

## 2.3. RAMAN SCATTERING

For any given symmetry species, this relation can be used to deduce the matrix form of the first-order field-induced Raman tensors from the tensors given in Table 2.3.3.1.

*Example:* We consider again the  $4mm$  class crystal. The representation  $\Gamma(\mathbf{f})$  of the magneto-optic tensor  $\mathbf{f}$  in the  $4mm$  class reduces as follows:

$$\Gamma(\mathbf{f}) = \Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}} = 2A_1 \oplus A_2 \oplus B_1 \oplus B_2 \oplus 2E.$$

Straightforward application of the mapping mentioned above then gives the following symmetry-restricted matrix forms of contributions to the magnetic-field-induced Raman tensors  $\mathbf{R}^{iH}$  for all symmetry species of the  $4mm$ -class crystals. The number of independent parameters for each species is the same as in the intrinsic nonsymmetric zero-field Raman tensors:

$$\begin{aligned} A_1 : & \begin{pmatrix} \cdot & ib'H_z & -ia'H_y \\ -ib'H_z & \cdot & ia'H_x \\ ia'H_y & -ia'H_x & \cdot \end{pmatrix} \\ A_2 : & \begin{pmatrix} \cdot & \cdot & ic'H_x \\ \cdot & \cdot & ic'H_y \\ -ic'H_x & -ic'H_y & \cdot \end{pmatrix} \\ B_1 : & \begin{pmatrix} \cdot & \cdot & id'H_y \\ \cdot & \cdot & id'H_x \\ -id'H_y & -id'H_x & \cdot \end{pmatrix} \\ B_2 : & \begin{pmatrix} \cdot & \cdot & -ie'H_x \\ \cdot & \cdot & ie'H_y \\ ie'H_x & -ie'H_y & \cdot \end{pmatrix} \\ E : & \begin{pmatrix} \cdot & ig'H_x & \cdot \\ -ig'H_x & \cdot & if'H_z \\ \cdot & -if'H_z & \cdot \\ \cdot & ig'H_y & -if'H_z \\ -ig'H_y & \cdot & \cdot \\ if'H_z & \cdot & \cdot \end{pmatrix}. \end{aligned}$$

Let us note that the conclusions mentioned above apply, strictly speaking, to non-magnetic crystals. In magnetic materials in the presence of spontaneous ordering (*ferro-* or *antiferromagnetic* crystals) the analysis has to be based on magnetic point groups.

## 2.3.4.4. Stress- (strain-) induced Raman scattering

Stress-induced Raman scattering is an example of the case when the external ‘force’ is a higher-rank tensor. In the case of stress, we deal with a symmetric second-rank tensor. Since symmetric stress ( $\mathbf{T}$ ) and strain ( $\mathbf{S}$ ) tensors have the same symmetry and are uniquely related *via* the fourth-rank *elastic stiffness tensor* ( $\mathbf{c}$ ),

$$T_{\alpha\beta} = c_{\alpha\beta\mu\nu} S_{\mu\nu},$$

it is immaterial for symmetry purposes whether stress- or strain-induced effects are considered. The linear strain-induced contribution to the susceptibility can be written as

$$\Delta\chi_{\alpha\beta}(\mathbf{S}) = \left( \frac{\partial\chi_{\alpha\beta}}{\partial S_{\mu\nu}} \right) S_{\mu\nu}$$

so that the respective strain coefficients (conventional symmetric scattering) transform evidently as

$$[\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_{\text{S}} \otimes [\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_{\text{S}},$$

*i.e.* they have the same symmetry as the *piezo-optic* or *elasto-optic* tensor. Reducing this representation into irreducible components  $\Gamma(j)$ , we obtain the symmetry-restricted form of the linear strain-induced Raman tensors. Evidently, their matrix form is the same as for quadratic electric-field-induced Raman tensors. In centrosymmetric crystals, strain-induced Raman scattering (in any order in the strain) is thus allowed for even-parity modes only.

## 2.3.5. Spatial-dispersion effects

For  $\mathbf{q} = 0$ , the normal modes correspond to a homogeneous phonon displacement pattern (all cells vibrate in phase). Phenomenologically, the  $\mathbf{q}$ -dependence of Raman tensors can be understood as a kind of morphic effect due to the gradients of the displacement field. Developing the contribution of the long-wavelength  $j$ th normal mode to the susceptibility in Cartesian components of the displacement of atoms in the primitive cell and their gradients, we obtain

$$\delta\chi_{\alpha\beta}^{(j)}(\mathbf{q}) = \sum_{\kappa} \left( \frac{\partial\chi_{\alpha\beta}}{\partial u_{\kappa,\gamma}^{(j)}} \right)_0 u_{\kappa,\gamma}^{(j)}(\mathbf{q}) + i \sum_{\kappa} \left( \frac{\partial\chi_{\alpha\beta}}{\partial(\nabla u_{\kappa,\gamma}^{(j)})_{\delta}} \right)_0 q_{\delta} u_{\kappa,\gamma}^{(j)}(\mathbf{q}), \quad (2.3.5.1)$$

where the derivatives are taken at  $\mathbf{q} = 0$ , and we use the obvious relation  $\nabla u_{\kappa,\gamma}^{(j)} = i\mathbf{q}u_{\kappa,\gamma}^{(j)}$ .

