The Magnetic Properties of Solids

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General Editor's Preface

Of all the electronic properties of solids magnetism is perhaps that of interest or concern to the widest range of scientists and technologists. At one extreme, quite small improvements in permeability or saturation magnetization can be of great economic significance to the engineer; at the other, magnetic phase transitions have supplied the model systems for some of the most abstract recent discussion of theoretical physicists. The very existence of the most striking form of magnetism—ferromagnetism— has provided generations of students with a stimulating oddity and confronts the solid state physicist with one of his most natural questions. 'Why is iron ferromagnetic?' belongs with 'Why is aluminium a conductor and diamond an insulator?' and 'Why is steel stronger than copper?' as one of the central questions posed by our everyday experience of solids. It is impossible to cover the whole range of magnetic phenomena and satisfy all interested parties in one book; the author has taken a clear decision to make the focus of his book the bulk magnetic properties of solid materials, their explanation in atomic terms and their applications. In this decision, as in the straightforwardness of his explanations and the obvious relish he has for the experimental challenges and pleasures the topic affords, Dr Crangle shows himself to be in the central tradition established by such pioneers of the subject as his teacher Professor W. Sucksmith and Professor L. F. Bates. In another respect however he breaks new ground by providing the first consistent textbook treatment of magnetism as a branch of solid state physics wholly in SI units. The many students who have found difficulty in reconciling their studies of magnetism in solids with their wholly SI based treatment of formal electricity and magnetism will be deeply grateful.

Imperial College   BRC
London,
1977

Preface

The magnetic properties of solids are important and they vary widely.
Attempts to understand them have led to a deep insight into the
fundamental structure of many different metallic or non-metallic solids,
although this understanding is often still far from complete. In addition to
the fundamental interest in their magnetic properties there is a large and
growing technology based on the applications of the properties of
magnetic materials.

The aim of this book is to provide a simple introduction to the study of
solid state magnetism, both intrinsic and technical. The level of the
treatment is that of a senior undergraduate studying physics in a British
university. It is hoped that the book will also meet the needs of a wider
group than this, such as chemists, electrical engineers, metallurgists and
materials scientists, some at a postgraduate level; or practising
scientists specializing in other areas who require an introduction to
magnetism.

The subject matter is treated selectively rather than comprehensively
and the size of the book is limited so that those who are studying several
other topics simultaneously may grasp most of the contents fairly easily.
The treatment is experimental and descriptive, with an accent on the basic
principles involved. The list of references and suggestions for further
reading should help the reader to find fuller and deeper accounts of
various parts of magnetism when he is ready to deal with them. Perhaps
the most outstanding of the important topics omitted is magnetic
resonance, except where it is used to measure applied magnetic fields or
hyperfine fields. Experiments employing inelastic scattering of neutrons are
not discussed, nor are spin waves. Also the newly discovered properties
connected with limited dimensionality and materials called spin glasses or
mictomagnets are left out.

The system of units used is SI. Wherever possible quantities are given
also in CGS electromagnetic units. No choice is made between the
Sommerfeld and the Kennelly systems of magnetic units but a distinctive
nomenclature is employed which should enable either to be used where

appropriate and ambiguity to be avoided. Susceptibilities are so defined that conversion between SI and CGS only requires movement of the decimal point.

Sheffield   JC
1976

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1

Introduction and Survey
of Basic Experimental Properties

The magnetic properties of solids are important and attempts to understand them have led to a deep insight into the fundamental structure of many solids, both metallic and non-metallic. However, in many cases the understanding is still far from complete. As in other areas of science the need to test theories that have themselves been set up to explain and correlate previous experimental information has suggested new experimental approaches. These have led to further theoretical development, and so on. In magnetism the process has been accelerated particularly by the recent development of several completely new experimental techniques. A very wide variety of magnetic behaviour has now been recognized in hundreds of different materials. One of the problems in magnetism is that there are serious mathematical difficulties in tackling parts of the subject with theories that are very realistic. Furthermore, it has not yet been possible in many areas to devise sufficiently sensitive experiments to test theoretical predictions and so to give an indication of which among diverging branches in a theory is correct. On the other hand, theoretical models based on one-dimensional or two-dimensional simplifications have sometimes been treated and major distortions of the theory due to the simplification have been found. But the range of available magnetic materials produced both by metallurgy and by chemistry is so very large that examples have often been found experimentally which satisfy the conditions of the simplified theory, often verifying it in a remarkable way.

