

2.3. RAMAN SCATTERING

In a general case, the second-order susceptibilities are not necessarily symmetric. However, they fulfil a general symmetry property which follows from the symmetry of the scattering with respect to time inversion. Since the anti-Stokes process can be regarded as a time-inverted Stokes process (exchanging the role of the incident and scattered photons), it can be shown that in non-magnetic materials the susceptibilities obey the relation

$$\chi_{\beta\alpha}^{(j)}(-\mathbf{q}, \omega_S, \omega) = \chi_{\alpha\beta}^{(j)}(\mathbf{q}, \omega_I, -\omega). \quad (2.3.3.10)$$

In the *quasi-static* limit, *i.e.* if the scattering frequency is negligibly small compared with the incident photon frequency ($0 \approx \omega \ll \omega_I \approx \omega_S$), it follows that the susceptibilities of non-magnetic materials become *symmetric* in the Cartesian indices α, β . This symmetry is very well fulfilled in a great majority of cases. Appreciable antisymmetric contributions are known to occur, *e.g.* under *resonant conditions*, where the quasi-static approximation breaks down as the energy of the incident (or scattered) photon approaches those of electronic transitions.

Thus, in the first approximation, we set ω equal to zero and remove the time dependence in the phonon amplitudes, treating the normal coordinates as *static*. Then the nonlinear susceptibilities correspond to susceptibility derivatives,

$$\chi_{\alpha\beta}^{(j)}(\mathbf{q}, \omega_I, -\omega) \rightarrow \mathbf{R}_{\alpha\beta}^j(\mathbf{q}) \equiv \chi_{\alpha\beta}^{(j)}(\mathbf{q}, \omega_I) = \frac{\partial \chi_{\alpha\beta}(\omega_I)}{\partial Q_j^*(\mathbf{q})}, \quad (2.3.3.11)$$

where we suppressed the explicit dependence on ω_I and introduced a simplified notation for the Raman tensor $\mathbf{R}^j(\mathbf{q})$, still keeping the dependence on the scattering wavevector.

In deriving the symmetry properties of the Raman tensor $\mathbf{R}^j(\mathbf{q})$ that follow from the crystal lattice symmetry, the main point is thus to determine its transformation properties under the symmetry operation of the crystal *space group*.

Since the magnitude of the scattering vector $q \equiv |\mathbf{q}|$ is very small compared with the Brillouin-zone dimensions, another conventional approximation is to neglect the \mathbf{q} dependence of the susceptibilities. Setting $\mathbf{q} \rightarrow 0$ enables us to analyse the symmetry of the Raman tensor in terms of the *factor group* G_0 , which is isomorphous to the point group of the crystal lattice. This approach is, again, appropriate for the vast majority of cases. An important exception is, for instance, the scattering by acoustic modes (*Brillouin scattering*) or scattering by longitudinal plasma waves in semiconductors (*plasmons*): in these cases the Raman tensor vanishes for $\mathbf{q} = 0$, since this limit corresponds to a homogeneous displacement of the system. Possible \mathbf{q} -dependent effects can be treated by expanding the Raman tensor in powers of \mathbf{q} and using compatibility relations between the symmetries at $\mathbf{q} = 0$ and at the full symmetries applicable in the $\mathbf{q} \neq 0$ case.

Let us mention that another notation is sometimes used in the literature for the Raman tensor. Since the square modulus of a second-rank tensor contracted with two vectors can be written as a fourth-rank tensor contracted with four vectors, one can introduce a fourth-rank tensor $\mathbf{I}^{(j)}$,

$$I_{\alpha\beta\mu\nu}^{(j)} = \frac{\partial \chi_{\alpha\beta}^*}{\partial Q_j} \frac{\partial \chi_{\mu\nu}}{\partial Q_j^*},$$

so that the scattering cross section of the j th mode is

$$\frac{d\sigma^{(j)}}{d\Omega d\omega_S} \approx e_{I\alpha} e_{I\mu} e_{S\beta} e_{S\nu} I_{\alpha\beta\mu\nu}^{(j)}.$$

If there are no antisymmetric components in the susceptibility derivatives, it can be shown that the fourth-rank tensor $\mathbf{I} = (I_{\alpha\beta\mu\nu})$ has at most 21 independent components, as for the elastic constants tensor.

