2.3. Raman scattering

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2.3.1. Introduction

The term Raman scattering, traditionally used for light scattering by molecular vibrations or optical lattice vibrations in crystals, is often applied in a general sense to a vast variety of phenomena of inelastic scattering of photons by various excitations in molecules, solids or liquids. In crystals these excitations may be collective (phonons, plasmons, polaritons, magnons) or single-particle (electrons, electron–hole pairs, vibrational and electronic excitation of impurities). Raman scattering provides an important tool for the study of the properties of these excitations. In the present chapter, we shall briefly review the general features of Raman scattering in perfect crystals on a phenomenological basis, paying special attention to the consequences of the crystal symmetry. Our focus will be mainly on Raman scattering by vibrational excitations of the crystal lattice – *phonons*. Nevertheless, most of the conclusions have general validity and may be (with possible minor modifications) transferred also to inelastic scattering by other excitations.

2.3.2. Inelastic light scattering in crystals – basic notions

Although quantum concepts must be used in any complete theory of inelastic scattering, basic insight into the problem may be obtained from a semiclassical treatment. In classical terms, the origin of inelastically scattered light in solids should be seen in the modulation of the dielectric susceptibility of a solid by elementary excitations. The exciting light polarizes the solid and the polarization induced *via* the modulated part of the susceptibility is re-radiated at differently shifted frequencies. Thus inelastic scattering of light by the temporal and spatial fluctuations of the dielectric susceptibility that are induced by elementary excitations provides information about the symmetry and wavevector-dependent frequencies of the excitations themselves as well as about their interaction with electromagnetic waves.

2.3.2.1. *Kinematics*

Let us consider the incident electromagnetic radiation, the scattered electromagnetic radiation and the elementary excitation to be described by plane waves. The incident radiation is characterized by frequency ω_I, wavevector $\mathbf{k}_I$ and polarization vector $\mathbf{e}_I$. Likewise, the scattered radiation is characterized by ω_S, $\mathbf{k}_S$ and $\mathbf{e}_S$:

$$\mathbf{E}_{I,S}(\mathbf{r}, t) = E_{I,S}\mathbf{e}_{I,S} \exp(i\mathbf{k}_{I,S}\mathbf{r} - \omega t). \qquad (2.3.2.1)$$

The scattering process involves the annihilation of the incident photon, the emission or annihilation of one or more quanta of elementary excitations and the emission of a scattered photon. The scattering is characterised by a *scattering frequency* ω (also termed the *Raman shift*) corresponding to the energy transfer $\hbar\omega$ from the radiation field to the crystal, and by a *scattering wavevector* $\mathbf{q}$ corresponding to the respective momentum transfer $\hbar\mathbf{q}$. Since the energy and momentum must be conserved in the scattering process, we have the conditions

$$\omega_I - \omega_S = \omega,$$
$$\mathbf{k}_I - \mathbf{k}_S = \mathbf{q}. \qquad (2.3.2.2)$$

Strictly speaking, the momentum conservation condition is valid only for sufficiently large, perfectly periodic crystals. It is further assumed that there is no significant absorption of the incident and scattered light beams, so that the wavevectors may be considered real quantities.

Since the photon wavevectors ($\mathbf{k}_I$, $\mathbf{k}_S$) and frequencies (ω_I, ω_S) are related by the dispersion relation $\omega = ck/n$, where c is the speed of light in free space and n is the refractive index of the medium at the respective frequency, the energy and wavevector conservation conditions imply for the magnitude of the scattering wavevector q

$$c^2q^2 = n_I^2\omega_I^2 + n_S^2(\omega_I - \omega)^2 - 2n_In_S\omega_I(\omega_I - \omega)\cos\varphi, \qquad (2.3.2.3)$$

where φ is the *scattering angle* (the angle between $\mathbf{k}_I$ and $\mathbf{k}_S$). This relation defines in the (ω, q) plane the region of wavevectors and frequencies accessible to the scattering. This relation is particularly important for scattering by excitations whose frequencies depend markedly on the scattering wavevector (*e.g.* acoustic phonons, polaritons *etc.*).

2.3.2.2. *Cross section*

In the absence of any excitations, the incident field $\mathbf{E}_I$ at frequency ω_I induces in the crystal the polarization $\mathbf{P}$, related to the field by the *linear* dielectric susceptibility tensor χ (ε_0 is the permittivity of free space):

$$\mathbf{P} = \varepsilon_0\chi(\omega_I)\mathbf{E}_I. \qquad (2.3.2.4)$$

The linear susceptibility $\chi(\omega_I)$ is understood to be independent of position, depending on the crystal characteristics and on the frequency of the radiation field only. In the realm of nonlinear optics, additional terms of higher order in the fields may be considered; they are expressed through the respective *nonlinear* susceptibilities.

The effect of the excitations is to modulate the wavefunctions and the energy levels of the medium, and can be represented macroscopically as an additional contribution to the linear susceptibility. Treating this modulation as a perturbation, the resulting contribution to the susceptibility tensor, the so-called *transition susceptibility* $\delta\chi$ can be expressed as a Taylor expansion in terms of *normal coordinates* Q_j of the excitations:

$$\chi \to \chi + \delta\chi, \quad \text{where} \quad \delta\chi = \sum_j \chi^{(j)}Q_j + \sum_{j,j'} \chi^{(j,j')}Q_jQ_{j'} + \dots.$$
$$(2.3.2.5)$$

The tensorial coefficients $\chi^{(j)}$, $\chi^{(j,j')}$, ... in this expansion are, in a sense, *higher-order susceptibilities* and are often referred to as *Raman tensors* (of the first, second and higher orders). They are obviously related to *susceptibility derivatives* with respect to the normal coordinates of the excitations. The time-dependent polarization induced by $\delta\chi$ *via* time dependence of the normal coordinates can be regarded as the source of the inelastically scattered radiation.

The central quantity in the description of Raman scattering is the *spectral differential cross section*, defined as the relative rate of energy loss from the incident beam (frequency ω_I, polarization $\mathbf{e}_I$) as a result of its scattering (frequency ω_S, polarization $\mathbf{e}_S$) in volume V into a unit solid angle and unit frequency interval. The corresponding formula may be concisely written as (see *e.g.* Hayes & Loudon, 1978)

$$\frac{d^2\sigma}{d\Omega\,d\omega_S} = \frac{\omega_S^3\omega_I V^2 n_S}{(4\pi)^2 c^4 n_I} \left\langle \left| \mathbf{e}_I \delta\chi \mathbf{e}_S \right|^2 \right\rangle_\omega. \qquad (2.3.2.6)$$

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* $(\mathrm{d}\sigma/\mathrm{d}\Omega)$ and the *total cross section* (σ_{tot}):

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

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 $10^5\,\mathrm{cm}^{-1}$, much lower than those of the reciprocal-lattice vectors K ($\approx 10^8\,\mathrm{cm}^{-1}$). 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 $0 \leq q \leq 2k$, *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

$$P_\alpha(\mathbf{q}) = \sum_j Z_{j\alpha}(\mathbf{q})Q_j(\mathbf{q}),$$

(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),

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

(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

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