

RESEARCH

Raman Scattering in Solids

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Inelastic scattering of visible or ultraviolet light from matter is called “Raman scattering” after one of its discoverers. The development of lasers as coherent light sources in the early 1960s caused an upturn for almost all methods of optical spectroscopy. In this context, Raman scattering has become an important tool for the studies of elementary excitations in gases, liquids, and solids in the past years. In this article, we review some of the principles of Raman scattering in solids and the application of Raman spectroscopy as a tool to study basic physical properties.

In optically homogeneous media light will propagate straight through the material. In the case of inhomogeneous media, however, especially if the inhomogeneities are comparable in size to the wavelength of light the radiation will be scattered into various directions in space. If the material shows only spatial inhomogeneities one will observe elastic scattering without a shift of frequency. Depending on the size and the nature of the optical inhomogeneity the effects are called Tyndall scattering, Mie scattering, Rayleigh scattering, etc. If the inhomogeneities vary in time the spectrum of the scattered light will show sidebands coming from inelastic scattering. The processes of Brillouin and Raman scattering fall in this category. The spectroscopy of the inelastically scattered light can provide important information about electronic, vibrational, or magnetic properties of the scattering system¹.

Historical overview

At the beginning of the past century, the pioneering work of Planck who quantized the electromagnetic field² and Einstein who explained the photoelectric effect³ prepared the ground for the study of inelastic light scattering processes. Since that time it has been clear that light can be described not only as an electromagnetic wave, but also as a particle “beam” consisting of single energy quanta. These so-called *photons* carry both energy and momentum. Therefore, they can participate in inelastic scattering processes which exchange energy and momentum between them and the scattering medium.

The first theoretical approach to inelastic light scattering was done by Smekal in 1923⁴. He considered a system with two quantized energy levels and predicted



Chandrasekhara Venkata Raman was born at Tiruchirapalli in Southern India on November 7th, 1888. He entered Presidency College, Madras, in 1902, and passed his B.A. examination in 1904, winning the first place and the gold medal in physics; in 1907 he gained his M.A.

degree, obtaining the highest distinctions. Since at that time a scientific career did not appear to present the best possibilities, Raman joined the Indian Finance Department in 1907; though the duties of his office took most of his time, Raman found opportunities for carrying on experimental research in the laboratory of the Indian Association for the Cultivation of Science at Calcutta (of which he became Honorary Secretary in 1919). In 1917 he was offered a chair of physics at Calcutta University, and decided to accept it. After 15 years at Calcutta he became professor at the Indian Institute of Science at Bangalore (1933-1948), and since 1948 he was director of the Raman Institute of Research at Bangalore, established and endowed by himself.

In 1922 he published his work on the “Molecular Diffraction of Light”, the first of a series of investigations with his collaborators which ultimately led to his discovery, on the 28th of February, 1928, of the radiation effect which bears his name (*Indian J. Phys.* **2**, 387 (1928)), and which gained him the 1930 Nobel Prize in Physics.

C.V. Raman has been honoured with a large number of honorary doctorates and memberships of scientific societies. He was elected a Fellow of the Royal Society early in his career (1924), and was knighted in 1929. Prof. Raman died on November 21st, 1970 in Bangalore.

Figure 1: Biography of Chandrasekhara Venkata Raman (taken from Nobel Lectures of The Nobel Foundation).

the existence of sidebands in the spectrum of the scattered light. This effect was observed by C.V. Raman (fig. 1) and K.S. Krishnan five years later⁵. They found that the light scattered by a liquid such as benzene contains sidebands in pairs symmetrically disposed around the incident frequency. The shifts were identical to the frequencies of some of the infrared vibrational spectral

