}$ **R**^{*j*}FF $\mathbf{F}\mathbf{F}$ + ...)·**e**_i|², which, in general, may modify the polarization selection rules. If, for example, the mode is *intrinsically* Raman inactive, *i.e.* **R**^{*j*}0 = 0 whereas **R**^{*j*}F ≠ 0, we deal with purely force-induced Raman scattering; its intensity is proportional to F² 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 Γ(*j*) can contribute to the first-order transition susceptibility by terms of order *n* in the force only if the identity