

## 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

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$$\begin{aligned}\omega_I - \omega_S = \omega &= \pm\omega_j \pm \omega_{j'}, \\ \mathbf{k}_I - \mathbf{k}_S = \mathbf{q} &= \pm\mathbf{q}_j \pm \mathbf{q}_{j'}.\end{aligned}\quad (2.3.6.1)$$

The combinations of signs in these equations correspond to four possibilities, in which either both phonons,  $j$  and  $j'$ , are created (Stokes process: ++), both annihilated (anti-Stokes process: --), or one is created and the other annihilated (difference process: +-, -+). If in the Stokes or anti-Stokes case both excitations are of the same type,  $j = j'$ , one speaks of *overtone*s. The corresponding terms in the transition susceptibility are the coefficients of a bilinear combination of normal coordinates in the expansion of  $\delta\chi$ .

In the quasi-static limit, the transition susceptibilities for the second-order scattering correspond, again, to the susceptibility derivatives. Thus, the spectral differential cross section for the second-order scattering (Stokes component) can be formally written as

$$\begin{aligned}\frac{d^2\sigma}{d\omega d\Omega} \approx & \sum_{\substack{j,j' \\ \mathbf{q}_j + \mathbf{q}_{j'} = \mathbf{q} \approx 0}} \left| e^{S\alpha} \frac{\partial^2 \chi_{\alpha\beta}}{\partial Q_j^*(\mathbf{q}_j) \partial Q_{j'}^*(\mathbf{q}_{j'})} e^{I\beta} \right|^2 \\ & \times \delta[\omega_j(\mathbf{q}_j) + \omega_{j'}(\mathbf{q}_{j'}) - \omega],\end{aligned}$$

with  $\omega = \omega_I - \omega_S > 0$ . In this formula, we have suppressed the universal factors [see (2.3.3.5)] and the explicit expression for the response function (thermal factors). Instead, the *delta* function (response function in the limit of zero damping) expresses the energy-conservation condition.

The wavevector selection rules in the long-wavelength limit, with  $\mathbf{q} = 0$ , imply that  $\mathbf{q}_j = -\mathbf{q}_{j'}$  (the same holds for anti-Stokes components, while  $\mathbf{q}_j = \mathbf{q}_{j'}$  for difference scattering), so the wavevectors themselves need not be small and, in principle, scattering by phonons with all wavevectors from the Brillouin zone can be observed.

Without invoking any symmetry arguments for the Raman activity, such as the restrictions imposed by crystal symmetry on the susceptibility derivatives, it is clear that the intensity of second-order scattering at a frequency  $\omega$  is controlled by the number of those combinations of phonons whose frequencies obey  $\omega = \omega_j(\mathbf{q}) + \omega_{j'}(-\mathbf{q})$ . The quantity determining this number is the combined density of states of phonon pairs, *i.e.*

$$\rho_2(\omega) = \sum_{j,j'} \sum_{\mathbf{q}} \delta[\omega_j(\mathbf{q}) + \omega_{j'}(\mathbf{q}) - \omega]. \quad (2.3.6.2)$$

This function can be calculated provided the *dispersion curves*  $\omega_j(\mathbf{q})$  of the excitations are known. The density of states is a continuous function and shows features known as the van Hove singularities corresponding to the *critical points*, where one or more components of the gradient  $\nabla_{\mathbf{q}}[\omega_j(\mathbf{q}) + \omega_{j'}(\mathbf{q})]$  vanish. Most of the critical points occur for wavevectors on the boundary, where the vanishing gradients of the individual dispersion curves are often dictated by the crystal symmetry, but they also occur in those regions of the reciprocal space where both dispersion curves have opposite or equal slopes at the same wavevector  $\mathbf{q}$ . To a first approximation, the second-order spectrum is thus essentially continuous, reflecting the two-phonon density of states, with peaks and sharp features at frequencies close to the positions of the van Hove singularities. This is to be contrasted with the first-order scattering, where (in perfect crystals) only single peaks corresponding to long-wavelength ( $\mathbf{q} \approx 0$ ) phonons occur.