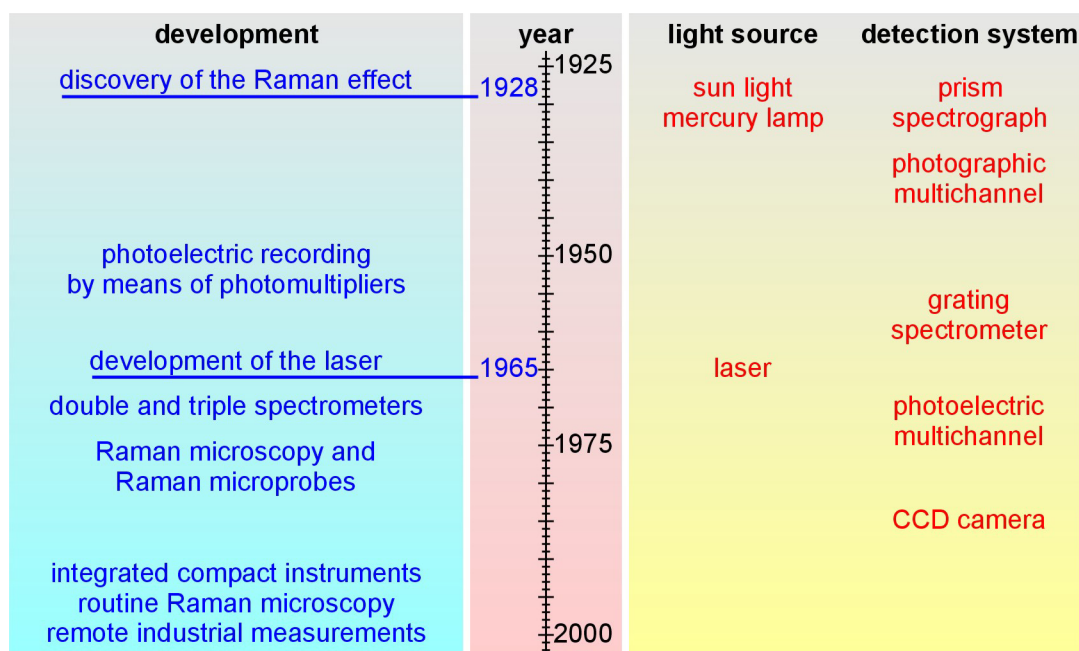


Figure 2: Development of Raman spectroscopy within the last 75 years.

lines of the liquid. At the same time, Landsberg and Mandelstam observed a similar effect in solids such as quartz⁶. This inelastic scattering of light by molecular and crystal vibrations is known as the *Raman effect*. It is caused by modulations of the susceptibility or polarizability of the scattering material by vibrations or other excitations.

In the past 75 years, Raman spectroscopy has become an important tool for the study of elementary excitations in gases, liquids, and solids. It is interesting to consider this evolution from the point of view of an experimentalist since the most impressive progress has been clearly related to the availability of new technologies (fig. 2). It is universally accepted that laser light sources were the driving force for a complete renewal of Raman instrumentation. In addition, decisive improvements have been permitted by the advent of other components such as photomultipliers, image intensifiers, solid state detector arrays, and sophisticated optical devices, and of course by the development of computer data processing. It is important to notice that this progress in instrumentation often relied on pioneering experimental studies 10 to 20 years before. A considerable amount of laboratory study in various countries has been the necessary basis for the evolution of the commercial instruments which are now available.

The Raman effect

Raman scattering is the inelastic scattering of light with momentum and energy transfer between the photons and the scattering material (fig. 3). The photon is characterized by its energy $E = \hbar\omega$ (where ω is an angular frequency) and momentum $\vec{p} = \hbar\vec{k}$. The incoming photon (I) will either be reflected (R) specularly at the surface of the sample or penetrate into it. There, it may participate in elastic or inelastic scattering processes with the

elementary excitations of the medium and leave the material as scattered photon (S). If its energy (E_S) is different from that of the incoming photon (E_I) the scattering process was associated with an energy transfer to the sample.

The Raman effect itself is based on three single processes happening all within the time limited by the Heisenberg uncertainty (fig. 4):

- (1) An incoming photon with wave vector \vec{k}_I and frequency ω_I is absorbed, and the absorbing material is excited from its initial state i to an intermediate virtual state v .
- (2) An elementary excitation with wave vector \vec{q} and frequency ω is created (Stokes process) or annihilated (Anti-Stokes process).
- (3) The material undergoes a transition from the intermediate state v to the final state f . This process is accompanied with the emission of the scattered photon with (\vec{k}_S, ω_S) .

In summary, one photon is scattered with a transfer of energy $\hbar\omega$ and momentum $\hbar\vec{q}$ to or from the medium.