 2.3.3.3. Raman tensor and selection rules at $\mathbf{q} \approx 0$

The scattering cross section, being a scalar quantity, must be invariant with respect to all symmetry elements of the space group of the crystal. This invariance has two important consequences: it determines which normal modes (j) can contribute to the scattering (*Raman activity* of the modes) and it also gives the restrictions on the number of independent components of the Raman tensor (*polarization selection rules*).

At $\mathbf{q} \approx 0$, the transformation properties of the incident and scattered light are described by the three-dimensional *polar vector representation* Γ_{PV} of the appropriate point group of the crystal, since the quantities that characterize the light ($\mathbf{E}_I, \mathbf{E}_S, \mathbf{P} \dots$) are all *polar vectors*, *i.e.* first-rank polar tensors (T_α). The transformation properties of a normal mode j must correspond to an irreducible matrix representation $\Gamma(j)$ of the crystal point group. We recall that in cases of two- or three-dimensional representations (degeneracy), the index j represents two indices.

In order that a particular normal mode j in a given crystal be Raman active, *i.e.* *symmetry-allowed* to contribute to the (first-order) scattering cross section, the necessary condition is that the corresponding irreducible representation $\Gamma(j)$ must be contained in the decomposition of the direct Kronecker product representation $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}$ at least once:

$$\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}} \supset \Gamma(j). \quad (2.3.3.12)$$

In this case, the Kronecker product $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}} \otimes \Gamma(j)$ contains the identity representation at least once, so the cross section remains invariant under the transformation of the crystal point group. In the phenomenological formulation, the susceptibility derivatives correspond to third derivatives of a particular potential energy Φ (interaction Hamiltonian),

$$R_{\alpha\beta}^j = \left(\frac{\partial \chi_{\alpha\beta}}{\partial Q_j^*} \right) \sim \left(\frac{\partial^3 \Phi}{\partial E_{I\alpha} \partial E_{S\beta}^* \partial Q_j^*} \right), \quad (2.3.3.13)$$

such that the product $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}} \otimes \Gamma(j)$ is the reducible representation of the Raman tensor. If condition (2.3.3.12) holds, then the Raman tensor \mathbf{R}^j does not vanish identically and may have at least one independent nonzero component. As the representation $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}$ is that of a second-rank polar tensor, equivalent formulation of the Raman activity of a normal mode j is that the corresponding normal coordinate Q_j must transform like one or more components of a polar tensor. The transition susceptibility $\delta\chi^{(j)}$ transforms accordingly. The task of determining whether a given normal mode j is Raman active or not thus consists of simply decomposing the representation $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}$ and identifying the irreducible components $\Gamma(j)$.

The second consequence of the invariance condition is the imposition of restrictions on the Cartesian components of the Raman tensor for modes allowed to participate in the scattering. By virtue of the properties of the irreducible representations $\Gamma(j)$, some components of the corresponding Raman tensor are required to vanish whereas others may have related values. This fact results in anisotropies in the observed cross section depending on the polarization directions of the incident and scattered light, and is usually referred to as *polarization selection rules*. As the scattering cross section of the excitation (j) is proportional to the scalar quantity

$$|\mathbf{e}_S \mathbf{R}^j \mathbf{e}_I|^2 \equiv \left| e_{S\alpha} R_{\alpha\beta}^j e_{I\beta} \right|^2,$$

one can generally ‘isolate’ a given component of the Raman tensor by suitably arranging the scattering geometry in the experiment, *i.e.* by choosing the orientation of the wavevectors \mathbf{k}_I and \mathbf{k}_S and the polarization vectors \mathbf{e}_I and \mathbf{e}_S with respect to crystallographic axes.

