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2.4. Brillouin scattering

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2.4.1. Introduction

Brillouin scattering originates from the interaction of an incident radiation with thermal acoustic vibrations in matter. The phenomenon was predicted by Brillouin in 1922 (Brillouin, 1922) and first observed in light scattering by Gross (Gross, 1930*a*,*b*). However, owing to specific spectrometric difficulties, precise experimental studies of Brillouin lines in crystals were not performed until the 1960s (Cecchi, 1964; Benedek & Fritsch, 1966; Gornall & Stoicheff, 1970) and Brillouin scattering became commonly used for the investigation of elastic properties of condensed matter with the advent of laser sources and multipass Fabry–Perot interferometers (Hariharan & Sen, 1961; Sandercock, 1971). More recently, Brillouin scattering of neutrons (Egelstaff *et al.*, 1989) and X-rays (Sette *et al.*, 1998) has been observed.

Brillouin scattering of light probes long-wavelength acoustic phonons. Thus, the detailed atomic structure is irrelevant and the vibrations of the scattering medium are determined by macroscopic parameters, in particular the density ρ and the elastic coefficients $c_{ijk\ell}$. For this reason, Brillouin scattering is observed in gases, in liquids and in crystals as well as in disordered solids.

Vacher & Boyer (1972) and Cummins & Schoen (1972) have performed a detailed investigation of the selection rules for Brillouin scattering in materials of various symmetries. In this chapter, calculations of the sound velocities and scattered intensities for the most commonly investigated vibrational modes in bulk condensed matter are presented. Brillouin scattering from surfaces will not be discussed. The current state of the art for Brillouin spectroscopy is also briefly summarized.

2.4.2. Elastic waves

2.4.2.1. *Non-piezoelectric media*

The fundamental equation of dynamics (see Section 1.3.4.2), applied to the displacement $\mathbf{u}$ of an elementary volume at $\mathbf{r}$ in a homogeneous material is

$$\rho\ddot{u}_i = \frac{\partial T_{ij}}{\partial x_j}. \tag{2.4.2.1}$$

Summation over repeated indices will always be implied, and $\mathbf{T}$ is the stress tensor. In non-piezoelectric media, the constitutive equation for small strains $\mathbf{S}$ is simply

$$T_{ij} = c_{ijk\ell}S_{k\ell}. \tag{2.4.2.2}$$

The strain being the symmetrized spatial derivative of $\mathbf{u}$, and $\mathbf{c}$ being symmetric upon interchange of k and ℓ, the introduction of (2.4.2.2) in (2.4.2.1) gives (see also Section 1.3.4.2)

$$\rho\ddot{u}_i = c_{ijk\ell}\frac{\partial^2 u_k}{\partial x_j \partial x_\ell}. \tag{2.4.2.3}$$

One considers harmonic plane-wave solutions of wavevector $\mathbf{Q}$ and frequency ω,

$$\mathbf{u}(\mathbf{r}, t) = \mathbf{u}_0 \exp i(\mathbf{Q}\cdot\mathbf{r} - \omega t). \tag{2.4.2.4}$$

For $\mathbf{u}_0$ small compared with the wavelength $2\pi/Q$, the total derivative $\ddot{u}$ can be replaced by the partial $\partial^2 u/\partial t^2$ in (2.4.2.3). Introducing (2.4.2.4) into (2.4.2.3), one obtains

$$c_{ijk\ell}\hat{Q}_j\hat{Q}_\ell u_{0k} = C\delta_{ik}u_{0k}, \tag{2.4.2.5}$$

where $\hat{\mathbf{Q}} = \mathbf{Q}/|\mathbf{Q}|$ is the unit vector in the propagation direction, δ_{ik} is the unit tensor and $C \equiv \rho V^2$, where $V = \omega/|\mathbf{Q}|$ is the phase velocity of the wave. This shows that u_0 is an eigenvector of the tensor $c_{ijk\ell}\hat{Q}_j\hat{Q}_\ell$. For a given propagation direction $\hat{\mathbf{Q}}$, the three eigenvalues $C^{(s)}$ are obtained by solving

$$\left|c_{ijk\ell}\hat{Q}_j\hat{Q}_\ell - C\delta_{ik}\right| = 0. \tag{2.4.2.6}$$