The corresponding conservation laws read

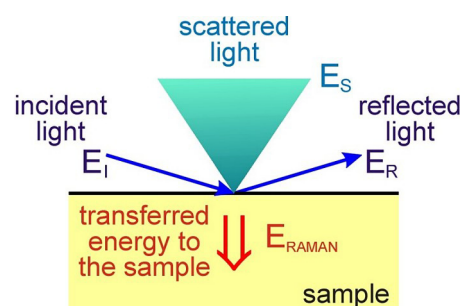


Figure 3: The Raman scattering process. For details see text.

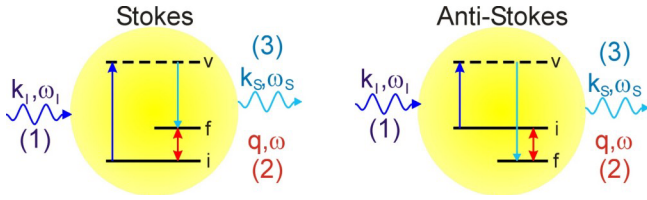


Figure 4: The Raman effect in the energy level picture. In Stokes processes the final state is above (left), in anti-Stokes processes it is below the initial state (right). For a description of the variables see text.

$$\begin{aligned}\hbar\omega_i &= \hbar\omega_s + \hbar\omega \\ \hbar\vec{k}_i &= \hbar\vec{k}_s + \hbar\vec{q}\end{aligned}\quad (1)$$

If the final state is above the initial state the energy transfer $\hbar\omega$ from the photon to the system was positive (Stokes process), otherwise the system transferred energy to the photon (anti-Stokes process). For anti-Stokes processes to happen, the system has already to be in an excited state before.

In most cases, the energy transfer is small compared to the energy of the incoming photons, $\hbar\omega \ll \hbar\omega_i$. So one finds for the momentum transfer

$$\hbar\vec{q} \equiv \frac{2n\hbar\omega_i}{c} \cdot \sin \frac{\phi}{2} \quad (2)$$

with n the refractive index of the medium, c the velocity of light, and ϕ the angle between the directions of the incident and the scattered photon. The maximum (at $\phi = 180^\circ$) is given by $\hbar q^{\max} = 2n\hbar\omega_i/c$. For standard Raman experiments in typical solids, q^{\max} of the order of 10^{-3} \AA^{-1} and thus 1000 times smaller than both the characteristic wave vectors for most atomic lattice vibrations (phonons) and the highest momentum of the conduction electrons in the crystal. Therefore, we come to the important conclusion that the Raman experiment can only probe excitations in the limit $\vec{q} \rightarrow 0$. This makes Raman scattering fundamentally different from many other methods for studying solid state excitations, such as neutron scattering.

In the Raman experiment, one measures the intensity $I(\omega)$ of the scattered light as a function of the frequency shift ω (Raman shift) of the photons (fig. 5). In addition and depending on the experimental set-up (see next section), one may also vary the polarization vectors of the light, the temperature of the sample, etc. $I(\omega)$ is usually given in units of *photon counts per second* per milliwatt of incoming light power (cps/mW). The frequency shift ω is measured in *wavenumbers* (cm^{-1}), where $8 \text{ cm}^{-1} = 1 \text{ meV}$. Due to the interaction of light with different elementary excitations in solids, Raman spectroscopy is a powerful tool for the investigation of different solid state properties (tab. 1). For this reason, a typical spectrum from a solid usually shows many different features.

As an example, let us take a Raman spectrum of a single crystal of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

(fig. 5) which is a high-temperature superconductor with magnetic order⁷. It consists of a broad continuum (green) superimposed by some more or less narrow lines. The Raman continuum originates in scattering from continuous excitations at $\vec{q} \rightarrow 0$, such as free carriers or spin fluctuations. By studying this continuum at different temperatures or light polarizations, one obtains information about the charge-carrier and spin dynamics. The Raman lines, however, are attributed to discrete excitations at $\vec{q} \rightarrow 0$. In the range of low Raman shifts (up to 1000 cm^{-1}) these are mostly optical phonons (lattice vibrations) (blue). Their position, width, and intensity give information about the lattice dynamics and/or the electronic configuration of the atoms. In addition, the spectra will always show a sharp line at $\omega = 0$ due to insufficient suppression of the incident laser light (laser line). In the higher energy region (above 1000 cm^{-1}), one observes Raman scattering for instance from magnetic excitations. The peak at 3000 cm^{-1} shown here (red) corresponds to the flip of two adjacent electron spins and is therefore referred to as two-magnon peak. Its position and shape gives information about the antiferromagnetic exchange energy which is responsible for antiferromagnetic order in the material.