2. SYMMETRY ASPECTS OF EXCITATIONS

For each normal mode (j) allowed in the scattering, the number of independent components of its Raman tensor is given by the multiplicity coefficients $c^{(j)}$ of the irreducible representation $\Gamma(j)$ in the decomposition

$$\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}} = c^{(1)}\Gamma(1) \oplus c^{(2)}\Gamma(2) \oplus \dots, \quad (2.3.3.14)$$

where the multiplicity coefficient $c^{(j)}$ corresponds to the number of times the given irreducible representation $\Gamma(j)$ enters the decomposition. If the representation $\Gamma(j)$ is two- or three-dimensional, then for each occurrence of $\Gamma(j)$ in (2.3.3.14) there are two or three degenerate partners (of the same frequency) whose Raman tensors are symmetry-related.

The matrix form of the Raman tensor corresponding to a given irreducible representation – *i.e.* *symmetry species* – $\Gamma(j)$ can be readily constructed by finding the appropriate bilinear basis functions that transform according to the corresponding irreducible representation $\Gamma(j)$. The required number of such independent bases is given by the multiplicity coefficient $c^{(j)}$. Alternatively, one may construct invariant polynomials (transforming as scalars) of order *four*, *i.e.* of the same order as the product $E_{I\alpha}E_{S\beta}Q_j$.

Making allowance for possible *antisymmetric* scattering, we have not explicitly supposed that the Raman tensor is symmetric. We recall that the derivative (2.3.3.13) is not necessarily symmetric in the α and β indices as long as the fields $E_{I\alpha}$ and $E_{S\beta}$ correspond to different frequencies (inelastic scattering). However, each second-rank polar tensor $T_{\alpha\beta}$ (nine components), transforming according to $\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}$, can be decomposed into a symmetric part $T'_{\alpha\beta} = T'_{\beta\alpha}$ (six components), transforming like a symmetric polar tensor $[\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_S$, and an antisymmetric part $T''_{\alpha\beta} = -T''_{\beta\alpha}$ (three components), transforming like an axial vector (for the definition of axial tensors, see Section 1.1.4.5.3) according to $\Gamma_{\text{AV}} = [\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_A$.

The symmetry-restricted forms of the (3×3) Raman tensors corresponding to all Raman-active symmetry species are summarized in Table 2.3.3.1 (see *e.g.* Hayes & Loudon, 1978) for each of the 32 crystal symmetry classes. Spectroscopic notation is used for the irreducible representations of the point groups. The symbols (x , y or z) for some Raman-active symmetry species in the noncentrosymmetric classes indicate that the respective components of polar vectors also transform according to these irreducible representations. Hence the normal coordinates of the phonons of these *polar* symmetry species (polar phonons) transform in the same way and, consequently, the corresponding component of the effective charge tensor $Z_{j\alpha}(\mathbf{q} = 0)$, see (2.3.3.4), is not required by symmetry to vanish. Polar phonons thus may carry a nonzero dipole moment and contribute to the polarization in the crystal, which manifests itself in *infrared activity* and also in the Raman scattering cross section (see Section 2.3.3.5).

For convenience, the Raman tensors are explicitly split into a symmetric and possible antisymmetric part (upper and lower row of each part of the table, respectively, in each case). The conventional *symmetric* Raman tensors are *appropriate for most cases of practical interest*. Besides the resonant conditions mentioned above, there are other exceptions. For instance, there are optical phonons that transform like *axial vectors*, such as in the case of A_2 (or A_{2g} , A'_2) modes in some uniaxial crystal classes, where the Raman tensor is *purely antisymmetric*. Antisymmetric scattering by these modes may become allowed at finite wave-vector \mathbf{q} . Antisymmetric Raman tensors are also needed for analysing the symmetry of scattering in magnetic materials (scattering by spin waves – *magnons*), or non-magnetic materials under a magnetic field, where the susceptibility itself is essentially nonsymmetric.

