2.3. RAMAN SCATTERING

representation is contained in the reducible representation of the nth-order Raman tensor.

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

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

vanish identically for symmetry reasons unless $[\Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}}] \otimes [\Gamma(\mathbf{F})]^n_S \supset \Gamma(j)$. Here $[\Gamma(\mathbf{F})]^n_S = [\Gamma(\mathbf{F}) \otimes \Gamma(\mathbf{F}) \otimes \dots \otimes \Gamma(\mathbf{F})]_S$ is the *symmetrized nth 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, $[\Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}}]$, 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 $[\Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}}]_S$.

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 $\mathbf{q} \to 0$ (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 jth optic mode is written as $\mathbf{R}^j(\mathbf{E}) = \mathbf{R}^{j0} + \mathbf{R}^{jE}\mathbf{E} + \frac{1}{2}\mathbf{R}^{jEE}\mathbf{EE} + \dots$.

Since the representation $\Gamma(\mathbf{E}) = \Gamma_{\mathrm{PV}}$, the coefficients of the linear term in the expansion for χ, *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:

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

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 $[\Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}}]_S \otimes [\Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}}]_S$ 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 $\mathbf{S}(\mathbf{E}) = \mathbf{dE}$ (*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_1	$(x_1x_2 + y_1y_2)z_3$; $z_1z_2z_3$; $(x_1z_2 + z_1x_2)x_3 + (y_1z_2 + z_1y_2)y_3$	(s)
	$(x_1z_2 - z_1x_2)x_3 + (y_1z_2 - z_1y_2)y_3$	(a)
A_2	$(x_1z_2 + z_1x_2)y_3 - (y_1z_2 + z_1y_2)x_3$	(s)
	$(x_1y_2 - y_1x_2)z_3$; $(x_1z_2 - z_1x_2)y_3 - (y_1z_2 - z_1y_2)x_3$	(a)
B_1	$(x_1x_2 - y_1y_2)z_3$; $(x_1z_2 + z_1x_2)x_3 - (y_1z_2 + z_1y_2)y_3$	(s)
	$(x_1z_2 - z_1x_2)x_3 - (y_1z_2 - z_1y_2)y_3$	(a)
B_2	$(x_1y_2 + y_1x_2)z_3$; $(x_1z_2 + z_1x_2)y_3 + (y_1z_2 + z_1y_2)x_3$	(s)
	$(x_1z_2 - z_1x_2)y_3 + (y_1z_2 - z_1y_2)x_3$	(a)
E	$[(x_1x_2 + y_1y_2)x_3, (x_1x_2 + y_1y_2)y_3]$; $[z_1z_2x_3, z_1z_2y_3]$; $[(x_1z_2 + z_1x_2)z_3, (y_1z_2 + z_1y_2)z_3]$; $[(x_1x_2 - y_1y_2)x_3, -(x_1x_2 - y_1y_2)y_3]$; $[(x_1y_2 + y_1x_2)y_3, (x_1y_2 + y_1x_2)x_3]$	(s)
	$[(x_1z_2 - z_1x_2)z_3, (y_1z_1 - z_1y_2)z_3]$; $[(x_1y_2 - y_1x_2)y_3, -(x_1y_2 - y_1x_2)x_3]$	(a)

references