Experimental

The experimental set-up used for Raman spectroscopy consists of the light source, the sample and the detection system for the scattered light. Early experiments (fig. 6) were carried out with mercury arcs, prism spectrographs, and photographic plates using exposure times that sometimes were many hours. Nowadays, modern Raman set-ups with lasers as intense and monochromatic light sources together with high-effective grating spectrometers and multichannel CCD cameras provide a fast and easy way to record a Raman spectrum in just a few seconds. The typical elements of an up-to-date Raman spectroscopy system for metals are illustrated in figure 7.

The sample is placed in a vacuum chamber. The

TABLE 1: EXCITATIONS PROBED		
Electrons	→ charge carrier dynamics and electronic structure	
Phonons	→ lattice dynamics and electron-phonon coupling	
Magnons	→ spin dynamics and magnetic order	

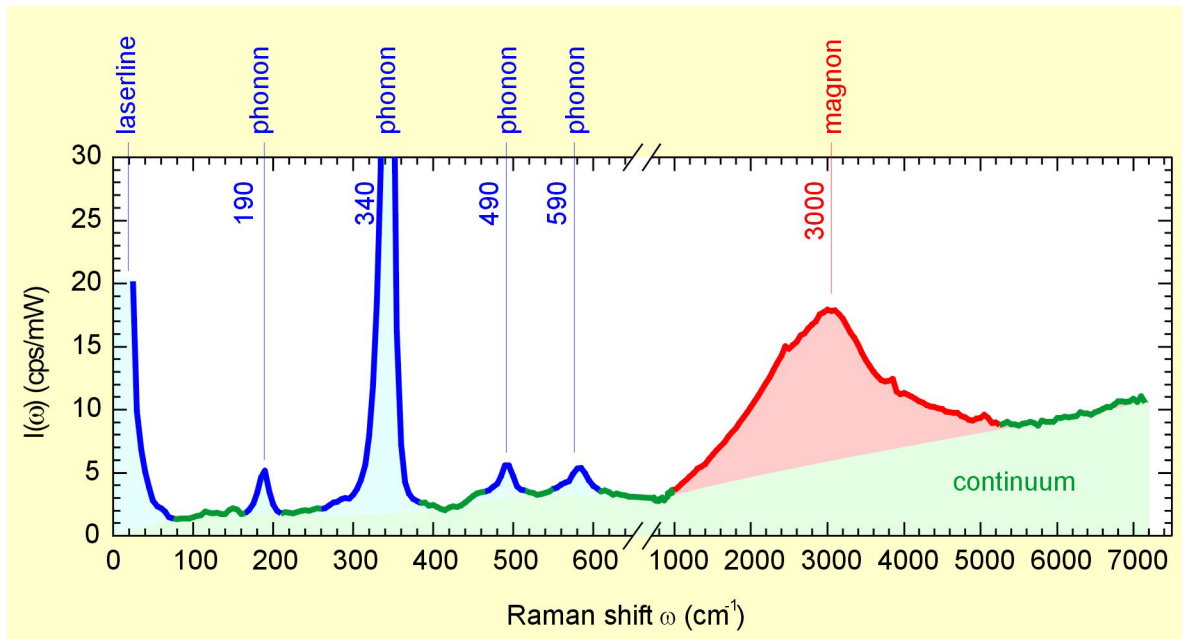


Figure 5: Raman spectrum from the high-temperature superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ taken at a temperature of 4 K.

quality of the sample surface is crucial since the Raman effect in a metal is very weak in comparison to scattering from most of the insulating materials. Hence, high or ultra-high vacuum is desirable. For low temperature studies, the sample is cooled using either a liquid helium cryostat or a closed-cycle refrigeration system.

