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Willes H. Weber Roberto Merlin (Eds.)

Raman Scattering in Materials Science

With 256 Figures



Springer

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Preface

The idea for this book began about two years ago when one of us (WHW) organized a focused session at the March Meeting of the American Physical Society on the applications of Raman scattering in materials characterization. The response to that session was overwhelming; we had twice as many papers as we anticipated, and it became clear at that time that Raman spectroscopy was becoming a standard tool for the materials scientist. Raman scattering has evolved from a technique practiced by dedicated laser physicists working in dark laboratories to a general-purpose characterization tool routinely applied to a wide range of materials science problems. With the addition of fiber optics, Raman probes are now in use for monitoring thin-film deposition processes and for such practical tasks as sorting waste polymers for recycling. There are two reasons for this evolution. First, the new generation of Raman instruments, with such improvements as array detectors, turnkey lasers, single-stage high-throughput spectrometers and holographic notch filters to reject Rayleigh light, made the implementation of Raman scattering simpler and less expensive. Second, many scientists in the field realized that the sort of detailed information obtainable from Raman scattering measurements could not be obtained as easily or at all with any other methods.

The purpose of the book is to provide a link between the fields of materials science and Raman spectroscopy. The first chapter gives an overview of the theory of Raman scattering in solids, with experimental examples drawn from well-known materials to illustrate most of the basic concepts. This chapter avoids rigorous mathematical treatments, but provides ample references to where such treatments can be found. The second chapter discusses the tremendous improvements in Raman instrumentation that have been made in the last decade and the impact this has had on the widespread use of Raman scattering. The remaining eight chapters focus on specific materials systems that comprise the mainstream of current research in materials science: bulk and alloy semiconductors; semiconductor heterostructures; high- T_c superconductors; catalysts materials; III-V nitrides; fullerenes, nanotubes, and other inorganic carbon-based materials; polymers; and manganites. These chapters form the heart of the book, and they provide extensive examples of Raman applications to current materials science problems. To augment these chapters, we have added short contributions on related subjects of historical or

VI Preface

topical interest. These short contributions are referred to as “boxes” and are generally invited by the author(s) of the chapter after which each appears. They range from an anecdotal account of a meeting with C.V. Raman to a purely technical account of strain mapping in semiconductor devices. The resulting book is the most thorough collection of Raman applications in materials science ever assembled in one volume.

April 2000
Ann Arbor

Willes H. Weber
Roberto Merlin

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1 Overview of Phonon Raman Scattering in Solids

R. Merlin, A. Pinczuk, and W.H. Weber

Abstract. This chapter provides a short review of the concepts underlying inelastic light scattering by phonons in solids. The discussion introduces the basic scattering mechanisms and the nomenclature used in the Raman community, but it avoids mathematical details. We give extensive references to the literature on topics that delve more deeply into theoretical issues. In addition, selected experimental results, obtained primarily from simple, well-known materials such as C, Si or GaAs, are shown to illustrate Raman spectroscopy applications to materials science.

The term Raman scattering is historically associated with the scattering of light by optical phonons in solids and molecular vibrations. In this book, the term refers to inelastic scattering by most elementary excitations associated with degrees of freedom of ions and electrons in crystalline and amorphous solids. The only exceptions are long wavelength acoustic phonons (sound waves) and acoustic magnons, which are identified with Brillouin scattering. Inelastic scattering processes are two-photon events that involve the simultaneous annihilation of an incident photon and the creation of a scattered photon [1]. If the frequency of the latter, ω_S , is smaller than that of the former, ω_L , a quantum of energy $\hbar(\omega_L - \omega_S)$ is added to the scattering medium and the event is referred to as a *Stokes* process (here, we use ω_L to designate the incident photon frequency, since the incident beam is invariably generated by a laser source). If, instead, $\omega_S > \omega_L$, we have an *anti-Stokes* process, where an elementary excitation of the medium is annihilated. For systems in thermal equilibrium, the anti-Stokes intensity depends strongly on temperature, since these processes can occur only when the medium is not in its ground state. The dominant form of Raman scattering, first-order scattering, involves a single quantum of excitation in the medium. However, it is not uncommon for materials to show strong higher-order processes leading to the creation or annihilation of two or more quanta.

