Light Scattering in Magnetic Solids

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Preface

Their magnetism works all night,
And dreams of Paradise and light.
HENRY VAUGHAN
1622–1695

Inelastic light scattering spectroscopy has been widely applied since its advent in the 1920s. The introduction of the laser source in the 1960s revitalized this technique and made observable many new phenomena. Meanwhile the theory of magnetism had been developed in terms of an operator formalism, where the fundamental excitations resulting from the quantized spin deviations are called magnons. Measurements by magnetic resonance, inelastic neutron scattering, and other techniques directly confirmed the existence of magnons and provided further tests for theory. In 1966 these separate subjects came together as a result of the observation of light scattering from magnons in the antiferromagnets FeF_2 and MnF_2. These first results posed immediate theoretical problems, and a burgeoning new field was started. Light scattering spectroscopy is now firmly established as a standard technique for measuring magnetic excitations in solids. The theoretical interpretation of such spectra is well developed, and considerable physical information about the magnetic properties of solids can be learned from their light scattering spectra.

The main objective of this book is to review the experimental and theoretical work on light scattering from *ordered* magnetic solids. We intend that the book should serve not only as a reference work but also as an introduction to this field of research. It unifies the diverse aspects of the subject, and we anticipate that it will stimulate future research and applications. We present the established work on light scattering from single magnons and pairs of magnons in both pure and impure magnets, with emphasis on the basic principles involved. The most recent developments, such as light scattering from magnetic surfaces and super-

lattices, are also treated. The scope of the book is best demonstrated by the list of contents: the introduction, which gives background material and introduces the subject matter; the basic theory for magnons and for light scattering; the experimental techniques of Raman and Brillouin scattering; one-magnon light scattering from pure ferromagnets and ferrimagnets, with details of the theory and experimental results for selected magnets; one-magnon light scattering from pure antiferromagnets, theory and experiment, with examples of simple antiferromagnets, canted antiferromagnets, and metamagnets; two-magnon light scattering from pure antiferromagnets; light scattering from impure magnets for the cases of magnetic and nonmagnetic impurities; light scattering at magnetic surfaces, dealing mainly with ferromagnets; and a concluding section, where new areas of interest are identified.

This book covers a wide variety of subject material that has not been reviewed extensively elsewhere. The more general work by W. Hayes and R. Loudon on *Scattering of Light by Crystals* (Wiley-Interscience, New York, 1978) contains a chapter on magnetic materials.

The book is written as a text for graduate students, but it will also suit academic staff and other researchers with general interests in magnetism and/or light scattering spectroscopy. The reader is assumed to have a basic knowledge of quantum mechanics, statistical mechanics, optics, and solid state physics. More advanced topics in quantum mechanics and other subjects such as scattering theory, group theory, and many-body theory are introduced where required. A knowledge of these subjects is not a prerequisite for reading this book.

Although the book is a general text, it is not intended to be a complete work. Many illustrative examples, chosen from a wide range of physical cases, are given, but this book is not a historical account, and so not all discoveries are mentioned or credited. The purpose is to provide an overview of the subject in a consistent manner, particularly with regard to the theoretical sections, as dictated by the authors' preference. Topics excluded from discussion, except in passing, are results from very complicated magnetic structures, magnetic materials in the paramagnetic phase, magnons interacting with other excitations, mixed-mode scattering, and higher energy electronic states. International (SI) units are used throughout except for frequency shifts, which by convention are given in cm^{-1}. An energy conversion table is given in Chapter 1.

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Contents

CHAPTER ONE
Introduction

The study of light scattering from spin waves (or magnons) has a relatively brief history dating from 1966. Experimental observations of inelastic light scattering phenomena began in 1928, but several major advances in the technique that occurred in the 1960s were needed before the weak magnon scattering could be detected. In this chapter we present an introduction to the subjects of light scattering spectroscopy and magnons in a historical context. The results from the first observations of light scattering by magnons in various types of magnetic solids are reviewed, emphasizing the new information that was obtained. Finally, we compare the light scattering technique with other methods of studying magnons.

