SCATTERING OF LIGHT BY CRYSTALS

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Preface

The experimental and theoretical study of light scattering has a lengthy history and some aspects of the phenomenon were well understood by the end of the nineteenth century. Its value as a tool for investigating the properties of matter, however, was fully realized only with the interpretation and observation of inelastic light scattering by Brillouin and Raman in the 1920s. More recently, the invention of the laser has extended and deepened the range of material properties accessible to measurement by light-scattering spectroscopy.

As with any field of science, the development and expansion of light-scattering work has necessarily led to a degree of fragmentation of the field. Thus, studies of gases, liquids, and solids are normally carried out by different groups of workers. There are further divisions associated with the size of the frequency shift of the light brought about by its inelastic scattering, the shifts being measured with increasing energy by intensity-fluctuation, Fabry-Perot, and diffraction-grating spectroscopy. A comprehensive account of the entire field would be extremely long.

This book is concerned with the scattering of light by solids, and its main emphasis is on the study of excitations in crystals by light-scattering spectroscopy. Chapter 1 surveys the scope of light-scattering experiments and presents the main theoretical tools available for calculation of scattering cross sections. The typical frequencies of excitations in crystals are such that they can normally be examined by either Brillouin scattering, using Fabry-Perot interferometric spectroscopy, or by Raman scattering, using grating spectrometers, and these techniques are described in Chapter 2.

The remainder of the book is devoted to a systematic account of the measurements and theories of light scattering by the various solid-state excitations. The major part of the published literature is concerned with light scattering by lattice vibrations and these receive the greatest emphasis here. Chapters 3 and 4 cover Raman scattering by nonpolar and polar optic vibrations, while Brillouin scattering by acoustic vibrations is discussed in Chapter 8. Vibrational effects are also of great importance in the light-scattering phenomena associated with structural phase changes; these are treated in Chapter 5. Raman scattering by magnetic and electronic excitations in crystals is described in Chapters 6 and 7.

The treatment is particularly intended for a graduate student or other research worker entering the field with the usual undergraduate background knowledge of quantum mechanics, electromagnetic theory, statistical mechanics, and solid-state physics, but without any prior knowledge of light-scattering theory. Some background in group theory would be useful but is not an essential prerequisite for reading the book. The book is also intended to serve as a reference text on the basic techniques and theory of light scattering by crystals. However, in view of its primary role as a textbook for students, there is no very serious attempt to assign due credit to those who made the first observations or first theories of the various phenomena. Rather, we have in each case chosen those experiments and theories that seem to illustrate and explain the features of interest in the simplest and most direct ways.

The book uses SI units throughout except for the retention of the inverse centimeter as a unit of frequency (1 $cm^{-1} = 3 \times 10^{10}$ Hz). This modest departure from the rules of the International System accords with almost universal usage in light-scattering research publications.

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CHAPTER ONE

Basic Features and Formal Theory of Light Scattering

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Much of the formal theory of light scattering is common to all varieties of measurement. It is the purpose of this first chapter to cover the common ground and to derive general results that can be applied in subsequent chapters to scattering by the various kinds of solid-state excitation. The main goals are a few basic formulas, summarized at the end of the chapter, for the kinematics and cross section of a light-scattering experiment.

1.1 HISTORICAL INTRODUCTION

We begin with a brief sketch of the historical development of light-scattering studies. Some of the earliest investigations were carried out by Tyndall (1868-1869). He found that white light, scattered at 90° to the incident light by very fine particles, was partly polarized and also slightly blue in color. He concluded that both the polarization and the blue color of light from the sky were caused by scattering of sunlight by dust particles in the atmosphere.

Lord Rayleigh (1899), following his earlier work (Strutt 1871a, b, c), treated the scattering of light by spherical particles of relative permittivity κ suspended in a medium of relative permittivity κ_0. If the particle separation is greater than the wavelength λ of the light so that the particles scatter independently of each other, and if in addition the particle radius is less than the wavelength of light, the intensity of the scattered light is (for a modern derivation, see Section 72 of Landau and Lifshitz 1960)

$$I_S = I\frac{9\pi^2 N\mathfrak{v}^2}{2\lambda^4 r^2}\left(\frac{\kappa-\kappa_0}{\kappa+2\kappa_0}\right)^2(1+\cos^2\phi), \tag{1.1}$$

where I is the intensity of the unpolarized incident light, N is the number of scattering particles of volume $\mathfrak{v}$, r is the distance to the point of observation, and ϕ is the angle through which the light is scattered. An important feature of this result, which we shall encounter many times in the course of the book, is the λ^{-4} dependence of the scattered intensity. This is known as Rayleigh's law, and it provides an explanation for the blueness of the sky. However, Rayleigh knew in 1899 that light is scattered by gas molecules in the air, and he suspected rightly at that time that particles of dust in the atmosphere are not essential for the blueness and polarization of light from the sky.