The sample is illuminated by a monochromatic, highly collimated and polarized beam of light with a power of typically 1...100 mW coming from one of various types of lasers which normally provide several lines throughout the visible and near infrared or ultra-violet spectral range. As the intensity of the light has to be extremely stable as a function of time mostly noble gas ion lasers (such as Ar^+ lasers) are used. In opaque materials the sample surface is oriented perpendicular to the optical axis of the system. To prevent directly reflected light from entering the spectrometer a large angle of incidence is used. Due to the relatively high refractive index of metals the exciting photons propagate at a small angle to the surface normal. For optimal

efficiency the beam is focused to some 100 μm diameter (at least in one direction). Even at low laser powers of the order of 1 mW corresponding to 10 W/cm^2 the spot temperature may be significantly higher than that of the sample holder. Typical values for this laser heating effect are between 1 and 10 K/mW.

The backscattered light is collected with an objective lens (fig. 8) with large aperture and focused on the entrance slit of a highly dispersive and selective grating spectrometer. In spite of the good selectivity of double and triple monochromators elastically scattered laser light cannot be completely suppressed and reduces the experimental accuracy at low frequencies. The selection of different polarization states of the incoming and scattered photons allows to determine the symmetry properties of the excitations in the solid, such as the vibration pattern of phonons.

After leaving the spectrometer the photons are counted by a highly sensitive CCD camera with a quantum efficiency up to 80% in the visible range. Most scientific-grade CCDs are cryogenically cooled down to about -100°C in order to suppress thermal noise effects. So, photon rates down to 10 per second can be measured within an exposure time of only 30 s with a statistical error of less than 10 %. Some more experimental details are compiled in table 2.

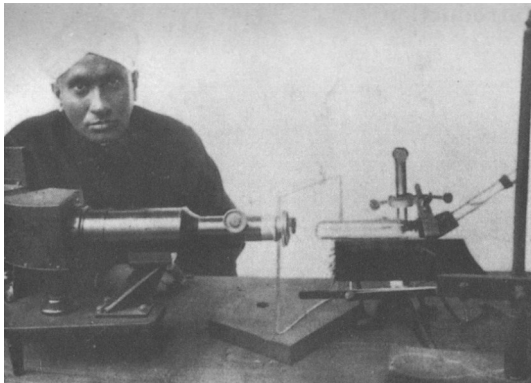


Figure 6: C.V. Raman with his apparatus for inelastic light scattering (taken from [26]).

TABLE 2: EXPERIMENTAL DETAILS		
Excitation energy	→	1 meV ... 1eV
Energy resolution	→	≤ 1 meV
Penetration depth of light	→	1000 Å

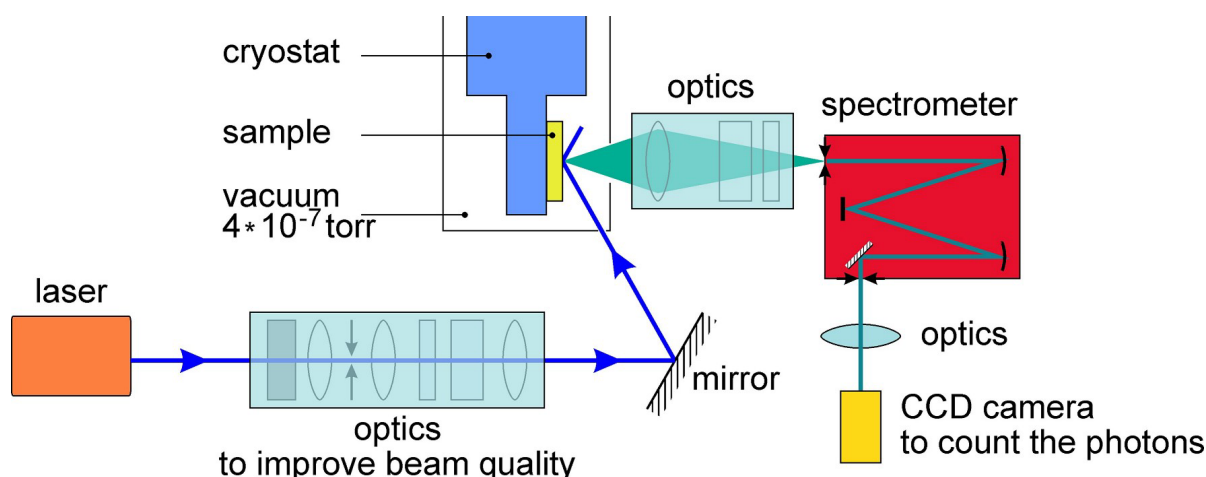


Figure 7: Typical experimental set-up for Raman spectroscopy in solids (schematic).