We note that the matrix form of the Raman tensors depends on the setting of the Cartesian axes with respect to the crystallographic axes. To avoid ambiguities and apparent disagreement with other sources, we give the results for alternative orientations

Table 2.3.3.1. *Symmetry of Raman tensors in the 32 crystal classes*

The symbols a, b, c, d, e, f, g, h and i in the matrices stand for arbitrary parameters denoting possible independent nonzero components (in general complex) of the Raman tensors. Upper row: conventional symmetric Raman tensors; lower row: antisymmetric part. Alternative orientations of the point group are distinguished by subscripts at 2 or m in the class symbol indicating the direction of the twofold axis or of the normal to the mirror plane.

Triclinic

$\frac{1}{\bar{1}}$	$\begin{pmatrix} a & d & f \\ d & b & h \\ f & h & c \end{pmatrix}$
	$\begin{matrix} A(x, y, z) \\ A_g \end{matrix}$
	$\begin{pmatrix} \cdot & e & g \\ -e & \cdot & i \\ -g & -i & \cdot \end{pmatrix}$

Monoclinic, unique axis z

$\begin{matrix} 2_z \\ m_z \\ 2_z/m \end{matrix}$	$\begin{pmatrix} a & d & \cdot \\ d & b & \cdot \\ \cdot & \cdot & c \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & f \\ \cdot & \cdot & h \\ f & h & \cdot \end{pmatrix}$
	$\begin{matrix} A(z) \\ A'(x, y) \\ A_g \end{matrix}$	$\begin{matrix} B(x, y) \\ A''(z) \\ B_g \end{matrix}$
	$\begin{pmatrix} \cdot & e & \cdot \\ -e & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & g \\ \cdot & \cdot & i \\ -g & -i & \cdot \end{pmatrix}$

Monoclinic, unique axis y

$\begin{matrix} 2_y \\ m_y \\ 2_y/m \end{matrix}$	$\begin{pmatrix} a & \cdot & d \\ \cdot & b & \cdot \\ d & \cdot & c \end{pmatrix}$	$\begin{pmatrix} \cdot & f & \cdot \\ f & \cdot & h \\ \cdot & h & \cdot \end{pmatrix}$
	$\begin{matrix} A(y) \\ A'(x, z) \\ A_g \end{matrix}$	$\begin{matrix} B(x, z) \\ A''(y) \\ B_g \end{matrix}$
	$\begin{pmatrix} \cdot & \cdot & e \\ \cdot & \cdot & \cdot \\ -e & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & g & \cdot \\ -g & \cdot & i \\ \cdot & -i & \cdot \end{pmatrix}$

Orthorhombic

$\begin{matrix} 222 \\ mm2 \\ mmm \end{matrix}$	$\begin{pmatrix} a & \cdot & \cdot \\ \cdot & b & \cdot \\ \cdot & \cdot & c \end{pmatrix}$	$\begin{pmatrix} \cdot & d & \cdot \\ d & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & f \\ \cdot & \cdot & \cdot \\ f & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & h \\ \cdot & h & \cdot \end{pmatrix}$
	$\begin{matrix} A \\ A_1(z) \\ A_g \end{matrix}$	$\begin{matrix} B_1(z) \\ A_2 \\ B_{1g} \end{matrix}$	$\begin{matrix} B_2(y) \\ B_1(x) \\ B_{2g} \end{matrix}$	$\begin{matrix} B_3(x) \\ B_2(y) \\ B_{3g} \end{matrix}$
	$\begin{pmatrix} \cdot & \cdot & e \\ -e & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & g \\ \cdot & \cdot & \cdot \\ -g & \cdot & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & i \\ \cdot & -i & \cdot \end{pmatrix}$	$\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & -i & \cdot \end{pmatrix}$

of the point groups in several cases where different settings of the twofold axes or mirror planes with respect to the Cartesian axes are commonly used. This concerns all monoclinic classes (unique

2.3. RAMAN SCATTERING

Table 2.3.3.1 (cont.)