The treatment of molecular scattering encounters a fundamental problem of which Rayleigh was aware. In dense media such as liquids and solids, and even gases at atmospheric pressure, the molecular separation is

small compared to the wavelength of light. There is now a coherence between the light beams scattered by different molecules, which no longer act as independent scatterers. Indeed, the light intensity scattered in any direction other than forward is zero for a perfectly homogeneous medium (see Sections 1.2 and 1.3). However, it was well known that apparently homogeneous fluids scatter light quite strongly. The scattering is especially pronounced when a fluid approaches its critical temperature, a phenomenon referred to as critical opalescence (Andrews 1869).

The problem of opalescence was explained by Smoluchowski (1908), who suggested that the density of an apparently homogeneous medium nevertheless varies from point to point because of thermal motions of the molecules. Light scattering is caused by density fluctuations, which become large at the critical point. Einstein (1910) showed that the wavevector of the scattering fluctuation conserves momentum between the incident and scattered photons.

These earlier workers were concerned with the intensity of the scattered light. Progress in understanding its frequency spectrum was first made by Brillouin (1914, 1922), who calculated the spectrum of light scattered by the density fluctuations associated with sound waves. He found that the spectrum of a fluid consists of a doublet split symmetrically around the frequency of the incident light. The splitting, which is very much smaller than the frequency of the incident light, is determined by the velocity of those sound waves whose wavelength is close to that of the light. The Brillouin doublets (called Mandelstam-Brillouin doublets in the Russian literature) were first observed by Gross (1930a, b, c, 1932) in liquid media. The liquids also showed a central unshifted component in the scattered light. This was explained by Landau and Placzek (1934) as the scattering by nonpropagating entropy fluctuations, although details of the calculation were not presented in the paper (see Chapter 8); it is generally referred to as Rayleigh scattering.

While progress was being made in the understanding of scattering by thermally induced density fluctuations, advances were also in progress on other fronts. Smekal (1923) studied the scattering of light by a system with two quantized energy levels and predicted the existence of sidebands in the scattered spectrum. This effect was subsequently observed in Raman's laboratory (Raman and Krishnan 1928a, b); it was found that the light scattered by liquids such as benzene contains sharp sidebands in pairs symmetrically disposed around the incident frequency with shifts identical to the frequencies of some of the infrared vibrational lines. At much the same time, Landsberg and Mandelstam (1928) discovered a similar phenomenon in quartz. This inelastic scattering of light by molecular and crystal vibrations is now known as the Raman effect. It is caused by modulation of the susceptibility (or, equivalently, polarizability) of the

medium by the vibrations (and, as described in this book, the scattering by other excitations in solids, including plasmons, excitons, and magnons, occurs by the same mechanism). The vibrational Raman effect was well documented and well understood by 1934 (Placzek 1934).

After the intense activity of the late 1920s and early 1930s, the study of light scattering proceeded at a more sedate pace, receiving more attention in India, Russia, France, and Canada than in other countries (for reviews of this period, see Menzies 1953; Fabelinskii 1957; and Loudon 1964). This was due in part to the weakness of light scattering, a second-order effect, compared with infrared absorption as techniques for determining vibrational properties. This situation was dramatically altered by the invention of the helium-neon laser in 1961 and by the subsequent development of improved optical spectrometers and detection techniques. These advances produced a renaissance in light-scattering studies, which began in 1964 and still has considerable momentum.

1.2 THE SCATTERING CROSS SECTION

1.2.1 Basic Definitions

The main meeting point of light-scattering experiments and theory is the scattering cross section. We describe here a simple kind of light-scattering experiment and define the types of cross section that can in principle be measured.

Consider the idealized experiment shown in Figure 1.1. An incident parallel beam of light from a laser source passes through a volume V of some material and is scattered in all directions from all the illuminated part of the sample. A detector is set up to examine the light scattered at angle ϕ to the direction of the incident beam. The range of acceptance of the detector symbolized by the lens, is limited to a small solid angle $d\Omega$, and the detector field stop restricts the volume v of the sample from which scattered light is received. The intensities of incident and scattered light are denoted $\mathcal{I}_I$ and $\mathcal{I}_S$, respectively.