To each $C^{(s)}$ there is an eigenvector $\mathbf{u}^{(s)}$ given by (2.4.2.5) and an associated phase velocity

$$V^{(s)} = \sqrt{C^{(s)}/\rho}. \tag{2.4.2.7}$$

The tensor $c_{ijk\ell}\hat{Q}_j\hat{Q}_\ell$ is symmetric upon interchange of the indices (i, k) because $c_{ijk\ell} = c_{k\ell ij}$. Its eigenvalues are real positive, and the three directions of vibration $\hat{\mathbf{u}}^{(s)}$ are mutually perpendicular. The notation $\hat{\mathbf{u}}^{(s)}$ indicates a unit vector. The tensor $c_{ijk\ell}\hat{Q}_j\hat{Q}_\ell$ is also invariant upon a change of sign of the propagation direction. This implies that the solution of (2.4.2.5) is the same for all symmetry classes belonging to the same Laue class.

For a general direction $\hat{\mathbf{Q}}$, and for a symmetry lower than isotropic, $\hat{\mathbf{u}}^{(s)}$ is neither parallel nor perpendicular to $\hat{\mathbf{Q}}$, so that the modes are neither purely longitudinal nor purely transverse. In this case (2.4.2.6) is also difficult to solve. The situation is much simpler when $\hat{\mathbf{Q}}$ is parallel to a symmetry axis of the Laue class. Then, one of the vibrations is purely longitudinal (LA), while the other two are purely transverse (TA). A pure mode also exists when $\hat{\mathbf{Q}}$ belongs to a symmetry plane of the Laue class, in which case there is a transverse vibration with $\hat{\mathbf{u}}$ perpendicular to the symmetry plane. For all these *pure mode directions*, (2.4.2.6) can be factorized to obtain simple analytical solutions. In this chapter, only pure mode directions are considered.

2.4.2.2. *Piezoelectric media*

In piezoelectric crystals, a stress component is also produced by the internal electric field $\mathbf{E}$, so that the constitutive equation (2.4.2.2) has an additional term (see Section 1.1.5.2),

$$T_{ij} = c_{ijk\ell}S_{k\ell} - e_{mij}E_m, \tag{2.4.2.8}$$

where $\mathbf{e}$ is the piezoelectric tensor at constant strain.

The electrical displacement vector $\mathbf{D}$, related to $\mathbf{E}$ by the dielectric tensor $\boldsymbol{\varepsilon}$, also contains a contribution from the strain,

$$D_m = \varepsilon_{mn}E_n + e_{mk\ell}S_{k\ell}, \tag{2.4.2.9}$$

where $\boldsymbol{\varepsilon}$ is at the frequency of the elastic wave.

In the absence of free charges, $\operatorname{div}\mathbf{D} = 0$, and (2.4.2.9) provides a relation between $\mathbf{E}$ and $\mathbf{S}$,

$$\varepsilon_{mn}Q_nE_m + e_{mk\ell}Q_mS_{k\ell} = 0. \tag{2.4.2.10}$$

For long waves, it can be shown that $\mathbf{E}$ and $\mathbf{Q}$ are parallel. (2.4.2.10) can then be solved for $\mathbf{E}$, and this value is replaced in (2.4.2.8) to give

$$T_{ij} = \left[c_{ijk\ell} + \frac{e_{mij}e_{nk\ell}\hat{Q}_m\hat{Q}_n}{\varepsilon_{gh}\hat{Q}_g\hat{Q}_h}\right]S_{k\ell} \equiv c^{(e)}_{ijk\ell}S_{k\ell}. \tag{2.4.2.11}$$

Comparing (2.4.2.11) and (2.4.2.2), one sees that the effective elastic tensor $\mathbf{c}^{(e)}$ now depends on the propagation direction $\hat{\mathbf{Q}}$. Otherwise, all considerations of the previous section, starting from (2.4.2.6), remain, with $\mathbf{c}$ simply replaced by $\mathbf{c}^{(e)}$.