Transforming to normal coordinates, using (2.3.3.1), we identify the  $\mathbf{q} = 0$  intrinsic Raman tensor  $\mathbf{R}^{j0}$  of the  $j$ th normal mode, explicitly expressed *via* Cartesian displacements of atoms,

$$R_{\alpha\beta}^{j0} \equiv \chi_{\alpha\beta}^{(j)}(0) \equiv \left( \frac{\partial\chi_{\alpha\beta}}{\partial Q_j} \right) = \sum_{\kappa} \left( \frac{\partial\chi_{\alpha\beta}}{\partial u_{\kappa,\mu}} \right) \frac{e_{\kappa,\mu}(0, j)}{\sqrt{Nm_{\kappa}}}, \quad (2.3.5.2)$$

and introduce the first-order  $\mathbf{q}$ -induced atomic displacement Raman tensor coefficients  $\mathbf{R}^{jq}$ :

$$\begin{aligned} R_{\alpha\beta\gamma}^{jq} & \equiv -i \left( \frac{\partial\chi_{\alpha\beta}}{\partial q_{\gamma}} \right) = -i \left( \frac{\partial^2\chi_{\alpha\beta}}{\partial Q_j \partial q_{\gamma}} \right) \\ & = \sum_{\kappa} \left( \frac{\partial\chi_{\alpha\beta}}{\partial(\nabla u_{\kappa,\mu})_{\gamma}} \right) \frac{e_{\kappa,\mu}(0, j)}{\sqrt{Nm_{\kappa}}}. \end{aligned} \quad (2.3.5.3)$$

Hence, to the lowest order in  $\mathbf{q}$ , the transition susceptibility is expressed as

$$\delta\chi_{\alpha\beta}^{(j)}(\mathbf{q}) \cong \left( R_{\alpha\beta}^{j0} + iR_{\alpha\beta\gamma}^{jq} q_{\gamma} \right) Q_j(0). \quad (2.3.5.4)$$

In a more general case, spatial dispersion should be considered together with the electro-optic contributions due to the internal macroscopic field  $\mathbf{E}$  and its gradients. Assuming the linear susceptibility to be modulated by the atomic displacements  $Q_j$  and the macroscopic electric field  $\mathbf{E}$  as well as by their gradients  $\nabla Q_j$  and  $\nabla \mathbf{E}$ , we can expand the transition susceptibility of the  $j$ th phonon mode  $Q_j(\mathbf{q})$  to terms linear in  $\mathbf{q}$  and formally separate the atomic displacement and electro-optic parts of the Raman tensor [see (2.3.3.15)]:

$$\begin{aligned} \delta\chi^{(j)}(\mathbf{q}) & = (\partial\chi/\partial Q_j) Q_j(\mathbf{q}) + i(\partial\chi/\partial \nabla Q_j) \mathbf{q} Q_j(\mathbf{q}) \\ & \quad + (\partial\chi/\partial \mathbf{E}) \mathbf{E}^j(\mathbf{q}) + i(\partial\chi/\partial \nabla \mathbf{E}) \mathbf{q} \mathbf{E}^j(\mathbf{q}), \end{aligned}$$

or concisely

$$\delta\chi^{(j)}(\mathbf{q}) = \mathbf{a}^j(\mathbf{q}) Q_j(\mathbf{q}) + \mathbf{b}(\mathbf{q}) \mathbf{E}^j(\mathbf{q}),$$

with

$$\mathbf{a}^j(\mathbf{q}) = (\mathbf{a}^{j0} + i\mathbf{a}^{jq} \mathbf{q}), \quad \mathbf{b}(\mathbf{q}) = (\mathbf{b}^0 + i\mathbf{b}^q \mathbf{q}). \quad (2.3.5.5)$$

## 2. SYMMETRY ASPECTS OF EXCITATIONS

Hence, setting  $\mathbf{E}^j(\mathbf{q}) = (d\mathbf{E}/dQ_j)Q_j(\mathbf{q})$ , we write for the total Raman tensor

$$\mathbf{R}^j(\mathbf{q}) = \mathbf{a}^j(\mathbf{q}) + \mathbf{b}(\mathbf{q})(d\mathbf{E}/dQ_j). \quad (2.3.5.6)$$