In addition to the fundamental interest in the magnetic properties of solids there is a great interest in the applications of magnetic materials. There has grown up a tendency to divide magnetism into two kinds. The first is called intrinsic magnetism, concerned with relating magnetic properties to electronic structure and other fundamentals in metals or non-metals. The second, technical magnetism, which is a large subject in itself, is concerned largely with the properties of magnetic domains and related phenomena. Of course, there is quite a lot of cross coupling between the two groups.

The aim of this book is to provide a simple introduction to magnetism

in solids, both intrinsic magnetism and technical magnetism. The level of the treatment is intended to be that of a senior undergraduate studying physics in a British university, although it can meet the needs of a wider group than this. The treatment is experimental and descriptive, with an accent on the basic principles involved. The rest of this first chapter is devoted mainly to an outline of the more obvious experimental magnetic properties, to highlight the needs for the explanations which follow.

1.1 Basic magnetic properties

That lodestone (magnetite, Fe_3O_4), a natural non-metallic solid, may attract iron was first described in known Greek writings about 800 B.C. But the scientific significance was not appreciated until some time later. This was the first technical magnetic material because it formed the first compass.

1.1.1 Ferromagnetic materials

The most widely recognized magnetic elements are iron, nickel and cobalt. These are all ferromagnetic, that is they possess atomic magnetic moments which are ordered (aligned) below some critical temperature. The most obvious properties of a ferromagnet are as follows.

If a piece of iron is examined at room temperature it may be obtained first in an unmagnetized state. If it is then placed in a relatively weak magnetic field a magnetic moment is induced. Such a field may be produced by wrapping a few turns of wire round the iron specimen and passing an electric current of the order of one ampere through it, or by placing the specimen in the vicinity of another specimen which is permanently magnetized. The magnetic state of the iron specimen depends on the magnetic field in a relatively complicated way. There are also differences in the definition of the magnetic state according to how it is measured. The different measuring techniques are described in Chapter 7. The magnetization is given by a measurement depending on the dipole moment of the specimen, for example the measurement of the change in field at some point outside the specimen due to the presence of the specimen. Otherwise the induction within the specimen can be measured from the charge flowing in a closed electrical circuit when the specimen is inserted in or removed from it. The difference here is that the induction includes in it the contribution of induction which would be produced by the applied field itself if the specimen were absent. While the magnetization is used more in fundamental measurements of ferromagnetic properties, the induction is used technically. The

relationship between the quantities differs according to the unit convention used and there is an unfortunate dichotomy between users. The unit systems are described in Section 1.2. The various quantities will now be used according to how they are defined in Section 1.2.

Starting with the unmagnetized piece of iron at room temperature we find that when a small increasing field is applied its magnetization increases at first slowly and reversibly. Beyond a critical field hysteresis develops. The magnetization does not return to zero when the field is switched off and if the field is cycled between small limits a minor hysteresis loop is followed. Eventually the magnetization rises more sharply with increasing field and at still higher fields saturation of the magnetization sets in. The hysteresis loop from saturation is a characteristic of the specimen and it is illustrated in Fig. 1.1a. The
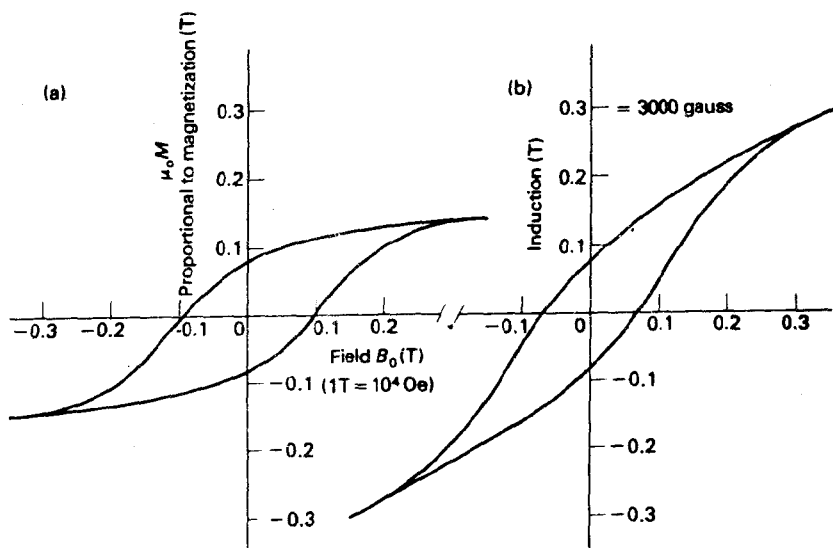

