

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

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

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 $\Gamma_{PV} \otimes \Gamma_{PV}$, can be decomposed into a symmetric part $T'_{\alpha\beta} = T'_{\beta\alpha}$ (six components), transforming like a symmetric polar tensor $[\Gamma_{PV} \otimes \Gamma_{PV}]_S$, 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 $\Gamma_{AV} = [\Gamma_{PV} \otimes \Gamma_{PV}]_A$.

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

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

Monoclinic, unique axis z

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

Monoclinic, unique axis y

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

Orthorhombic

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

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

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Table 2.3.3.1 (cont.)

Hexagonal

	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$	$\begin{pmatrix} . & . & e \\ . & . & d \\ e & d & . \end{pmatrix}$ $\begin{pmatrix} . & . & -d \\ . & . & e \\ -d & e & . \end{pmatrix}$	$\begin{pmatrix} c & f & . \\ f & -c & . \\ . & . & . \end{pmatrix}$ $\begin{pmatrix} f & -c & . \\ -c & -f & . \\ . & . & . \end{pmatrix}$
6 6 6/m	A(z) A' A _g	E ₁ (x, y) E'' E _{1g}	E ₂ E'(x, y) E _{2g}
	$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & i \\ . & . & g \\ -i & -g & . \end{pmatrix}$ $\begin{pmatrix} . & . & -g \\ . & . & i \\ g & -i & . \end{pmatrix}$	

	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & b \end{pmatrix}$		$\begin{pmatrix} . & . & . \\ . & . & d \\ . & d & . \end{pmatrix}$ $\begin{pmatrix} . & . & -d \\ . & . & . \\ -d & . & . \end{pmatrix}$	$\begin{pmatrix} . & f & . \\ f & . & . \\ . & . & . \end{pmatrix}$ $\begin{pmatrix} f & . & . \\ . & -f & . \\ . & . & . \end{pmatrix}$
622 6mm 6m, 2y 62x, my 6/mmm	A ₁ A ₁ (z) A ₁ ' A ₁ ' A _{1g}	A ₂ (z) A ₂ A ₂ ' A ₂ ' A _{2g}	E ₁ (x, y) E ₁ (y, -x) E'' E'' E _{1g}	E ₂ E ₂ E'(x, y) E'(y, -x) E _{2g}
		$\begin{pmatrix} . & h & . \\ -h & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & g \\ . & -g & . \end{pmatrix}$ $\begin{pmatrix} . & . & -g \\ . & . & . \\ g & . & . \end{pmatrix}$	

Cubic

	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & a \end{pmatrix}$	$\begin{pmatrix} b & . & . \\ . & b & . \\ . & . & -2b \end{pmatrix}$ $\begin{pmatrix} -\sqrt{3}b & . & . \\ . & \sqrt{3}b & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & c \\ . & c & . \end{pmatrix}$ $\begin{pmatrix} . & . & c \\ . & . & . \\ c & . & . \end{pmatrix}$ $\begin{pmatrix} . & c & . \\ c & . & . \\ . & . & . \end{pmatrix}$
23 m3	A A _g	E E _g	F(x, y, z) F _g
			$\begin{pmatrix} . & . & . \\ . & . & d \\ . & -d & . \end{pmatrix}$ $\begin{pmatrix} . & . & d \\ . & . & . \\ -d & . & . \end{pmatrix}$ $\begin{pmatrix} . & d & . \\ -d & . & . \\ . & . & . \end{pmatrix}$

	$\begin{pmatrix} a & . & . \\ . & a & . \\ . & . & a \end{pmatrix}$	$\begin{pmatrix} b & . & . \\ . & b & . \\ . & . & -2b \end{pmatrix}$ $\begin{pmatrix} -\sqrt{3}b & . & . \\ . & \sqrt{3}b & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & c \\ . & c & . \end{pmatrix}$ $\begin{pmatrix} . & . & c \\ . & . & . \\ c & . & . \end{pmatrix}$ $\begin{pmatrix} . & c & . \\ c & . & . \\ . & . & . \end{pmatrix}$
432 43m m3m	A ₁ A ₁ A _{1g}	E E E _g	F ₁ (x, y, z) F ₁ F _{1g}
			$\begin{pmatrix} . & . & . \\ . & . & d \\ . & -d & . \end{pmatrix}$ $\begin{pmatrix} . & . & d \\ . & . & . \\ -d & . & . \end{pmatrix}$ $\begin{pmatrix} . & d & . \\ -d & . & . \\ . & . & . \end{pmatrix}$

(infrared activity) and for Raman scattering are incompatible. This is often expressed as the *mutual exclusion rule* or *complementarity principle*: The excitations in a crystal belonging to a centrosymmetric class cannot be simultaneously active in infrared absorption and in Raman scattering. Let us note, however, that even-parity excitations are not necessarily all Raman active, and that odd-parity excitations are not necessarily infrared active.

In the remaining noncentrosymmetric crystal classes, the excitations have no defined parity with respect to inversion and can be, in principle, both Raman and infrared active.

Example: Consider a Raman scattering experiment on a crystal of tetragonal symmetry, class 4/mmm. Raman-active phonons, allowed in conventional symmetric scattering, are of the symmetry species A_{1g}, B_{1g}, B_{2g} and E_g. (the A_{2g} species admits purely antisymmetric scattering only). Straightforward application of Table 2.3.3.1 makes it possible to determine the polar-

ization selection rules, *i.e.* to determine which symmetry species will contribute to the scattering cross section in various experimental configurations. Choosing the Cartesian axes $x \equiv [100]$, $y \equiv [010]$, $z \equiv [001]$ consistent with the standard setting of the 4/mmm point group, *i.e.* the fourfold rotation axis $4 \parallel \mathbf{z}$, let us further introduce the notation $x' \equiv [110]$, $y' \equiv [\bar{1}10]$. Then the contributions to the cross section for different symmetry species can be distinguished by their dependence on the polarization vectors \mathbf{e}_I and \mathbf{e}_S of the incident and scattered light:

$$A_{1g} : |(e_{Ix}e_{Sx} + e_{Iy}e_{Sy})a + e_{Iz}e_{Sz}b|^2$$

$$B_{1g} : |(e_{Ix}e_{Sx} - e_{Iy}e_{Sy})d|^2$$

$$B_{2g} : |(e_{Ix}e_{Sy} + e_{Iy}e_{Sx})e|^2$$

$$E_g : [(e_{Ix}e_{Sz} + e_{Iz}e_{Sx})^2 + (e_{Iy}e_{Sz} + e_{Iz}e_{Sy})^2]|f|^2.$$