P. Mohn

Solid-State Sciences

Magnetism in the Solid State

An Introduction

固态磁性导论

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Peter Mohn

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Preface

During 1986 and 1987, when I was working at the Imperial College of Science and Technology in London with E.P. Wohlfarth, I was asked to prepare some lecture notes following his lecture "*Magnetic properties of metals and alloys*". Peter Wohlfarth had planned to use these lecture notes in a book about itinerant magnetism he wanted us to write together. Due to his untimely death this project was never realized.

Back in Vienna I started to write up the lecture notes for a graduate course, which to some extent was based on these original lectures but in many respects has been modernized by including more recent results of band structure calculations and band theoretical results. During a two month visit of Melbourne University in 1993, I met G. Fletcher from Monash University (Melbourne) who kindly offered to critically read the manuscript. His comments are highly appreciated.

The present greatly enlarged version was mainly written during a sabbatical at the university of Uppsala during 2000. I am grateful to Börje Johansson for making this possible and to Clas Persson for reading the manuscript and providing me with lots of useful comments.

The aim of the book is to present a largely phenomenological introduction to the field of solid state magnetism at a relatively elementary level. The two basic concepts of magnetism in solids namely the localized and the delocalized description are presented as the extreme approaches. The true nature of magnetism lies, as often in life, somewhere in between, sometimes showing a tendency towards the more localized side, sometimes tending to the delocalized side. It is perhaps this mixing of concepts which makes magnetism appear complicated and difficult. Another source of confusion is the different language used by theoreticians and experimentalists. I have tried very hard to clarify these rather more semantic problems and to use a uniform nomenclature throughout the book. It is my belief and my experience that the approach presented here provides a useful introduction not only for the physicist, but also for the interested reader coming from fields like chemistry, electrical engineering or even geo-sciences. The mathematical concepts used are kept rather simple and hardly ever go beyond an undergraduate course in mathematics for physicists, chemists or engineering. Since the book emerged from a lecture course I have given at Vienna University of Technology for the last 15 years, the chapters in the book are not completely self-contained. The first-time reader is thus advised to read the chapters in the sequence that they appear in the book. It is my sincere hope that after having read this book the reader will agree that for once the Encyclopedia Brittanica is in error when it states *Few subjects in science are more difficult to understand than magnetism*, (Encyclopedia Brittanica, 15th edition 1989).

The present book does not attempt to cover the whole field of solid state magnetism, but tries to provide an overview by selecting special topics. The idea is to create an interest in this fascinating field in which quantum mechanics, thermodynamics and computer simulations join forces to explain "Magnetism in the Solid State".

Vienna, *Peter Mohn*
June 2002

Since this book has been so well received by the scientific community that the first printing has been sold within three years, I was asked by the publishers to produce an updated version for a second printing. I am grateful to all colleagues (mainly students) who reported typos, ambiguous or unclear formulations etc. I considered all of them seriously and thus made a number of changes, which I hope will improve the text.

Vienna, *Peter Mohn*
September 2005

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Contents

1. A Historical Introduction

Already in archaic times it was known that a type of stone which was found close to a place called Magnesia in northern Greece attracts iron. The Greek philosopher and mathematician Thales of Milet (about 625-564 b.c.) [1] even attributed a soul and thus life to this attracting material. The first known application of magnetism is the compass as it was used by the Chinese [2]. The oldest description of a compass is found in the book *Meng Chhi Pi Than* (from the year 1086) of the author Shen Kua who not only describes the compass needle to point to the south direction but also refers to a slight easterly deviation meaning the declination of the compass. Although only described therein for the first time, it seems probable that the compass was already used in the 7th and 8th century since during this time the natural magnet lodestone (formed by the mineral magnetite; Fe_3O_4) was already replaced by iron needles. The Chinese used the compass mainly for terrestrial navigation; only at the end of the 12th century did it also appear on ships.

In Europe the compass was first mentioned in 1187 by the Englishman A. Neckam [3] in his works *De utensilibus* and *De naturis rerum.* Other sources about the use of magnetic needles can be found in a poem by G. de Provins [4] and in a letter of the crusader P. de Mericourt in his *Epistola de magnete* [5]. It is interesting that, although it was well known that magnets only attract iron and iron rich metals, the medieval literature also reports tales about magnetic mountains or islands whose magnetism was said to be able to remove the copper or bronze nails out of boats. It took until 1600 for Gilbert [6] to notice that the use of the right kind of iron is necessary to produce strong magnets. Figure 1.1 shows how a piece of iron can be magnetized by coldworking in the earth's magnetic field.