Figure 1.1 Magnetization (a) and induction (b) hysteresis loops of a hard magnetic material. The unit of the ordinate in (a) is $\mu_0 M$, equal to the magnetic polarization J.

remanence is thereby defined, which is the magnetization remaining when the field is switched off from saturation; and the coercivity is also defined, which is the reverse field required to reduce the magnetization to zero from saturation. The induction hysteresis loop has a different shape (Fig. 1.1b) and the induction coercivity has a different value. The hysteresis properties of ferromagnets are largely properties of arrangements of magnetic domains, and these are described in Chapter 6.

After saturation has been reached the magnetization increases very slowly and approximately linearly with increasing field. This is the intrinsic magnetization, which is the value of the magnetization within a domain. It is what remains when the different orientations of all the domains present have been allowed for. It is reached in strong fields because of the effect of increasing field on the domain orientation. The intrinsic magnetization of a ferromagnet does not become zero when the applied field is zero but it remains at a value only a little below its value in a strong field. This is the spontaneous magnetization, that which is spontaneously present within the domains when no field is applied externally. In iron at room temperature the difference between the spontaneous magnetization and the intrinsic magnetization measured in a strong field of about 5 T (50 kOe) is only detectable with difficulty.
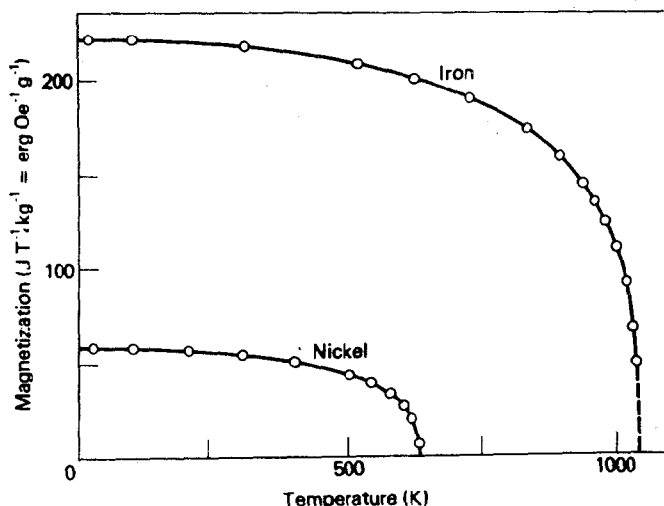

Figure 1.2   Spontaneous magnetization plotted against temperature for iron and nickel.