The definitions of the tensors  $\mathbf{a}^j$  and  $\mathbf{a}^{jq}$  correspond to (2.3.5.2) and (2.3.5.3). Analogously, the tensors  $\mathbf{b}^0$  and  $\mathbf{b}^q$  are defined by

$$b_{\alpha\beta\gamma}^0 = \left( \frac{\partial \chi_{\alpha\beta}}{\partial E_\gamma} \right), \quad b_{\alpha\beta\gamma\delta}^q = -i \left( \frac{\partial^2 \chi_{\alpha\beta}}{\partial q_\gamma \partial E_\delta} \right) = \left( \frac{\partial \chi_{\alpha\beta}}{\partial (\nabla E_\delta)_\gamma} \right). \quad (2.3.5.7)$$

The  $\mathbf{q}$ -independent part  $\mathbf{a}^{j0}$  of the atomic displacement Raman tensor corresponds to the standard  $\mathbf{q} = 0$  Raman tensors  $\mathbf{R}^{j0}$ , whose symmetry properties and matrix form were discussed in Section 2.3.3.3.

Like  $\mathbf{a}^{j0}$ , the form of the  $\mathbf{q}$ -dependent contribution  $\mathbf{a}^{jq}$  also depends on the symmetry properties of the corresponding normal coordinate  $Q_j(\mathbf{q} \approx 0)$ . Since  $\mathbf{q}$  (or  $\nabla Q_j$ ) and  $\mathbf{E}$  are polar vectors, the symmetry properties of the  $\mathbf{a}^{jq}$  are identical to those of the coefficients  $\mathbf{R}^{jE}$  of the electric-field-induced Raman tensor discussed in Section 2.3.4.2: they transform according to the  $\mathbf{q} = 0$  representation  $[\Gamma_{PV} \otimes \Gamma_{PV}]_S \otimes \Gamma_{PV} \otimes \Gamma(j)$ . Hence, the symmetry-restricted matrix form of the  $\mathbf{q}$ -dependent contribution to the atomic displacement Raman tensor  $\mathbf{a}^{jq}$  is exactly the same as that of the corresponding electric-field-induced Raman tensor  $\mathbf{R}^{jE}$ . In general, these linear terms must vanish for even-parity modes in centrosymmetric crystals (where the lowest-order non-vanishing contributions to the Raman tensor are quadratic). The third-rank tensor  $\mathbf{b}^0$  corresponds to the first-order susceptibility derivative  $\mathbf{b}$  and the fourth-rank tensor  $\mathbf{b}^q$  to its first-order  $\mathbf{q}$ -dependent part.

As mentioned above, the  $\mathbf{q}$ -independent third-rank polar tensor  $\mathbf{b}^0$  is nonzero only in noncentrosymmetric (piezoelectric) crystals, where it contributes to Raman tensors for polar longitudinal optical (LO) phonons. The corresponding electro-optic terms in  $\mathbf{R}^j$ , connected with the accompanying longitudinal electric field  $\mathbf{E}$ , are given by  $\mathbf{b}^0(d\mathbf{E}/dQ_j)$ . Symmetry arguments imply that the  $\mathbf{q}$ -independent part of such terms must have the same form as the atomic displacement Raman tensor for polar LO phonons, since the corresponding normal coordinates transform as components of polar vectors.

The  $\mathbf{q}$ -dependent part of the electro-optic contribution, the polar fourth-rank tensor  $\mathbf{b}^q = (b_{\alpha\beta\gamma\delta}^q)$ , transforms as  $[\Gamma_{PV} \otimes \Gamma_{PV}]_S^2 \otimes \Gamma_{PV} \otimes \Gamma_{PV}$  and its symmetry properties are similar to those of the quadratic electro-optic tensor (however, as  $\mathbf{q}$  and  $\mathbf{E}$  are not interchangeable, there is no symmetry in the last two indices  $\gamma, \delta$ ). Thus, for finite  $\mathbf{q}$ , the term  $\mathbf{b}^q\mathbf{q}$  has nonzero components in all crystal classes. The corresponding contribution to the Raman tensor, however, is possible only in noncentrosymmetric crystals. Again, because of the  $(d\mathbf{E}/dQ_j)$  factor, the symmetry-restricted matrix form of this contribution for polar LO phonons will be equivalent to that of the  $\mathbf{a}^j\mathbf{q}$  term. As far as symmetry is concerned, the distinction between atomic displacement and electro-optic contributions is therefore immaterial.

