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.*

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

vanish identically for symmetry reasons unless $[\Gamma_{\rm PV} \otimes \Gamma_{\rm PV}] \otimes [\Gamma(\mathbf{F})]^n_S \supset \Gamma(j)$. Here $[\Gamma(\mathbf{F})]^n_S = [\Gamma(\mathbf{F}) \otimes \Gamma(\mathbf{F}) \otimes \ldots \otimes \Gamma(\mathbf{F})]_S$ 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, $[\Gamma_{\rm PV} \otimes \Gamma_{\rm PV}]$, 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 $[\Gamma_{\rm PV} \otimes \Gamma_{\rm PV}]_S$.

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

$$\chi_{\alpha\beta}(\mathbf{E}) = \chi_{\alpha\beta}(0) + \frac{\partial\chi_{\alpha\beta}}{\partial E_\gamma}E_\gamma + \frac{\partial^2\chi_{\alpha\beta}}{\partial E_\gamma \partial E_\delta}E_\gamma E_\delta + \ldots. \qquad (2.3.4.3)$$

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 $\mathbf{R}^j(\mathbf{E}) = \mathbf{R}^{j0} + \mathbf{R}^{jE}\mathbf{E} + \frac{1}{2}\mathbf{R}^{jEE}\mathbf{E}\mathbf{E} + \ldots$.

Since the representation $\Gamma(\mathbf{E}) = \Gamma_{\rm PV}$, 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:

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

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

In order to separate these contributions, we write formally $\chi(\mathbf{E}) = \chi(\mathbf{E}, Q_p(\mathbf{E}), \mathbf{S}(\mathbf{E}))$ and get, to first order in the field,

$$\begin{aligned}\delta\chi(\mathbf{E}) &= (\partial\chi/\partial\mathbf{E})\mathbf{E} + \sum_p (\partial\chi/\partial Q_p) Q_p(\mathbf{E}) + (\partial\chi/\partial\mathbf{S})\mathbf{S}(\mathbf{E}) \\ &= \sum_j \mathbf{R}^{jE}\mathbf{E}Q_j, \text{ where we define} \\ \mathbf{R}^{jE} &= (\partial\mathbf{R}^j/\partial\mathbf{E}) + \sum_p (\partial\mathbf{R}^j/\partial Q_p)(\mathrm{d}Q_p/\mathrm{d}\mathbf{E}) + (\partial\mathbf{R}^j/\partial\mathbf{S})\mathbf{d}.\end{aligned} \tag{2.3.4.4}$$

The first term in these equations involves the susceptibility derivative $\mathbf{b} = (\partial\chi/\partial\mathbf{E})$ at constant Q_p and $\mathbf{S}$. The second term involves the second-order susceptibility derivatives with respect to the normal coordinates: $\chi^{(j,p)} = (\partial^2\chi/\partial Q_j \partial Q_p) = (\partial R^j_{\alpha\beta}/\partial Q_p)$. Since $Q_p(\mathbf{E}) \sim Z_{pv}E_v$, where the quantity $\mathbf{Z}_p = (Z_{pv})$ is the effective charge tensor (2.3.3.4) of the normal mode p, its nonzero contributions are possible only if there are infrared-active optical phonons (for which, in principle, $\mathbf{Z}_p \neq 0$) in the crystal. The third term is proportional to the field-induced elastic strain $\mathbf{S}(\mathbf{E}) = \mathbf{dE}$ *via* the elasto-optic tensor $\mathbf{p} = (\partial\chi/\partial\mathbf{S})$ and can occur only in piezoelectric crystals.

Example: As an illustration, we derive the matrix form of linear electric-field-induced Raman tensors (including possible antisymmetric part) in a tetragonal crystal of the 4*mm* class. The corresponding representation $[\Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}}] \otimes \Gamma_{\mathrm{PV}}$ in this class reduces as follows:

$$\begin{aligned}[\Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}}]_S \otimes \Gamma_{\mathrm{PV}} &= 3\mathrm{A}_1 \oplus \mathrm{A}_2 \oplus 2\mathrm{B}_1 \oplus 2\mathrm{B}_2 \oplus 5\mathrm{E}, \\ [\Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}}]_A \otimes \Gamma_{\mathrm{PV}} &= \mathrm{A}_1 \oplus 2\mathrm{A}_2 \oplus \mathrm{B}_1 \oplus \mathrm{B}_2 \oplus 2\mathrm{E}.\end{aligned}$$