Some applications of inelastic light scattering in solids

Most light-scattering experiments are concerned with the vibrational properties of molecules and crystals. Vibrational frequencies are determined by the mass of the involved atoms and the force constants between them and normally lie in the range where light scattering is a convenient tool. In addition, the probability for vibrational scattering is usually larger than that for other excitations in the same frequency range. Although the direct study of crystal-lattice vibrations is limited to processes with negligible momentum transfer ($\vec{q} \rightarrow 0$, see section 2), the spectral resolution available in Raman scattering exceeds that of other spectroscopic methods. Light-scattering studies have made significant contributions to our understanding of the dynamics of structural phase transitions and of magnetism in solids. The phase transitions we are generally familiar with are of first order (e.g. melting) and can be traced back to discontinuous changes in thermodynamic quantities

such as energy or entropy. Phase transitions of second order, however, are by implication less abrupt as the thermodynamic quantities mentioned above change continuously. Raman scattering can be used to study both types of transitions. In the following, we shall give some examples.

Raman himself studied the first-order transition of quartz from the α to the β phase at $\sim 570^\circ\text{C}$.⁸ He found a specific phonon mode at 220 cm^{-1} decreasing in frequency as the transition temperature is approached from below. He concluded that excitations of this mode had a direct bearing on the phase transition. The discovery about 50 years ago that BaTiO_3 with its relatively simple perovskite structure was ferroelectric stimulated interest in the fundamental nature of ferroelectricity and in structural instabilities in perovskites. Subsequently, various perovskites including BaTiO_3 , KTaO_3 , and SrTiO_3 were studied using Raman spectroscopy. Other examples are hydrogen-bonded ferroelectrics. Among those, KH_2PO_4 (generally abbreviated as KDP) and its isomorphs have attracted most attention from spectroscopists.⁹ As a last example, we mention that Raman spectroscopy was also used for the investigation of the cooperative Jahn-Teller effect (CJTE).¹⁰ Because of the interaction of the lattice vibrations with low-lying electronic states of an ion in a solid, the environment of the ion changes towards a lower symmetry and its energy is reduced. These low lying states have been observed by Raman scattering experiments.¹¹ After the discovery of the colossal magnetoresistive effects in manganites and related compounds¹² Raman spectroscopy and the investigation of the CJTE has again attracted great interest. In this context, Raman spectroscopy is currently being used to study the ionic orbital ordering in those materials and contributes essentially to the understanding of their unconventional magnetic properties.¹³

Magnetic excitations in crystals generally have smaller light-scattering cross sections than vibrational excitations, and the observation of magnetic scattering had to wait for the advent of laser sources in Raman spectroscopy. The first successful experiment was that in antiferromagnetic FeF_2 .¹⁴ Light scattering has since

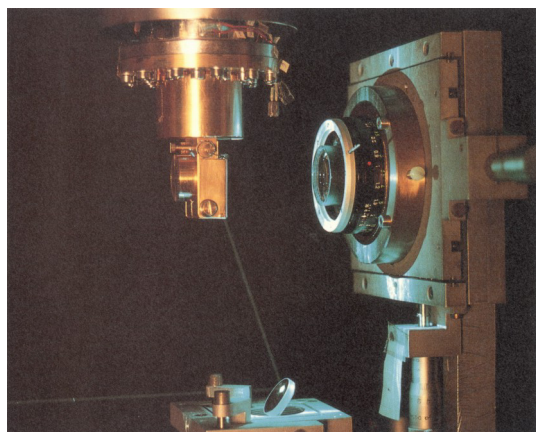


Figure 8: View of the experimental set-up used by the authors at the Bavarian Academy of Sciences. It shows parts of the schematic sketch from fig. 7: the mirror (bottom), the sample holder with the cold finger of the cryostat (top left), and the optics for collecting the scattered light (right).