2.4.3. Coupling of light with elastic waves

2.4.3.1. *Direct coupling to displacements*

The change in the relative optical dielectric tensor $\boldsymbol{\kappa}$ produced by an elastic wave is usually expressed in terms of the strain, using the Pockels piezo-optic tensor $\mathbf{p}$, as

$$(\Delta\kappa^{-1})_{ij} = p_{ijk\ell} S_{k\ell}. \qquad (2.4.3.1)$$

The elastic wave should, however, be characterized by both strain $\mathbf{S}$ *and* rotation $\mathbf{A}$ (Nelson & Lax, 1971; see also Section 1.3.1.3):

$$A_{[k\ell]} = \tfrac{1}{2}\left(\frac{\partial u_k}{\partial x_\ell} - \frac{\partial u_\ell}{\partial x_k}\right). \qquad (2.4.3.2)$$

The square brackets on the left-hand side are there to emphasize that the component is antisymmetric upon interchange of the indices, $A_{[k\ell]} = -A_{[\ell k]}$. For birefringent crystals, the rotations induce a change of the local $\boldsymbol{\kappa}$ in the laboratory frame. In this case, (2.4.3.1) must be replaced by

$$(\Delta\kappa^{-1})_{ij} = p'_{ijk\ell} \frac{\partial u_k}{\partial x_\ell}, \qquad (2.4.3.3)$$

where $\mathbf{p}'$ is the new piezo-optic tensor given by

$$p'_{ijk\ell} = p_{ijk\ell} + p_{ij[k\ell]}. \qquad (2.4.3.4)$$

One finds for the rotational part

$$p_{ij[k\ell]} = \tfrac{1}{2}[(\kappa^{-1})_{i\ell}\delta_{kj} + (\kappa^{-1})_{\ell j}\delta_{ik} - (\kappa^{-1})_{ik}\delta_{\ell j} - (\kappa^{-1})_{kj}\delta_{i\ell}]. \qquad (2.4.3.5)$$

If the principal axes of the dielectric tensor coincide with the crystallographic axes, this gives

$$p_{ij[k\ell]} = \tfrac{1}{2}(\delta_{i\ell}\delta_{kj} - \delta_{ik}\delta_{\ell j})(1/n_i^2 - 1/n_j^2). \qquad (2.4.3.6)$$

This is the expression used in this chapter, as monoclinic and triclinic groups are not listed in the tables below.

For the calculation of the Brillouin scattering, it is more convenient to use

$$(\Delta\kappa)_{mn} = -\kappa_{mi}\kappa_{nj} p'_{ijk\ell} \frac{\partial u_k}{\partial x_\ell}, \qquad (2.4.3.7)$$

which is valid for small $\Delta\kappa$.

2.4.3.2. *Coupling via the electro-optic effect*

Piezoelectric media also exhibit an electro-optic effect linear in the applied electric field or in the field-induced crystal polarization. This effect is described in terms of the third-rank electro-optic tensor $\mathbf{r}$ defined by

$$(\Delta\kappa^{-1})_{ij} = r_{ijm} E_m. \qquad (2.4.3.8)$$

Using the same approach as in (2.4.2.10), for long waves E_m can be expressed in terms of $S_{k\ell}$, and (2.4.3.8) leads to an effective Pockels tensor $\mathbf{p}^e$ accounting for both the piezo-optic and the electro-optic effects:

$$p^e_{ijk\ell} = p_{ijk\ell} - \frac{r_{ijm} e_{nk\ell} \hat{Q}_m \hat{Q}_n}{\varepsilon_{gh} \hat{Q}_g \hat{Q}_h}. \qquad (2.4.3.9)$$

The total change in the inverse dielectric tensor is then

$$(\Delta\kappa^{-1})_{ij} = (p^e_{ijk\ell} + p_{ij[k\ell]}) \frac{\partial u_k}{\partial x_\ell} = p'_{ijk\ell} \frac{\partial u_k}{\partial x_\ell}. \qquad (2.4.3.10)$$

The same equation (2.4.3.7) applies.

