2.3. RAMAN SCATTERING

The symbol $\langle\ldots\rangle_\omega$ stands for the power spectrum (correlation function) of the transition susceptibility fluctuations. The spectral differential cross section is the quantity that can be directly measured in a Raman scattering experiment by analysing the frequency spectrum of the light scattered into a certain direction. By integrating over frequencies ω_S for a particular Raman band and, in addition, over the solid angle, one obtains, respectively, the *differential cross section* ($d\sigma/d\Omega$) and the *total cross section* (σ_{tot}):

$$\frac{d\sigma}{d\Omega} = \int \left(\frac{d^2\sigma}{d\Omega\, d\omega_S}\right) d\omega_S, \quad \sigma_{tot} = \int \left(\frac{d\sigma}{d\Omega}\right) d\Omega.$$

These quantities are useful in comparing the integrated scattered intensity by different excitations.

2.3.2.3. *Experimental aspects*

In a scattering experiment on crystals, the choice of the scattering geometry implies setting the propagation directions $\mathbf{k}_I$ and $\mathbf{k}_S$ and the polarization of the incident and scattered light with respect to the crystallographic axes and defining thus the direction of the scattering wavevector $\mathbf{q}$ as well as the particular component (or a combination of components) of the transition susceptibility tensor $\delta\chi$. In practice, the incident radiation is almost exclusively produced by a suitable laser source, which yields a monochromatic, polarized narrow beam, with a well defined wavevector $\mathbf{k}_I$. The light scattered in the direction of $\mathbf{k}_S$ is collected over a certain finite solid angle $\Delta\Omega$. Its polarization is analysed with a suitable polarization analyser, and the scattered intensity as a function of frequency ω_S (or Raman shift ω) is analysed using a spectrometer.

To characterize the Raman scattering geometry in a particular experimental arrangement, standard notation for the scattering geometry is often used, giving the orientation of the wavevectors and polarization vectors with respect to a reference Cartesian coordinate system, namely: $\mathbf{k}_I(\mathbf{e}_I, \mathbf{e}_S)\mathbf{k}_S$. Thus, for example, the symbol $x(zy)z$ means that right-angle scattering geometry is used, where the incident beam polarized in the $z = [001]$ direction propagates along the $x = [100]$ axis, while the scattered beam is collected in the z direction and the polarization analyser is set parallel with the $y = [010]$ direction. The measured intensity, being proportional to $|\chi_{zy}|^2$, gives information on this particular component of the transition susceptibility tensor. By virtue of the momentum conservation, the scattering wavevector $\mathbf{q}$ in this case is oriented along the $[10\bar{1}]$ direction.

In a typical Raman experiment with visible light ($\omega \ll \omega_I \approx \omega_S$), the magnitudes of the wavevectors $k_I \approx k_s = k$ are of the order of 10^5 cm^{-1}, much lower than those of the reciprocal-lattice vectors K ($\approx 10^8$ cm^{-1}). Consequently, the range of the magnitudes of the scattering wavevectors q accessible by varying the scattering geometry from $\varphi = 0°$ (forward scattering) to $\varphi = 180°$ (back scattering) is $0 \le q \le 2k$, *i.e.* by about three orders of magnitude lower than the usual dimensions of the Brillouin zone. The use of back-scattering geometry is imperative in the case of opaque samples, which show stronger absorption for the exciting (or scattered) light.

It should be noted that the general formula for the spectral differential cross section (2.3.2.5) applies to the situation *inside* the crystal. Since in real experiments the observer is always *outside* the crystal, several corrections have to be taken into account. These are in particular due to refraction, reflection and transmission of the incident and scattered light at the interfaces, as well as absorption of light in the crystal. Attention must be paid in the case of anisotropic or gyrotropic crystals, where birefringence or rotation of the polarization direction of both incident and scattered light may occur on their paths through the crystal, between the interfaces and the scattering volume.