The spontaneous magnetization depends on temperature (Fig. 1.2), having its largest value at the absolute zero. It falls at an increasing rate with increasing temperature and becomes zero at a characteristic temperature T_C called the Curie temperature. As the temperature rises the intrinsic magnetization varies increasingly with field (Fig. 1.3) and it becomes non-linearly dependent on the field as the Curie temperature is approached. This causes certain difficulties in measuring the spontaneous magnetization when T approaches T_C, with consequent difficulties in the exact experimental definition of T_C from magnetization measurements. The
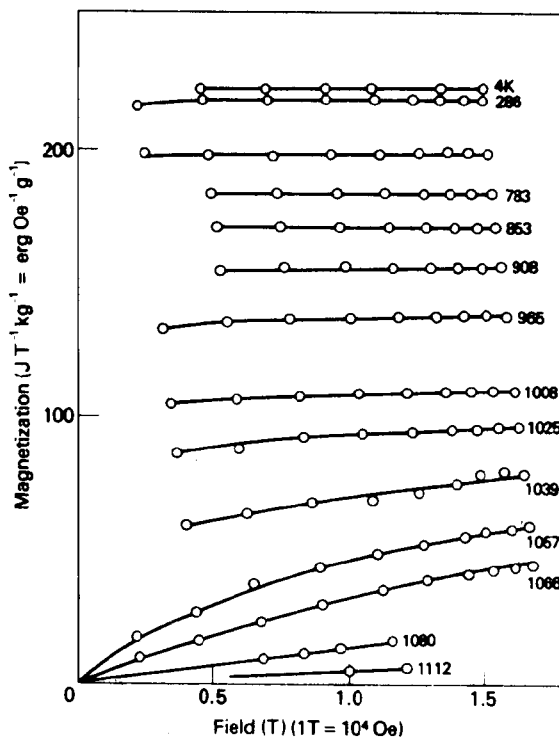
Figure 1.3 Graphs of magnetization of nickel plotted against field for different temperatures

maximum value of the spontaneous magnetization (at $T = 0$) is directly related to the average magnetic moment per atom of the ferromagnet and it gives a measure of the number of magnetic carriers per atom.

If the magnetization of a single crystal of a ferromagnet is measured in a field increasing from zero it is found that the approach to saturation differs according to the orientation of the field with respect to the crystal axes. Some directions are directions of easy magnetization and others are hard directions. In iron (Fig. 1.4) the cube edge direction (100) is easy while the direction of the cube diagonal (111) is hard. This is a fundamental effect called magnetocrystalline anisotropy. The directionality of the magnetic moments of individual atoms interacts with the symmetry of their crystalline environment. Measurements on the effect lead to basic information on the nature of the magnetic atoms. The effect is very important in technical magnetism. Magnetocrystalline energy plays a large part in determining the thickness, energy and mobility of domain

boundary walls. This is important in both soft and in hard technical
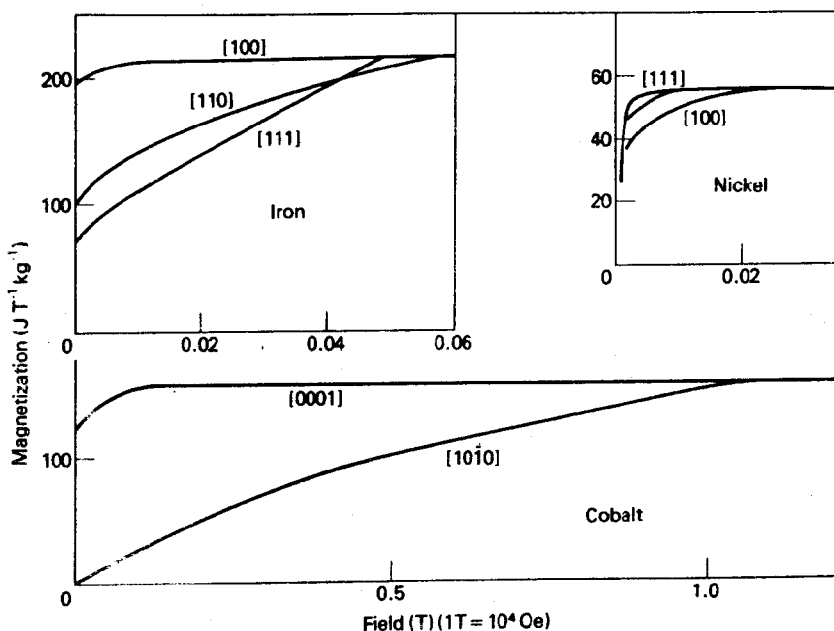magnetic materials.

Figure 1.4   Magnetization as a function of field in single crystals of iron, nickel and cobalt, for different crystallographic directions.