2.4.4. Brillouin scattering in crystals

2.4.4.1. *Kinematics*

Brillouin scattering occurs when an incident photon at frequency ν_i interacts with the crystal to either produce or absorb an acoustic phonon at $\delta\nu$, while a scattered photon at ν_s is simultaneously emitted. Conservation of energy gives

$$\delta\nu = \nu_s - \nu_i, \qquad (2.4.4.1)$$

where positive $\delta\nu$ corresponds to the anti-Stokes process. Conservation of momentum can be written

$$\mathbf{Q} = \mathbf{k}_s - \mathbf{k}_i, \qquad (2.4.4.2)$$

where $\mathbf{Q}$ is the wavevector of the emitted phonon, and $\mathbf{k}_s$, $\mathbf{k}_i$ are those of the scattered and incident photons, respectively. One can define unit vectors $\mathbf{q}$ in the direction of the wavevectors $\mathbf{k}$ by

$$\mathbf{k}_i = 2\pi\mathbf{q}n/\lambda_0, \qquad (2.4.4.3a)$$

$$\mathbf{k}_s = 2\pi\mathbf{q}'n'/\lambda_0, \qquad (2.4.4.3b)$$

where n and n' are the appropriate refractive indices, and λ_0 is the vacuum wavelength of the radiation. Equation (2.4.4.3*b*) assumes that $\delta\nu \ll \nu_i$ so that λ_0 is not appreciably changed in the scattering. The incident and scattered waves have unit polarization vectors $\mathbf{e}$ and $\mathbf{e}'$, respectively, and corresponding indices n and n'. The polarization vectors are the principal directions of vibration derived from the sections of the ellipsoid of indices by planes perpendicular to $\mathbf{q}$ and $\mathbf{q}'$, respectively. We assume that the electric vector of the light field $\mathbf{E}_{\rm opt}$ is parallel to the displacement $\mathbf{D}_{\rm opt}$. This is exactly true for many cases listed in the tables below. In the other cases (such as skew directions in the orthorhombic group) this assumes that the birefringence is sufficiently small for the effect of the angle between $\mathbf{E}_{\rm opt}$ and $\mathbf{D}_{\rm opt}$ to be negligible. A full treatment, including this effect, has been given by Nelson *et al.* (1972).

After substituting (2.4.4.3) in (2.4.4.2), the unit vector in the direction of the phonon wavevector is given by

$$\hat{\mathbf{Q}} = \frac{n'\mathbf{q}' - n\mathbf{q}}{|n'\mathbf{q}' - n\mathbf{q}|}. \qquad (2.4.4.4)$$

The Brillouin shift $\delta\nu$ is related to the phonon velocity V by

$$\delta\nu = VQ/2\pi. \qquad (2.4.4.5)$$

Since $\nu\lambda_0 = c$, from (2.4.4.5) and (2.4.4.3), (2.4.4.4) one finds

$$\delta\nu \cong (V/\lambda_0)[n^2 + (n')^2 - 2nn'\cos\theta]^{1/2}, \qquad (2.4.4.6)$$

where θ is the angle between $\mathbf{q}$ and $\mathbf{q}'$.

2.4.4.2. *Scattering cross section*

The power $\mathrm{d}P_{\rm in}$, scattered from the illuminated volume V in a solid angle $\mathrm{d}\Omega_{\rm in}$, where $P_{\rm in}$ and $\Omega_{\rm in}$ are measured inside the sample, is given by

$$\frac{\mathrm{d}P_{\rm in}}{\mathrm{d}\Omega_{\rm in}} = V\frac{k_B T\pi^2 n'}{2n\lambda_0^4 C} M I_{\rm in}, \qquad (2.4.4.7)$$

where $I_{\rm in}$ is the incident light intensity inside the material, $C = \rho V^2$ is the appropriate elastic constant for the observed phonon, and the factor $k_B T$ results from taking the fluctuation–

references