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, *mm*2, 4, $\bar{4}$, 422, 4*mm*, $\bar{4}2m$, 3, 32, 3*m*, 6, $\bar{6}$, 622, 6*mm*, $\bar{6}2m$, 23, 432, $\bar{4}3m$) 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 $\mathbf{q} \to 0$. 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 $\mathbf{q} \to 0$ 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

$$\delta\chi_{\alpha\beta}^{(j)}(\mathbf{q} \approx 0, \omega_I) = \frac{d\chi_{\alpha\beta}}{dQ_j}Q_j$$

$$= \frac{\partial\chi_{\alpha\beta}}{\partial Q_j}Q_j + \frac{\partial\chi_{\alpha\beta}}{\partial E_\gamma}E_\gamma^j$$

$$= \left(\frac{\partial\chi_{\alpha\beta}}{\partial Q_j} + \frac{\partial\chi_{\alpha\beta}}{\partial E_\gamma}\frac{dE_\gamma}{dQ_j}\right)Q_j,$$

(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 jth 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.

references