Suitable sets of symmetrized (s) and antisymmetrized (a) basis functions (third-order polynomials) for the representations of the 4*mm* point group can be easily derived by inspection or using projection operators. The results are given in Table 2.3.4.1. Using these basis functions, one can readily construct the Cartesian form of the linear contributions to the electric-field-induced Raman tensors $\mathbf{R}^j(\mathbf{E}) = \mathbf{R}^{jE}\mathbf{E}$ for all symmetry species of the 4*mm*-class crystals. The tensors are split into symmetric (conventional allowed scattering) and antisymmetric part.

	Symmetric	Antisymmetric
A_1 :	$\begin{pmatrix} a_1E_z & . & a_2E_x \\ . & a_1E_z & a_2E_y \\ a_2E_x & a_2E_y & b_1E_z \end{pmatrix}$	$+\begin{pmatrix} . & . & a_3E_x \\ . & . & a_3E_y \\ -a_3E_x & -a_3E_y & . \end{pmatrix}$
A_2 :	$\begin{pmatrix} . & . & c_2E_y \\ . & . & -c_2E_x \\ c_2E_y & -c_2E_x & . \end{pmatrix}$	$+\begin{pmatrix} . & c_1E_z & c_3E_y \\ -c_1E_z & . & -c_3E_x \\ -c_3E_y & c_3E_x & . \end{pmatrix}$
B_1 :	$\begin{pmatrix} d_1E_z & . & d_2E_x \\ . & -d_1E_z & -d_2E_y \\ d_2E_x & -d_2E_y & . \end{pmatrix}$	$+\begin{pmatrix} . & . & d_3E_x \\ . & . & -d_3E_y \\ -d_3E_x & d_3E_y & . \end{pmatrix}$
B_2 :	$\begin{pmatrix} . & e_1E_z & e_2E_y \\ e_1E_z & . & e_2E_x \\ e_2E_y & e_2E_x & . \end{pmatrix}$	$+\begin{pmatrix} . & . & e_3E_y \\ . & . & e_3E_x \\ -e_3E_y & -e_3E_x & . \end{pmatrix}$
E :	$\begin{pmatrix} (f_1+f_2)E_x & f_4E_y & f_5E_z \\ f_4E_y & (f_1-f_2)E_x & . \\ f_5E_z & . & f_3E_x \end{pmatrix}$	$+\begin{pmatrix} . & g_4E_y & g_5E_z \\ -g_4E_y & . & . \\ -g_5E_z & . & . \end{pmatrix}$
	$\begin{pmatrix} (f_1-f_2)E_y & f_4E_x & . \\ f_4E_x & (f_1+f_2)E_y & f_5E_z \\ . & f_5E_z & f_3E_y \end{pmatrix}$	$+\begin{pmatrix} . & -g_4E_x & . \\ g_4E_x & . & g_5E_z \\ . & -g_5E_z & . \end{pmatrix}$

2.3.4.3. *Raman scattering in a magnetic field*

In a magnetic field, the dielectric susceptibility tensor of a crystal is known to obey the general relation (Onsager reciprocity theorem for generalized kinetic coefficients)

$$\chi_{\alpha\beta}(\mathbf{H}) = \chi_{\beta\alpha}(-\mathbf{H}). \tag{2.3.4.5}$$

Further, in the absence of absorption, the susceptibility must be Hermitian, *i.e.*

$$\chi_{\alpha\beta}(\mathbf{H}) = \chi^*_{\beta\alpha}(\mathbf{H}). \tag{2.3.4.6}$$

Hence, $\boldsymbol{\chi}(\mathbf{H})$ is neither symmetric nor real. Expanding $\boldsymbol{\chi}(\mathbf{H})$ in the powers of the field,

$$\chi_{\alpha\beta}(\mathbf{H}) = \chi_{\alpha\beta}(0) + \frac{\partial\chi_{\alpha\beta}}{\partial H_\mu}H_\mu + \frac{\partial^2\chi_{\alpha\beta}}{\partial H_\mu \partial H_\nu}H_\mu H_\nu + \ldots, \tag{2.3.4.7}$$

it follows that all terms of the magnetic-field-induced Raman tensor that are of odd powers in $\mathbf{H}$ are purely imaginary and antisymmetric in α and β, whereas all terms of even powers in $\mathbf{H}$ are real and symmetric.