Group-theoretical arguments may again be invoked in deriving the selection rules that determine the Raman activity of a particular combination of excitations (Birman, 1974). The susceptibility derivative again transforms as a tensor. For a given pair of excitations ( $j, \mathbf{q}$ ) and ( $j', -\mathbf{q}$ ) responsible for the modu-

Table 2.3.6.1. Thermal factors for second-order Raman scattering

$n(\omega)$  is given by (2.3.3.7).

Factor	Process	Raman shift
$[n(\omega_j) + 1][n(\omega_{j'}) + 1]$	Stokes	$(\omega = \omega_j + \omega_{j'})$
$[n(\omega_j) + 1]n(\omega_{j'})$	Difference	$(\omega = \omega_j - \omega_{j'})$
$n(\omega_j)n(\omega_{j'})$	Anti-Stokes	$(\omega = -\omega_j - \omega_{j'})$

lation, the combined excitation symmetry is obtained by taking the direct product of the irreducible representations of the space group corresponding to the participating excitations,

$$\Gamma(j, j') = D_{j,\mathbf{q}} \otimes D_{j',-\mathbf{q}}. \quad (2.3.6.3)$$

The representation  $\Gamma(j, j')$ , unlike  $D_{j,\mathbf{q}}$ , corresponds to a zero-wavevector representation of the crystal space group and is therefore equivalent to a (reducible) representation of the crystal point group. It can be decomposed into irreducible components. Raman scattering of the pair is allowed if a Raman-active  $\mathbf{q} = 0$  representation is contained in this decomposition of  $\Gamma(j, j')$  or, alternatively, if the product  $[\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_S \otimes \Gamma(j, j')$  contains the totally symmetric representation  $\Gamma(1)$ .

The selection rules for the second-order scattering are, in general, far less restrictive than in the first-order case. For example, it can be shown that for a general wavevector  $\mathbf{q}$  in the Brillouin zone there are no selection rules on the participation of phonons in the second-order scattering, since the representations  $\Gamma(j, j')$  contain all Raman-active symmetries. In specific crystal structures, however, restrictions occur for the wavevectors corresponding to special symmetry positions (points, lines or planes) in the Brillouin zone. This implies that the selection rules may suppress some of the van Hove singularities in the second-order spectra.

*Morphic* effects in second-order scattering, due to an applied external force  $\mathbf{F}$  (see Section 2.3.4.1), may be investigated using the same criteria as in first-order scattering, *i.e.* decomposing the  $\mathbf{q} = 0$  representation  $\Gamma(\mathbf{F}) \otimes [\Gamma_{\text{PV}} \otimes \Gamma_{\text{PV}}]_S \otimes \Gamma(j, j')$  and searching for the matrix form of the corresponding second-order Raman tensors.

Generalization to third- and higher-order processes is obvious.

Concluding this section, we note that in a Raman-scattering experiment, higher-order features in the spectra can in principle be distinguished from first-order features by different behaviour of the differential scattering cross section with temperature. For example, the respective thermal factors entering the expression for the second-order scattering cross section are given in Table 2.3.6.1.

#### 2.3.7. Conclusions

In this overview of Raman scattering in crystals, we have almost exclusively based our considerations on a phenomenological, semi-classical viewpoint without going into details of the underlying microscopic theory. This is surely an appropriate approach to a discussion of the fundamental consequences of crystal symmetry on the selection rules governing the varied phenomena of inelastic light scattering and on the symmetry-restricted form of the corresponding tensorial quantities encountered in this vast and fruitful field. We have attempted to treat the most important symmetry aspects of the inelastic scattering of light by collective excitations in perfect crystals, concentrating on scattering by optical phonons – in the traditional sense of Raman scattering studies. Within a limited scope, we tried to give some insight into the nature of the phenomena relevant in connection with this topic. Our coverage is certainly not exhaustive (nor original); we have also deliberately omitted all scattering phenomena connected with purely electronic excitations, although the corresponding symmetry aspects can be analysed on the same footing. The essence of the truth is rather simple: As long as the