1.1 LIGHT SCATTERING SPECTROSCOPY

In 1928 Raman announced the discovery of the effect that bears his name and that was to win for him the Nobel Prize in Physics. During the course of a systematic investigation of the scattering of light in liquids and solids he had observed frequency shifts in the scattered light that were dependent on the sample used (Raman 1928; Raman and Krishnan 1928). Shortly afterwards, Landsberg and Mandelstam (1928) published details of the same effect in quartz. This inelastic scattering was found to be due to vibrations (within the liquid or solid) modulating the permittivity of the medium.

The inelastic light scattering process, now known as the Raman effect, is depicted schematically in Figure 1.1. Incident light of energy $\hbar\omega_I$

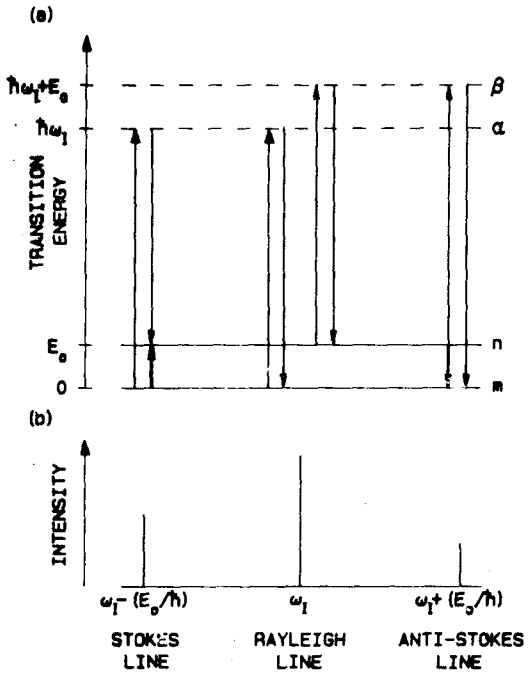

FIGURE 1.1 (*a*) The quantum mechanical energy level representation of light scattering, and (*b*) the corresponding spectrum. The arrows denote transitions involving stationary states m and n and virtual levels α and β.

interacts with the system, raising the energy to some virtual intermediate state before a relaxation occurs to a lower stationary state with the simultaneous emission of light. The energy of the final state may be greater or less than the energy of the initial state. In the former case the frequency of the scattered light is $\omega_I - (E_0/\hbar)$, and the process is called Stokes scattering. Here $h(=2\pi\hbar)$ is Planck's constant and $E_0 = E_n - E_m$, where E_m and E_n are the energies of the initial and final states, respectively, for this transition. The second case, where the energy of the initial state is greater than that of the final state, gives rise to anti-Stokes scattering. If the energies of the initial and final states are the same, then the scattered light is not shifted in frequency. This is conventionally called Rayleigh scattering. Examples of all three processes are given in Figure 1.1.

Raman's discovery had been predicted earlier by Smekal (1923). Kramers and Heisenberg (1925) developed the old-style quantum theory of Smekal to derive a scattering formula from classical wave theory by

means of the correspondence principle. They considered a transition from an initial electronic state m (of energy E_m) to a final state n (of energy E_n) and found that the total intensity of the spontaneously scattered radiation is proportional to (see Placzek 1934)

$$\omega_S^4 |\mathbf{P}_{mn}|^2 \tag{1.1}$$

where

$$\mathbf{P}_{mn} = \frac{1}{\hbar} \sum_r \left[\frac{(\mathbf{E}_I M_{mr}) M_{rn}}{\omega_{rm} - \omega_I} + \frac{M_{mr}(\mathbf{E}_I M_{rn})}{\omega_{rn} + \omega_I} \right] \tag{1.2}$$