Let us discuss in more detail the symmetry properties of the first-order term, which can be written as

$$\Delta\chi_{\alpha\beta}(\mathbf{H}) = if_{\alpha\beta\mu}H_\mu, \tag{2.3.4.8}$$

where the tensor $\mathbf{f}$, referred to as the *magneto-optic tensor*, is real and purely antisymmetric in the first two indices:

$$f_{\alpha\beta\nu} \equiv -i(\partial\chi_{\alpha\beta}/\partial H_\nu) = -f_{\beta\alpha\nu}.$$

The representation $\Gamma(\mathbf{f})$ of the magneto-optic tensor $\mathbf{f}$ may thus be symbolically written as

$$\begin{aligned}\Gamma(\mathbf{f}) &= [\Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}}]_A \otimes \Gamma_{\mathrm{AV}} = \Gamma_{\mathrm{AV}} \otimes \Gamma_{\mathrm{AV}} = \Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}} \\ &= \Gamma(T_\alpha T_\beta),\end{aligned} \tag{2.3.4.9}$$

since the antisymmetric part of the product of two polar vectors transforms like an axial vector, and the product of two axial vectors transforms exactly like the product of two polar vectors. Hence, the representation $\Gamma(\mathbf{f})$ is equivalent to the representation of a general nonsymmetric second-rank tensor and reduces in exactly the same way (2.3.3.14).

$$\Gamma(\mathbf{f}) = \Gamma_{\mathrm{PV}} \otimes \Gamma_{\mathrm{PV}} = c^{(1)}\Gamma(1) \oplus c^{(2)}\Gamma(2) \oplus \ldots.$$

We arrive thus at the important conclusion that, to first order in the field, only the modes that normally show intrinsic Raman activity (either symmetric and antisymmetric) can take part in magnetic-field-induced scattering. Moreover, the magnetic-field-induced Raman tensors for these symmetry species must have the same number of components as the general nonsymmetric Raman tensors at zero field.

In order to determine the symmetry-restricted matrix form of the corresponding field-induced Raman tensors (linear in $\mathbf{H}$) in Cartesian coordinates, one can use the general method and construct the tensors from the respective (antisymmetric) basis functions. In this case, however, a simpler method can be adopted, which makes use of the transformation properties of the magneto-optic tensor as follows.

From the definition of the tensor $\mathbf{f}$, it is clear that its Cartesian components $f_{\alpha\beta\nu}$ must have the same symmetry properties as the product $[E_\alpha E_\beta]_A H_\nu$. The antisymmetric factor $[E_\alpha E_\beta]_A$ transforms, however, as $\varepsilon_{\alpha\beta\mu}H_\mu$, where $\varepsilon_{\alpha\beta\mu}$ is the fully antisymmetric third-rank pseudotensor (*Levi–Civita tensor*). Consequently, $f_{\alpha\beta\nu}$ must transform in the same way as $\varepsilon_{\alpha\beta\mu}H_\mu H_\nu$, which in turn transforms identically to $\varepsilon_{\alpha\beta\mu}E_\mu E_\nu$. Therefore, comparison of the matrices corresponding to the irreducible components $\Gamma(j)$ provides a simple mapping between the components of the Cartesian forms of the linear field-induced Raman tensors $\mathbf{R}^j(\mathbf{H}) = \mathbf{R}^{jh}\mathbf{H}$ and the intrinsic Raman tensors $\mathbf{R}^{j0}$. Explicitly, this mapping is given by

$$R^{jH}_{\alpha\beta\nu} \equiv \frac{\partial^2\chi_{\alpha\beta}}{\partial Q_j \partial H_\nu} = if^{(j)}_{\alpha\beta\nu} \;\leftarrow\; i\varepsilon_{\alpha\beta\mu}R^{jo}_{\mu\nu}. \tag{2.3.4.10}$$