The occurrence of  $\mathbf{q}$ -dependent terms leads to polarization selection rules that are generally different from those of intrinsically ( $\mathbf{q} = 0$ ) Raman-active modes. For this reason, this phenomenon is sometimes referred to as *forbidden* scattering. It is often observed under resonance conditions.

We recall that the terms linear in  $\mathbf{q}$ , *i.e.* proportional to displacement gradients and elastic strains, are fundamental for the description of inelastic light scattering by those excitations for which the transition susceptibility identically vanishes in the limit  $\mathbf{q} \rightarrow 0$  regardless of lattice point symmetry. This is the case for scattering by acoustic phonons (*Brillouin scattering*) and also for scattering by plasma waves (plasmons in semiconductors).

We have explicitly considered only the  $\mathbf{q}$ -dependent effects, due to gradients of phonon fields. In general, spatial dispersion

may be also due to the gradients of the electric (or magnetic) field of the incident or scattered photons. The corresponding effects are often referred to as  $\mathbf{k}$ -dependent effects. In view of the wavevector conservation condition (2.3.2.2), the three wavevectors  $\mathbf{q}$ ,  $\mathbf{k}_I$  and  $\mathbf{k}_S$  are always related, which simplifies the symmetry analysis. Without going into details, we note that, microscopically, the  $\mathbf{k}$ -dependent effects come from photon–electron interactions beyond the usual dipole approximation, *i.e.* from multipolar effects. The symmetry-allowed matrix form of the  $\mathbf{k}$ -induced contributions, depending on the nature of the leading microscopic mechanism, can be obtained by standard group-theoretical techniques.

*Example:* As an example we give the symmetry-restricted form for the linear  $\mathbf{q}$ -dependent contribution to the Raman tensors for *Raman-inactive* triply degenerate  $F_{1u}$  modes in the  $m3m$  ( $O_h$ ) class:

$$\mathbf{R}^j = 0; \\ \mathbf{R}^{jq} = \begin{pmatrix} cq_x & bq_y & bq_z \\ bq_y & aq_x & . \\ bq_z & . & aq_x \end{pmatrix}, \begin{pmatrix} aq_y & bq_x & . \\ bq_x & cq_y & bq_z \\ . & bq_z & aq_y \end{pmatrix}, \\ \begin{pmatrix} aq_z & . & bq_x \\ . & aq_z & bq_y \\ bq_x & bq_y & cq_z \end{pmatrix}.$$

The same form of the  $\mathbf{q}$ -dependent contribution holds for Raman-active optic  $F_2$  modes in the  $\bar{4}3m$  ( $T_d$ ) class. The conventional ( $\mathbf{q} = 0$ ) intrinsic Raman tensor of  $F_2$  is nonzero, but has off-diagonal components only. Since these modes are also infrared-active, there is a concomitant splitting of LO and TO frequencies as well as a possible electro-optic contribution to the Raman tensor due to the accompanying longitudinal macroscopic field. If one chooses  $\mathbf{q} \parallel \mathbf{z}$ , for instance, the first two matrices correspond to two degenerate TO modes and the third one to the LO mode. Combining the  $\mathbf{q}$ -independent and  $\mathbf{q}$ -dependent contributions, we get for each triplet of (2TO + LO)  $F_2$  modes

$$\mathbf{R}^{j0} + \mathbf{R}^{jq} = \begin{pmatrix} . & . & bq_z \\ . & . & c_{TO} \\ bq_z & c_{TO} & . \end{pmatrix} \quad j_1 = F_2(\text{TO}_x), \\ \begin{pmatrix} . & . & c_{TO} \\ . & . & bq_z \\ c_{TO} & bq_z & . \end{pmatrix} \quad j_2 = F_2(\text{TO}_y), \\ \begin{pmatrix} aq_z & c_{LO} & . \\ c_{LO} & aq_z & . \\ . & . & dq_z \end{pmatrix} \quad j_3 = F_2(\text{LO}_z).$$

The difference in the parameters  $c_{TO}$  and  $c_{LO}$  is due to the electro-optic contribution to the Raman tensor for the LO mode. In the back-scattering geometry for scattering from the (001) face of the crystal, only the  $\text{LO}_z$  modes can take part. Intrinsic allowed components  $|c_{LO}|^2$  are observable in the crossed ( $xy$ ) polarization geometry, whereas the  $\mathbf{q}$ -dependent terms  $|aq_z|^2$  appear as ‘forbidden’ scattering in parallel ( $xx$ ) or ( $yy$ ) geometries.

### 2.3.6. Higher-order scattering

In higher-order processes, the scattering involves participation of two or more quanta ( $j$  and  $j'$ ) of the elementary excitations. Let us discuss briefly the second-order scattering by phonons, where the energy and wavevector conservation conditions read