Tetragonal

4 4 4/m	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$	$\begin{pmatrix} d & e & . \\ e & -d & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & f \\ . & . & h \\ f & h & . \end{pmatrix}$	$\begin{pmatrix} . & . & -h \\ . & . & f \\ -h & f & . \end{pmatrix}$
	A(z) A A _g	B B(z) B _g	E(x, y) E(x, -y) E _g	
	$\begin{pmatrix} . & c & . \\ -c & . & . \\ . & . & . \end{pmatrix}$		$\begin{pmatrix} . & . & g \\ . & . & i \\ -g & -i & . \end{pmatrix}$	$\begin{pmatrix} . & . & -i \\ . & . & g \\ i & -g & . \end{pmatrix}$

422 4mm 4̄2 _x m _{xy} 4m _x 2 _{xy} 4/mmm	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$		$\begin{pmatrix} d & . & . \\ . & -d & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & e & . \\ e & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & f \\ . & . & . \\ f & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & f \\ . & f & . \end{pmatrix}$
	A ₁ A ₁ (z)	A ₂ (z) A ₂	B ₁ B ₁	B ₂ B ₂	E(-y, x) E(x, y)	
	A ₁ A ₁	A ₂ A ₂	B ₁ B ₁	B ₂ (z) B ₂ (z)	E(y, x) E(-x, y)	
	A _{1g}	A _{2g}	B _{1g}	B _{2g}	E _g	
		$\begin{pmatrix} . & c & . \\ -c & . & . \\ . & . & . \end{pmatrix}$			$\begin{pmatrix} . & . & g \\ . & . & i \\ -g & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & g \\ . & -g & . \end{pmatrix}$

Trigonal

3 3	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$	$\begin{pmatrix} c & f & e \\ f & -c & d \\ e & d & . \end{pmatrix}$	$\begin{pmatrix} f & -c & -d \\ -c & -f & e \\ -d & e & . \end{pmatrix}$
	A(z) A _g	E(x, y) E _g	
	$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & i \\ . & . & g \\ -i & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & i \\ g & -i & . \end{pmatrix}$

32 _x 3m _x 3̄m _x	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$		$\begin{pmatrix} f & . & . \\ . & -f & d \\ . & d & . \end{pmatrix}$	$\begin{pmatrix} . & -f & -d \\ -f & . & . \\ -d & . & . \end{pmatrix}$
	A ₁ A ₁ (z)	A ₂ (z) A ₂	E(x, y) E(y, -x)	
	A _{1g}	A _{2g}	E _g	
		$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & g \\ . & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & . \\ g & . & . \end{pmatrix}$

32 _y 3m _y 3̄m _y	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$		$\begin{pmatrix} . & f & . \\ f & . & d \\ . & d & . \end{pmatrix}$	$\begin{pmatrix} f & . & -d \\ . & -f & . \\ -d & . & . \end{pmatrix}$
	A ₁ A ₁ (z)	A ₂ (z) A ₂	E(x, y) E(y, -x)	
	A _{1g}	A _{2g}	E _g	
		$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & g \\ . & -g & . \end{pmatrix}$	$\begin{pmatrix} . & . & -g \\ . & . & . \\ g & . & . \end{pmatrix}$

direction parallel to **y** or **z**), tetragonal class 4̄2m, trigonal classes 32, 3m and 3̄m, as well as hexagonal class 6̄2m.

1̄, 2/m, mmm, 4/m, 4/mmm, 3̄, 3̄m, 6/m, 6/mmm, m3, m3m,

2.3.3.4. Centrosymmetric crystals

In those point groups that contain the inversion operation, *i.e.* in the eleven centrosymmetric (*nonpolar*) crystal classes

the irreducible representations are divided into two groups, odd and even, according to the parity. Since second-rank polar tensors must transform according to the *even* parity representations only, whereas polar vectors transform according to *odd* parity representations, the selection rules for electric dipole absorption