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

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

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)

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

   references