The magnitude of the scattered intensity is determined by a variety of factors. One of these is the transmission of the light through the sample surfaces, which varies with φ in a complicated way, particularly for samples with edges or corners. The resulting dependence of $\mathcal{I}_S$ on φ obscures the basic physics of the scattering process. It is therefore customary to convert the directly measured intensities $\mathcal{I}_I$ and $\mathcal{I}_S$, solid angle $d\Omega$, and scattering angle φ into corresponding intensities I_I and I_S, solid angle $d\Omega$, and scattering angle ϕ *inside* the scattering sample. These

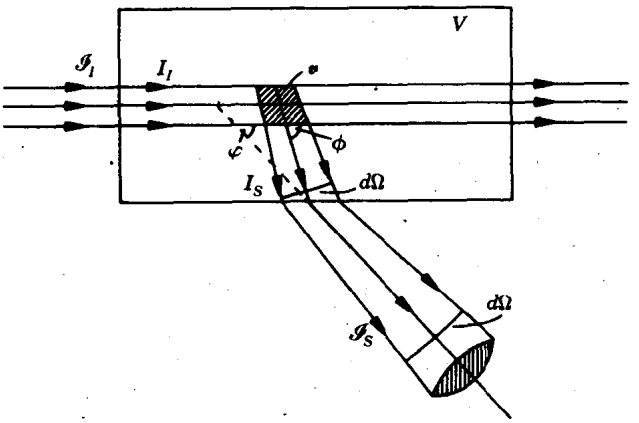

Figure 1.1 Idealized scattering experiment.

conversions can all be made from a knowledge of the sample shape and its refractive indices and the beam geometries (Lax and Nelson 1976). The variation of the scattering volume v with scattering angle can be similarly determined.

The experiment thus provides results for the variation of I_S with ϕ. An additional complication occurs for scattering by a crystalline medium, where the scattered intensity depends not only on the scattering angle but also on the orientations of the crystal symmetry axes relative to the light beams. The isotropy of a gas, liquid, or amorphous solid removes this latter dependence.

The spread of frequencies in the incident laser light is normally very small, and its intensity can be regarded as monochromatic with a single angular frequency ω_I. However, the scattered intensity is usually distributed across a range of frequencies, as shown in Figure 1.2. The peak in the center of the spectrum is the contribution of the incident photons that have been elastically scattered with no change in frequency. The remaining peaks correspond to inelastic scattering and their shifts from ω_I normally occur in two somewhat separate frequency ranges. The Brillouin component, resulting from scattering by sound waves, occurs close to the frequency of the incident light; typical shifts are approximately 1 cm^{-1} or smaller. The Raman component, resulting from scattering by internal vibrations of molecules or optic vibrations in crystals, lies at higher shifts, normally larger than 10 cm^{-1} and often of order 100–1000 cm^{-1}. The basic mechanisms for Brillouin and Raman scattering are essentially the same, but the experimental techniques are different; they are considered separately in Chapter 8 and Chapters 3 and 4, respectively.

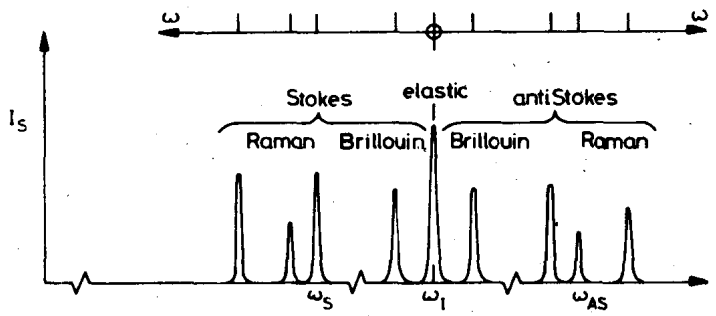

Figure 1.2 Schematic spectrum of scattered light.

The inelastic contributions are further subdivided; those scattered frequencies smaller than ω_I are denoted ω_S and are known as the Stokes component, while the scattered frequencies larger than ω_I are denoted ω_{AS} and they form the anti-Stokes component. Each scattered photon in the Stokes component is associated with a gain in energy $\hbar\omega$ by the sample, where

$$\omega = \omega_I - \omega_S. \tag{1.2}$$

Similarly, the sample loses energy $\hbar\omega$ for each scattered photon in the anti-Stokes component, where

$$\omega = \omega_{AS} - \omega_I. \tag{1.3}$$

The occurrence of scattered photons at particular frequencies ω_S and ω_{AS} depends upon the ability of the scattering sample to absorb or emit energy in quanta of magnitude $\hbar\omega$ determined by (1.2) or (1.3) The intensity peaks in the inelastic spectrum thus correspond to the various excited states of the sample. The most important application of inelastic light-scattering spectroscopy is the determination of excitation energies by measurement of frequency shifts from ω_I in the scattered light. Measurements of the frequency widths of the intensity peaks also provide information on the excited-state lifetimes.

Measurement of the Stokes part of the spectrum for a fixed scattering angle determines a function

$$\frac{d^2\sigma}{d\Omega\, d\omega_S} \equiv \text{spectral differential cross section.} \tag{1.4}$$

This is defined as the rate of removal of energy from the incident beam as

a result of its scattering in volume $\mathfrak{v}$ into a solid-angle element $d\Omega$ with a scattered frequency between ω_S and $\omega_S + d\omega_S$, divided by the product of $d\Omega\, d\omega_S$ with the incident-beam intensity. The various quantities are determined inside the scattering medium (see Figure 1.1). The spectral differential cross section has the dimensions of area divided by frequency.

