

## 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 <sub>1</sub>	E
<b>q</b> ∥ <b>z</b>	z(xx)z, z(yy)z	~  a <sub>LO</sub>   <sup>2</sup>	—
<b>q</b> ⊥ <b>z</b>	x(zz)x, x(zz)y	~  b <sub>TO</sub>   <sup>2</sup>	—
	$\bar{y}(xz)y, \bar{x}(yz)x$	—	~  f <sub>TO</sub>   <sup>2</sup>
	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<sub>1</sub>(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<sub>1g</sub> and E<sub>g</sub> 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) A<sub>1</sub> 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 A<sub>1</sub> phonons are longitudinal (LO<sub>∥</sub>) and both E modes (2TO<sub>⊥</sub>) are transverse, remaining degenerate, whereas at **q** ∥ **x** or **q** ∥ **y**, the A<sub>1</sub> phonons become transverse (TO<sub>⊥</sub>) and the E phonons split into a pair of (TO<sub>⊥</sub>, LO<sub>⊥</sub>) 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

	<b>q</b> ∥ <b>z</b>	<b>q</b> ∥ <b>x</b>	
	—	—	A <sub>1</sub> (TO <sub>∥</sub> )
A <sub>1</sub> (LO <sub>∥</sub> )	—	—	E <sub>x</sub> (LO <sub>⊥</sub> )
E(2TO <sub>⊥</sub> )	—	—	E <sub>y</sub> (TO <sub>⊥</sub> )

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 A<sub>1</sub> 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<sub>⊥</sub>) 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**<sup>*i*</sup>(**F**) expanded in powers of **F**:

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

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

(2.3.4.1)

Here, **R**<sup>*j*</sup><sub>0</sub> = χ<sup>(*j*)</sup>(0) = (∂χ<sub>αβ</sub>/∂Q<sub>*j*</sub>) 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**<sub>s</sub>(**R**<sup>*j*</sup><sub>0</sub> + **R**<sup>*jF*</sup>**F** +  $\frac{1}{2}$ **R**<sup>*jFF*</sup>**F****F** + ...)·**e**<sub>i</sub>|<sup>2</sup>, which, in general, may modify the polarization selection rules. If, for example, the mode is *intrinsically* Raman inactive, *i.e.* **R**<sup>*j*</sup><sub>0</sub> = 0 whereas **R**<sup>*jF*</sup> ≠ 0, we deal with purely force-induced Raman scattering; its intensity is proportional to F<sup>2</sup> 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

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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)