Another effect observed in ferromagnets is the occurrence of small
dimensional changes. The state of strain alters as the
direction of the spontaneous magnetization rotates with respect to the
crystal axes. This is magnetostriction. There is also a small volume
magnetostriction as the spontaneous magnetization is altered by changing
the temperature. Magnetostriction is fundamental and is due to the
link between atomic magnetic moments and the crystalline lattice. It is
important in technical magnetism, affecting the pinning of domain wall
boundaries to crystalline imperfections.

The specific heat capacity of ferromagnetic materials contains a
significant magnetic component C_m superimposed on that part of the total
specific heat capacity (mostly from the lattice and from the conduction
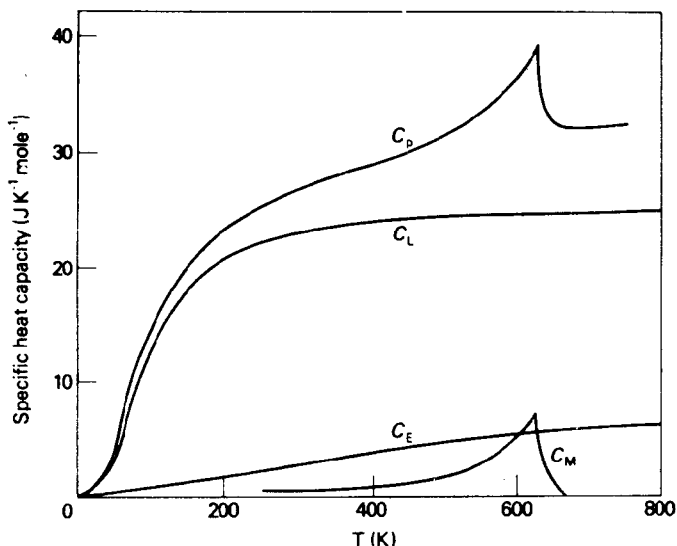electron gas) which would be present if the material were non-magnetic.

Figure 1.5 Specific heat capacity of nickel, as a function of temperature. The magnetic (C_M), lattice (C_L) and electronic contributions (C_E) to the total (C_p) are shown.

The sharp cusp in the graph of heat capacity against temperature (Fig. 1.5) at the Curie temperature is typical of a second-order thermodynamic phase change. It is associated with the disappearance of long-range magnetic order at T_C. The small magnetic heat capacity remaining just above T_C arises from the presence of residual short-range magnetic order, the amount of which diminishes rapidly with increasing temperature. The entropy ΔS_m of the magnetic state may be obtained from measurements of the heat capacity. It is given by

$$\Delta S_m = \int \frac{C_m}{T} \, dT$$

evaluated over the whole range of temperature of the ferromagnetic state. The entropy of the magnetic state is related to the spin quantum number S (and hence the magnetic moment) of the magnetic atoms by

$$\Delta S_m = cR \ln(2S + 1)$$

where c is the fraction of the atoms present carrying the magnetic moment and R is the gas constant.

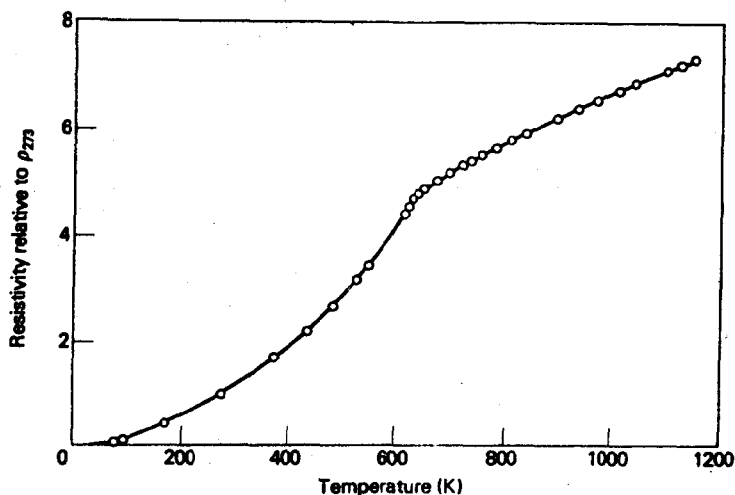There is also a link between the magnetic state of a ferromagnet and its

Figure 1.6 Relative resistance of nickel as a function of temperature. The Curie temperature is 631 K.

electrical resistivity. The dependence of the resistivity is illustrated in Fig. 1.6. Details of the relationship between magnetic order and resistivity are discussed in the book by Dugdale in this series. Since disorder of any kind contributes to resistivity we may expect the onset of magnetic order when a ferromagnetic specimen is cooled through its Curie temperature to be accompanied by a fall in resistivity.