become one of the standard methods for determining frequencies and other properties of magnetic excitations. Magnetic scattering occurs in paramagnetic materials and in the various types of magnetically ordered structures at low temperatures. The magnetic excitations have the form of propagating waves of small rotations of spins out of equilibrium (magnons, see tab. 1) at temperatures small compared to the transition temperature of the ordered state. Magnon frequencies are typically smaller than phonon frequencies, and ferromagnets and ferrimagnets have only excitations at frequencies which are best observed by Brillouin scattering techniques (Fabry-Perot rather than grating spectrometers). The magnon frequencies in antiferromagnets, however, can be quite high and observable in the Raman experiment. Due to their impressive physical properties and their complex phase diagrams, antiferromagnetic transition-metal oxides such as doped manganites¹⁵ or high- T_c superconductors¹⁶, are currently studied with great success.

Spin waves are one example of electronic excitations that produce inelastic light scattering. More generally, light scattering can be used to study any type of electronic excitations whose frequencies lie in the accessible range. The excitations can be those of electrons bound to particular ions or of electrons that can move freely through the crystal. An example of bound charges are electrons and holes weakly bound to donors and acceptors in semiconductors like Si or Ge. Raman spectroscopy can be used to study the effect of doping.¹⁷ On the other hand, spectroscopists deal with inelastic light scattering from free carriers. Although this is a weak effect it can readily be studied with state-of-the-art equipment. One can obtain important information on how the electric transport takes place, and the microscopic origin of the resistivity can be studied. Raman scattering is therefore complementary to infrared spectroscopy since all events limiting the electric current, such as scattering between electrons and crystal defects, lattice vibrations, or spin waves etc., lead to characteristic structures in the spectra. So, light scattering has been used extensively to study the excitations of free electrons and holes in various materials. Among those are semiconductors¹⁸, normal metals and alloys¹⁹, as well as superconductors²⁰. The latter transport electricity without losses below a critical temperature. This new state of matter requires the electrons to be bound into pairs. The glue between them is usually provided by lattice vibrations but the binding can also originate in other types of excitations, such as magnons. Once again, new information about the properties of superconductors have been obtained because the Raman experiment is also sensitive to the direction of the motion of the electrons.²¹ Equivalent to the superconducting state in metals is the frictionless mass transport in liquid Helium at very low temperatures (superfluidity). This effect has also been studied and analysed by Raman spectroscopy.²²

Outlook

Because of the variety of Raman-active excitations in solids, Raman spectroscopy has become a powerful tool to gain insight into some of their basic properties. In the field of fundamental solid state physics, results from Raman scattering experiments are contributing essentially to the understanding of various effects. Among those are the mechanism of high-temperature superconductivity where Raman scattering helps to clarify the symmetry of the energy gap and its relation to the normal state carrier dynamics.²³ Another area is the investigation of ferromagnetic oxides which are important for the development of spinel electronic devices and the discovery of a new kind of orbital excitation in these materials.¹⁵ Last but not least, Raman scattering is used for the characterization of quantum dots in semiconductors which may become the integral part of quantum computers in the near future.²⁴

In parallel, the technique of Raman scattering has evolved to be a highly efficient, easy-to-use, and time-saving tool for almost all disciplines of natural science in the recent years. Now several commercial "plug-and-play" Raman instruments are available which allow a high throughput screening of whole series of chemical or biological samples.²⁵ By observing different phonon bands for different atoms, ions, or bonds between them one can determine both their composition and molecular structure simultaneously. Fully integrated software and hardware allows a complete experimental control of all parameters. Huge spectral libraries are available which can be searched in order to match specified Raman peaks found in the samples or even their entire spectra. Furthermore by using scanning Raman spectroscopy, one is able to map the concentrations of one specific component within the sample, e.g. active ingredients in a pharmaceutical tablet. The evolution of these Raman spectroscopy techniques is still in progress. In the future, Raman spectroscopy is expected to develop to an everyday method for the characterization of most kinds of samples in science and technology.

Acknowledgments

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