An analogous definition can be made for the anti-Stokes part of the spectrum. However, it is shown in Section 1.4.5 that the Stokes and anti-Stokes cross sections for the great majority of scattering experiments are related to a very good approximation by

$$n(\omega)\frac{d^2\sigma}{d\Omega\, d\omega_S} = \{n(\omega)+1\}\frac{d^2\sigma}{d\Omega\, d\omega_{AS}}, \tag{1.5}$$

where the frequencies satisfy (1.2) and (1.3). The Bose-Einstein thermal factor is explicitly

$$n(\omega) = \frac{1}{\exp(\hbar\omega/k_B T)-1}, \tag{1.6}$$

where k_B is Boltzmann's constant and T is the sample temperature. Figure 1.3 shows the ratio $n(\omega)/\{n(\omega)+1\}$ as a function of $k_B T/\hbar\omega$. The anti-Stokes spectrum has a smaller strength than the Stokes spectrum, and it is usually more convenient to measure the latter. Most theoretical treatments consider only the Stokes component, relying on (1.5) to generate the corresponding results for the anti-Stokes component.

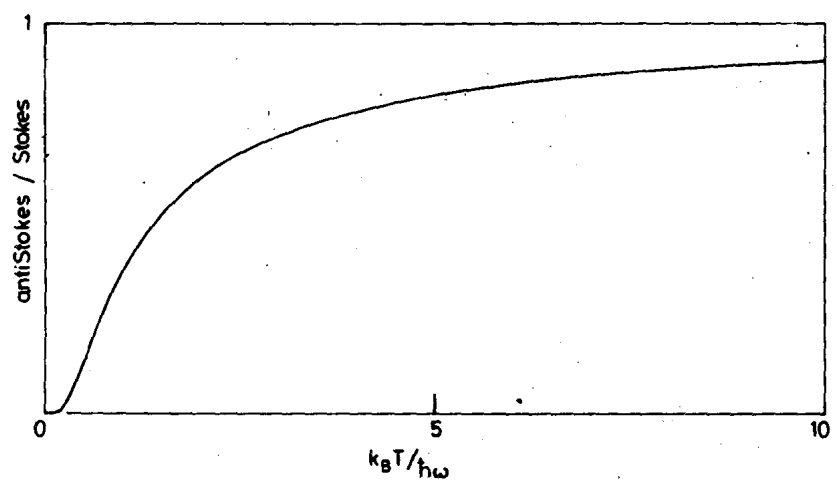

Figure 1.3 Ratio $n(\omega)/\{n(\omega)+1\}$ of the anti-Stokes to the Stokes cross section as a function of temperature and frequency shift.

The *differential cross section* is obtained by integration of the spectral differential cross section,

$$\frac{d\sigma}{d\Omega} = \int d\omega_S \frac{d^2\sigma}{d\Omega\, d\omega_S} \equiv \text{differential cross section.} \tag{1.7}$$

The integration can equally be taken over the frequency ω, since ω_S and ω differ by the constant frequency ω_I as in (1.2). The range of integration is usually restricted to include just a single intensity peak in the scattered spectrum. The differential cross section then determines the total scattering into solid angle $d\Omega$ associated with a particular excited state of the sample. It is often easier to calculate than the spectral differential cross section but it contains less information of potential value in interpreting the scattering process.

Finally, the *cross section* is obtained by integration of the differential cross section over all directions in space

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} \equiv \text{cross section.} \tag{1.8}$$

The cross section determines the total scattering in all directions caused by a particular excited state, and its experimental evaluation requires measurements of the scattered intensity at a large number of scattering angles. Such series of measurements are rarely made because the sample excitation energies, and lifetimes are in most cases independent of the scattering angle used in their determination (for exceptions, see Sections 4.3, 7.3, and 8.1). The cross section, however, can be computed from a restricted set of measurements of the differential cross section if a theoretical expression for the angular variation of the latter is available.

The three varieties of cross section are introduced above in decreasing order of importance. All three are referred to simply as the cross section when the distinction is clear from the context. The cross sections for an extended medium are proportional to the scattering volume $\mathcal{V}$ and quoted results are usually expressed in terms of a unit volume of scatterer. Note that a cross section for 1 m^3 of scatterer expressed in square meters is numerically equal to 100 times the same cross section for 1 cm^3 of scatterer expressed in square centimeters.

1.2.2 Classical Theory of Elastic Scattering

Several typical features of light-scattering theory can be simply illustrated by a classical description of elastic scattering by an atom. Only the main results need be quoted, since a full account is given in Chapter 11 of