Close to 75 years after the phenomenon was discovered [2], Raman scattering has become one of the most versatile spectroscopic tools to study the low-lying excitations of condensed matter systems. The group of excitations that can be accessed in Raman experiments is large and is growing as different areas of condensed matter science evolve. In solid-state media, it includes phonons, magnons, and impurity vibrational modes as well as the elementary

excitations of bulk and low-dimensional electronic systems. While the focus of this chapter is on Raman scattering by phonons, the conceptual discussion of conservation laws and selection rules applies, with few modifications, to electronic excitations as well. For a general description of electronic Raman scattering, particularly for doped semiconductors, we refer the reader to Chap. 7 of the book by Hayes and Loudon [3], and the review by Klein [4]. Magnetic scattering is discussed by Cottam and Lockwood [5] and in Chap. 6 of [3]. Extensive information on the various forms of Raman scattering and a list of original references can be found in the proceedings of topical conferences [6–10] and the series *Light Scattering in Solids* [11–18].

The strongest inelastic light scattering processes are due to coupling of light to the electric moments of the scattering medium [3,19–22]. Light scattering processes in which light couples to magnetic moments are by far too weak to interpret experiments. Further, the intensities of scattering processes in which there is direct coupling of light to the motion of the ions are negligible [23]. At the relatively high frequency of light employed in current experiments, the dominant contributions to electric moments are due to excitation of electrons across energy bandgaps (these are the so-called *interband* transitions in solids) [19,22]. The coupling of incident and scattered light to the medium may be understood as the modulation of the electric susceptibility by elementary excitations [19]. It is well known that coupling of light to optical transitions of the scattering medium is enhanced when ω_L and ω_S are close to interband gaps. Such optical resonances result in large enhancements of Raman scattering cross-sections and intensities [24–26]. Events involving light at frequencies ω_L and ω_S that are close to interband transition energies are referred to as resonant Raman processes (see Sect. 1.2).

The reader may find excellent classical, i.e., macroscopic presentations of the derivation of the Raman cross-section intensities in [1,3]. In classical as well as in quantum-mechanical descriptions [19,22,24–26], the intensities are calculated as *differential cross-sections*, which represent the rate at which energy is removed from the incident beam. The calculations of the cross-sections incorporate parameters that describe modulations of the electric-dipole density by elementary excitations of the scattering media. In classical descriptions, these modulations are represented by derivatives of the electric susceptibility. Macroscopic theories offer relatively simple, one could say intuitive, understandings of many light scattering phenomena [27]. With the use of the methods of group theory, macroscopic theories also yield symmetry-based selection rules for the polarization of the incident and scattered light [3,21,22].

Microscopic, that is quantum-mechanical, formulations are required in any attempt to describe resonant inelastic light scattering processes [24–26]. The microscopic description incorporates explicit interactions that account for the coupling between the photons and the electronic states of the material. The quantum formulation also requires precise consideration of the interactions between electrons and the elementary excitations of the media. In the specif-

ic case of phonons, these are the diverse forms of the electron–phonon interaction. Inelastic light scattering resonances in bulk semiconductors have been investigated in considerable detail [25,26,28]. In particular, resonant scattering by optical phonons and by electronic excitations are reviewed in [26], and specific examples are given in several of the following chapters.