Here ω_I is the angular frequency of the incident light with electric vector $\mathbf{E}_I \exp(-i\omega_I t)$. The scattered light has frequency $\omega_S = \omega_I - \omega_{mn}$, where $\omega_{mn} = (E_n - E_m)/\hbar$. There are similar definitions for ω_{rn} and ω_{rm}, where r denotes other electronic states and M_{rn} and M_{mr} are the corresponding transition moments. Normally ω_I is much greater than $|\omega_{mn}|$, in which case $\omega_S \approx \omega_I$. The Kramers–Heisenberg intensity relation, (1.1) and (1.2), was of fundamental importance in the development of quantum mechanics. Dirac (1927) subsequently rederived these results using his quantum theory of radiation. The term Raman scattering is now used to describe light scattering from many other excitations including magnons.

Simultaneously with the Raman effect another type of scattering was being considered. Brillouin (1922) and Mandelstam (1926) had predicted light scattering from sound waves in dense media. Their Stokes–anti-Stokes doublet can be thought of as a translational Raman spectrum. Shortly after the discovery of the Raman effect, Gross (1930) found a triplet structure in liquids. The frequency shift of the outer components was much smaller than in previous vibrational scattering, consistent with the expected acoustic wave scattering. These two lines comprise what is now commonly called the Brillouin (or Mandelstam–Brillouin) spectrum. The central elastic component was explained by Landau and Placzek (1934) as scattering from nonpropagating density fluctuations, and is often erroneously called the Rayleigh line. The choice of names for the various features in the light scattering spectrum has an interesting history (see Young 1982), and rather than add to the confusion we define here the terms of interest in this work. Following common usage, we use the name "Raman scattering" to denote light scattering spectra recorded with grating spectrometers, typically with frequency shifts in the range 5–4000 cm^{-1}. For spectra recorded with Fabry–Perot interferometers, typically in the frequency range up to 5 cm^{-1}, we use the name "Brillouin scattering." The division between scattering regimes is only approximate. The central component is referred to as "Rayleigh scattering." Frequency

TABLE 1.1 Energy Conversion Factors

The energy of a magnon can be expressed in various units, and it is often necessary to convert between them. The conversion factor is found by looking along the appropriate row to the column giving the required units.

	Wavenumber (cm^{-1})	Frequency (THz)	Temperature (K)	Electron Volts (meV)	Joules (J)
$1\ cm^{-1}$	$1\ cm^{-1}$	0.029979	1.4388	0.12399	1.9865×10^{-23}
1 THz	33.356	1 THz	0.020836	4.1357	6.6262×10^{-22}
1 K	0.69503	47.992	1 K	0.086173	1.3807×10^{-23}
1 meV	8.0655	0.24180	11.605	1 meV	1.6022×10^{-22}
1 J	5.0340×10^{22}	1.5092×10^{21}	7.2429×10^{22}	6.2415×10^{21}	1 J

shifts are described in wavenumber units (cm^{-1}) by convention, and conversion factors to other energy related units are given in Table 1.1.

1.2 MAGNONS

Spin waves (or magnons) are low-lying excitations that occur in ordered magnetic materials. The characteristics of the magnons in any particular material depend on the nature of the interactions and on the type of magnetic ordering. We are principally concerned with three types of magnetic material: ferromagnets, simple antiferromagnets, and ferrimagnets, and these are represented schematically in Figure 1.2. Other kinds of magnetic behavior, such as exhibited by metamagnets and canted antiferromagnets, are described later. In ferromagnets there is an interaction between neighboring electronic spins, which gives rise to a parallel alignment at low enough temperature. In simple antiferromagnets and ferrimagnets the sign of the interaction is such that an antiparallel ordering of spins is favored. However, ferrimagnets differ from antiferromagnets in