We conclude this section by remarking that, owing to the obvious difficulties in taking all the properties of the experimental setup and the corrections into consideration, measurements of absolute Raman intensities tend to be extremely rare. There exist, however, several crystals for which absolute determination of the cross section for particular excitations has been made with reasonable reliability and which may serve as secondary standards.

2.3.3. First-order scattering by phonons

In what follows, we shall be more specific and by underlying excitations we shall explicitly understand lattice vibrations – *phonons* – although the treatment is also applicable to other types of collective excitations in a crystal.

Let us recall (see Chapter 2.1) that atomic displacements in the crystal lattice can be expressed as linear combinations of the *normal modes of vibrations* – eigenvectors of the dynamical matrix.

$$\mathbf{u}_{\kappa l} = \sum_{\mathbf{q}}\sum_{j} \mathbf{u}_{\kappa l}(\mathbf{q}, j) = \frac{1}{\sqrt{Nm_\kappa}}\sum_{\mathbf{q}}\sum_{j} Q_j(\mathbf{q})\mathbf{e}_\kappa(\mathbf{q}, j)\exp(i\mathbf{q}\mathbf{r}_l),$$

$$(2.3.3.1)$$

where $\mathbf{l}$ denotes the *primitive* unit cell, κ ($\kappa = 1, \ldots, s$) is the index of the atom (mass m_κ) in the unit cell and N is the number of unit cells in the crystal. The *eigenvectors* $\mathbf{e}_\kappa(\mathbf{q}, j)$, also called *polarization vectors*, are normalized vectors describing the displacement pattern of atoms in the reference unit cell in a jth normal mode of vibration ($j = 1, 2, 3, \ldots, 3s$) with a wavevector $\mathbf{q}$. The normal modes can be classified according to irreducible representations of the crystal space group and labelled correspondingly. In the case of degeneracy, the branch index j stands, in fact, for two indices: one for the irreducible representation, and the other distinguishing the degenerate partners of the same frequency. The coefficients $Q_j(\mathbf{q})$ are called *normal coordinates* and represent the time-dependent amplitudes of the normal modes, vibrating with frequencies $\omega_j(\mathbf{q})$. The reality of the displacements and the hermiticity of the dynamical matrix impose the following conditions:

$$\mathbf{e}_\kappa(\mathbf{q}, j) = \mathbf{e}_\kappa^*(-\mathbf{q}, j), \quad \omega_j(\mathbf{q}) = \omega_j(-\mathbf{q}), \quad Q_j(\mathbf{q}) = Q_j^*(-\mathbf{q}).$$

$$(2.3.3.2)$$

In the limit of $\mathbf{q} \to 0$, three of the vibrational branches correspond to homogeneous displacements of the crystal with vanishing frequency along three independent directions. These branches are termed *acoustic*. The remaining $3s - 3$ branches (provided that $s > 1$) are called *optic*; they correspond to relative displacement of sublattices with nonzero frequency.

For completeness, we note that in a phenomenological treatment the amplitude of the polarization set up by atomic displacements of the normal modes with wavevector $\mathbf{q}$ can be expressed as

$$P_\alpha(\mathbf{q}) = \sum_{j} Z_{j\alpha}(\mathbf{q})Q_j(\mathbf{q}), \tag{2.3.3.3}$$

introducing the ($3s \times 3$) *effective charge* matrix of the jth normal mode of vibration (per unit cell of volume V_c),

$$Z_{j\alpha}(\mathbf{q}) = \left(\frac{\partial P_\alpha(\mathbf{q})}{\partial Q_j(\mathbf{q})}\right) = \frac{1}{V_c}\sum_{\kappa} z_{\alpha\beta}^{(\kappa)}\frac{e_{\kappa\beta}(\mathbf{q}, j)}{\sqrt{Nm_\kappa}}. \tag{2.3.3.4}$$

The quantity $z_{\alpha\beta}^{(\kappa)}$ represents the *microscopic* effective charge of the κth atom in the unit cell. Owing to dynamic contributions of ionic deformability, it is not a scalar but rather a (3×3) tensor in general. Hence, in general, the direction of the contribution of a mode to the electrical polarization (2.3.3.3) need not correspond

references