The study of resonant effects continues to be of great interest because enhanced cross-sections enable Raman scattering observations of otherwise weak processes. Early research demonstrated resonant enhancement in the spectra of optical phonons [29–32] and excitations of an electron gas at semiconductor surfaces [33]. In the latter case, light scattering occurs within ultrathin layers of thickness that in some instances are 10 nm or even smaller. The enhanced cross-sections revealed in this research played a key role in seminal light scattering studies of vibrational modes in semiconductor superlattices and quantum wells [34–37], as discussed in Chap. 3. Resonances are also crucial in studies of *low*-dimensional electron systems in semiconductor heterostructures and field-effect-devices [38–41]. Low dimensional electron systems that reside in semiconductor quantum structures are of great interest in contemporary materials science, device applications and fundamental physics.

1.1 Light Scattering Mechanisms and Selection Rules

1.1.1 Conservation Laws

Consider a monochromatic light beam of frequency ω_L . The magnitude of the propagation vector, \mathbf{k}_L , is $|\mathbf{k}_L| = \omega_L \eta(\omega_L)/c$ where $\eta(\omega_L)$ is the refractive index. Due to the scattering, a fraction of the incident photons are annihilated with creation of a scattered field in which the photons have frequency ω_S . The propagation vector of the scattered light is \mathbf{k}_S , with $|\mathbf{k}_S| = \omega_S \eta(\omega_S)/c$. We define the *scattering frequency* as

$$\omega = \omega_L - \omega_S , \quad (1.1)$$

and the *scattering wave vector* as

$$\mathbf{k} = \mathbf{k}_L - \mathbf{k}_S . \quad (1.2)$$

Inelastic scattering must satisfy conservation of energy and momentum. To consider these conservation laws we recall that in perfect crystals, that is, in idealized materials that display perfect translation symmetry, the elementary excitations can be labeled by the wave vector \mathbf{q} , also known as the crystal momentum [42]. These modes are represented by a dispersion relation that specifies a frequency ω_q for each value of \mathbf{q} [42]. In first-order processes, only a single elementary excitation participates. In such situations, momentum

conservation translates into the requirement that the scattering wave vector equal the wave vector of the excitation:

$$\mathbf{k} = \mathbf{q} . \quad (1.3)$$

Similarly, conservation of energy leads to

$$\omega = \omega_q . \quad (1.4)$$

In higher-order scattering processes ω becomes the sum of the frequencies of two or more quanta for which the total wave vector is \mathbf{k} (see Sect. 1.3).

1.1.2 Kinematics: Wave Vector Conservation

Processes that conserve crystal momentum obey (1.3). The magnitude and orientation of the scattering wave vector are determined by the geometry of the scattering experiment. Figure 1.1 shows three standard arrangements for the propagation of incident and scattered beams. The smallest and the largest scattering wave vector are obtained, respectively, in the forward ($\theta = 0^\circ$) and the backscattering ($\theta = 180^\circ$) geometries. In the forward case, the magnitude of the scattering wave vector is

$$|\mathbf{k}_{\min}| = [\eta(\omega_L)\omega_L - \eta(\omega_S)\omega_S] (1/c) , \quad (1.5)$$

whereas, in the backscattering configuration, we have

$$|\mathbf{k}_{\max}| = [\eta(\omega_L)\omega_L + \eta(\omega_S)\omega_S] (1/c) . \quad (1.6)$$

It follows from (1.6) that for typical experiments, in the visible and near infrared, $\mathbf{k}_{\max} \leq 10^6 \text{ cm}^{-1}$. This wave vector is much smaller, by about two orders of magnitude, than the value corresponding to the Brillouin zone boundary

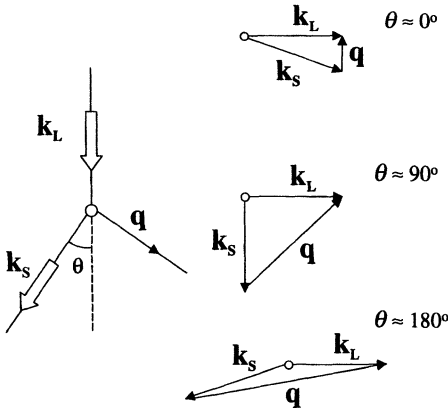


Fig. 1.1. Diagrams showing various scattering geometries