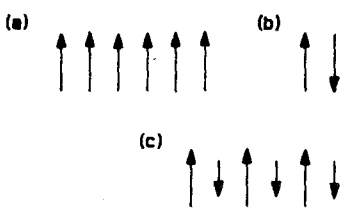

FIGURE 1.2 Schematic arrangement of the spins in ordered magnetic materials: (*a*) ferromagnets, (*b*) antiferromagnets, and (*c*) ferrimagnets.

that the "up" and "down" spins are of unequal magnitudes. Ferrimagnets therefore have a nonzero spontaneous magnetization at low temperatures, and in this respect they are similar to ferromagnets. As the temperature is raised the long-range magnetic order decreases in all three materials, and eventually there is a phase transition to a disordered (paramagnetic) state. The critical temperature at which this occurs is known as the Curie temperature T_C in ferromagnets and ferrimagnets and the Néel temperature T_N in antiferromagnets.

The first advance in explaining the properties of ordered magnetic materials was the mean field theory (also known as molecular field theory or Weiss theory) of ferromagnetism proposed by Weiss (1907). This theory did not attempt to give the origin of the interaction producing the parallel spin alignment in ferromagnets, but it made the hypothesis that its effect could be described in terms of an effective field B_W acting on each spin in addition to any applied magnetic field. By assuming that B_W is proportional to the magnetization, Weiss was able to account for the observed decrease in magnetization with increasing temperature and for the existence of a phase transition at T_C. Mean field theory was extended to antiferromagnets by Néel (1932) and subsequently to ferrimagnets; it has been fairly successful in describing the overall *static* properties of magnetic materials.

It was only after the advent of the quantum theory that progress was made in understanding the nature of the interaction that produces magnetic ordering. Heisenberg (1928) was able to show, at least in general terms, that it is electrostatic in origin and due to the quantum-mechanical exchange interaction. This is discussed in most standard texts on quantum mechanics or magnetism (e.g., Schiff 1955; Mattis 1965), and we refer the reader to these for details. The argument may be summarized as follows. We consider two neighboring ions (labeled a and b), each of which has one electron, and we denote the normalized spatial electronic wavefunctions by ψ_a and ψ_b. The electrons have spin $\frac{1}{2}$ and obey Fermi–Dirac statistics. Therefore their total wavefunction, which may be written as the product of a spatial part Ψ and a spin part χ_S, must be antisymmetric. The two possible spin states are the symmetric $\chi_{S=1}$ and the antisymmetric $\chi_{S=0}$, where S is the total spin quantum number. These have to be combined, respectively, with antisymmetric (Ψ_-) and symmetric (Ψ_+) orbital wavefunctions, which are given in the Heitler–London theory by

$$\Psi_\pm(\mathbf{r}_1, \mathbf{r}_2) = 2^{-1/2}[\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) \pm \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)] \qquad (1.3)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ denote the positions of the electrons. The two electrons interact with one another and with the ionic cores by means of the Coulomb interaction, and when the total energy is calculated from

first-order perturbation theory, it is found that the result may be expressed as $C \pm E$. Here C represents the Coulomb contribution, E is an additional quantum mechanical term known as the exchange integral, and the upper and lower signs are associated with the signs in (1.3). An expression for E can easily be written down in terms of an overlap integral involving the electronic wavefunctions ψ_a and ψ_b, and in principle E can be either a positive or a negative quantity. If $E > 0$, the spatial wavefunction Ψ_- corresponds to the lower energy state, and this means that the spins will be parallel ($S = 1$) as in a ferromagnet. The situation $E < 0$ would likewise be associated with antiferromagnetism or ferrimagnetism. The interaction energy can be written in terms of the spin operators $\mathbf{S}_1$ and $\mathbf{S}_2$ of the two electrons as

$$(C - \tfrac{1}{4}\hbar^2 J) - J\mathbf{S}_1 \cdot \mathbf{S}_2 \tag{1.4}$$

where $J = 2E/\hbar^2$. The above result is obtained by noting that the eigenvalues of $\mathbf{S}_1 \cdot \mathbf{S}_2$ are $\frac{1}{4}\hbar^2$ and $-\frac{3}{4}\hbar^2$ for the states of total spin $S = 1$ and $S = 0$, respectively (see Phillips and Rosenberg 1966). On generalizing this to a whole system of spins we arrive at the exchange Hamiltonian