1.1.2   Paramagnetism

Many solids are paramagnetic. When a field is applied to them they become magnetized, usually much more weakly than a ferromagnetic material. The magnetization depends linearly on the field and it always disappears when the field is removed (Fig. 1.7). The rate of change of magnetization with field is called the paramagnetic susceptibility, referred to unit mass of the specimen (χ), to one mole (χ_m) or to unit volume (κ).

Above their Curie temperature ferromagnets become paramagnetic and their susceptibility depends on temperature. The reciprocal of the susceptibility varies linearly with temperature, or nearly so (Fig. 1.8), with an intercept on the positive temperature axis at the paramagnetic Curie temperature θ_p. θ_p is usually of the same order as T_C but the two quantities are rarely exactly equal. This dependence of susceptibility on temperature of the form
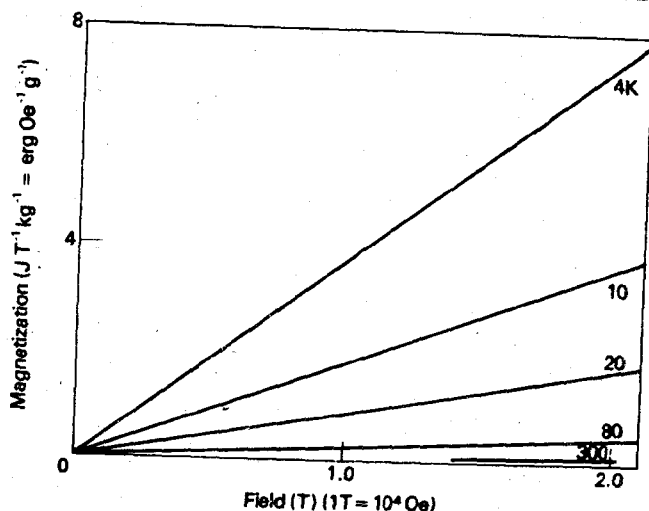
$$\chi = C/(T - \theta_p)$$

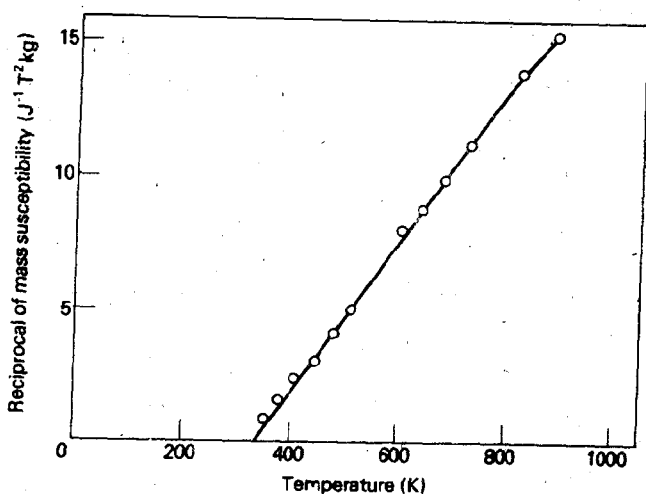**Figure 1.7** Magnetization of hydrated copper sulphate as a function of field at different temperatures.

Figure 1.8 Reciprocal susceptibility plotted against temperature for nickel–32% copper alloy, illustrating the Curie–Weiss law. θ_p is 336 K.

is known as the Curie–Weiss law.

Some other materials of which ordinary hydrated copper sulphate, $Cu\,SO_4 \cdot 5H_2O$, is an example (Fig. 1.9), follow a similar law at all ordinary