$$\mathcal{H} = -\sum_{\langle i,j \rangle} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j \tag{1.5}$$

where the summation is over all distinct pairs i and j, and we henceforth disregard the constant terms in (1.4). The above result is the Heisenberg Hamiltonian, and it forms the basis for most theoretical treatments of magnetic insulators.

A proper theory of the exchange interaction J_{ij} is much more complicated than the simple example outlined above. Apart from the direct exchange mechanism there is also an indirect mechanism that was proposed by Kramers (1934), known as superexchange. The general principle is that the overlap of wavefunctions may take place through the intermediary of a third ion, rather than by a direct overlap, and this situation can account for exchange effects over larger distances. The role of exchange interactions in magnetic insulators has been reviewed by Anderson (1963), while the more complex subject of exchange in metallic systems is discussed by Herring (1966).

The concept of spin waves, as the lowest lying magnetic states above the ground state, was introduced by Bloch (1930). He envisaged some of the spins as deviating slightly from their ground state, with these disturbances propagating with a wavelike behavior through the crystal. This is a dynamic effect that is ignored in mean field theory, where the exchange interactions are replaced by a static effective field. From spin wave theory Bloch (1930) was able to predict that the magnetization of a

ferromagnet at low temperatures (compared with T_C) should deviate from the zero-temperature value with a $T^{3/2}$ dependence, instead of the exponential dependence given by mean field theory. The spin wave result was substantially confirmed by measurements due to Fallot (1936) and Weiss (1937). Following the work of Bloch (1930) there have been a number of alternative formulations of spin wave theory. These include a semiclassical theory due to Heller and Kramers (1934) in terms of precessing spins. It is particularly helpful in gaining a physical interpretation of spin waves, and the concept is represented schematically in Figure 1.3.

Because the spins are properly described by quantum-mechanical operators, the spin waves are also quantized with the basic quantum being referred to as the *magnon* (by analogy with the photon and phonon). An operator approach, based on second quantization and utilizing the approximate boson character of the magnons, was developed by Holstein and Primakoff (1940). In principle this enabled interactions between magnons to be investigated, but a rigorous treatment of this topic did not come about until the work of Dyson (1956). In Chapter 2 we give an introductory account of the theory of magnons, and more advanced topics are presented later in the book.

The early experimental evidence for magnons came from measurements of thermodynamic properties. We have already referred to the magnetization dependence, and similarly the magnons produce a characteristic contribution to the specific heat that has been investigated and confirmed experimentally. Details are given in the review articles by Keffer (1966) and Phillips and Rosenberg (1966). Ferromagnetic res-

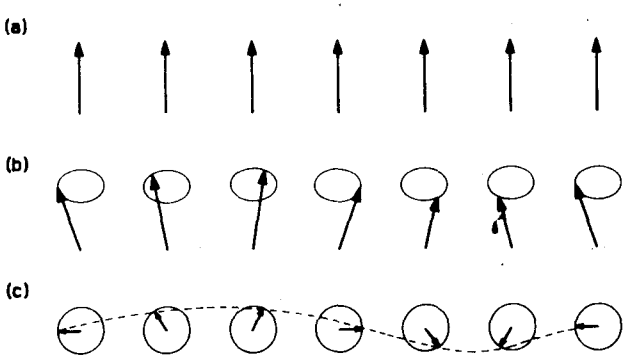

FIGURE 1.3 Semiclassical representation of a spin wave in a ferromagnet: (*a*) the ground state, (*b*) a spin wave of precessing spin vectors (viewed in perspective), and (*c*) the spin wave (viewed from above) showing a complete wavelength.