During the next centuries people tried to produce stronger magnets; in particular Knight [7] succeeded in building a magnetic "magazine" which was strong enough to reverse the magnetization of any other known magnet put into it. Also in the medical science of the 18th century the use of magnets came into fashion. In particular the German physician Mesmer claimed to be highly successful in curing various diseases by magnetizing the patient. In 1775 he published his results and claimed that his discovery of what he called *Magnetismus animalis* is of medical relevance. His influence was so strong that his name even entered the English language and is still present in the

Fig. 1.1. Coldworking of a permanent magnet in the direction of the earth's magnetic field (septentrio=north, auster=south) taken from Gilbert [6]

word *mesmerizing*. In a rather satirical way Lorenzo da Ponte comments on the Mesmer hysteria of his time in the textbook to Mozart's opera *Cosi fan tutte* [8] where in one scene two young men, who pretend to have poisoned themselves, are brought back to life by the application of a giant horseshoe magnet. This is not the only lyrical approach to magnetism. A rather different one can be found in the operetta *Patience* by Gilbert and Sullivan where W.S. Gilbert wrote in 1881:[1]

A magnet hung in a hardware shop,
And all around him was loving crop
Of scissors and needles, nails and knives,
Offering love for all their lives;
But for iron the magnet felt no whim,

[1] I am grateful to G. Fletcher for bringing this "magnetism chant" to my attention. It has also been referred to by J.H. van Vleck [9].

Though he charmed iron, it charmed not him;
From needles and nails and knives he'd turn,
For he'd set his love on a Silver Churn!
... But this magnetic, peripathetic
Lover he lived to learn,
By no endeavour
Can magnet ever
Attract a Silver Churn!

The effect of electric currents on compass needles was discovered by Oersted in 1820. As early as in 1831 Faraday formulated the induction principle which finally gave rise to a new scientific discipline: electromagnetism. The first electromagnets were built by Sturgeon [10] whose work started also a new and more systematic search for improving magnets. With the development of exact sciences the need for well defined stable magnetic fields also grew and reached its climax with the work of F. Bitter during the 1930s who succeeded in producing fields up to 15T in a bore of 5cm diameter. He developed segmented coils (which could tolerate the enormous mechanical stress) which were water cooled and had a power consumption of about 5MW. This line of experimental setup soon came to an end not only because of the enormous power consumption and cooling problems, but also because of the development of superconducting magnets. Although the mechanical stress problems remain, coils from technical superconductors like Nb-Ti and Nb_3Sn with upper critical fields of 15 and 23T, respectively, are readily available. The highest fields produced in the laboratory come from pulsed magnets, where a capacitance battery is discharged through a coil. Experiments are then performed at the peak flux usually for periods less than 1ms. These appliances reach up to 120T. A further increase can be achieved by implosion coils, where at the time of the main flux from a pulsed current, an implosion charge is ignited which contracts the coil area and thus increases the flux. Due to the high cost of these "self destroying" experiments their application is rather limited.

The development of "microscopic" models of the magnetic properties of free atoms, molecules and (much later) solids, started in the late 19th and early 20th century. It required the formulation of Maxwell's electrodynamics and the ideas of Boltzmann's statistical thermodynamics to treat the properties of ensembles of electric and magnetic carriers. If one assumes that a molecule has a magnetic moment of magnitude μ, the paramagnetic susceptibility χ_{para} of an ensemble of such molecules will be given by

$$\chi_{\mathrm{para}} = \frac{N\mu^2}{3k_{\mathrm{B}}T} \quad . \tag{1.1}$$

These persistent magnetic moments are thought to be represented by tiny permanent magnets, which themselves are supposed to be rigid and hence incapable of induced polarization. At $T = 0\mathrm{K}$ these elementary magnets will all be aligned parallel to an applied field. At finite T, temperature agitation will reduce the average number of aligned moments in the way expressed in (1.1). The linear temperature dependence of the inverse susceptibility was noticed experimentally by P. Curie [11] and was later derived theoretically by Langevin [12]. Equation (1.1) is in fact known as Curie's law and describes the susceptibility of all systems in the classical limit (high temperature).

While the Langevin paramagnetism always yields a positive contribution to the susceptibility there must also exist a different mechanism which leads to a diamagnetic behavior. Langevin also showed that induced polarization leads to a diamagnetic response by assuming that an applied field induces an additional electric current in the electron system. Due to the classical induction law, the magnetic field produced by this current is opposed to the direction of the applied field (Lenz's rule) and thus weakens it, which in turn leads to a negative value of the susceptibility. On calculating the statistical average of the two-dimensional projection over a three-dimensional motion Langevin missed out a factor of 2, which was only later corrected by Pauli [13] so the diamagnetic susceptibility χ_{dia} reads

$$\chi_{\text{dia}} = -\frac{Ne^2}{6mc^2}\sum_i \langle r_i^2 \rangle \quad . \tag{1.2}$$

In (1.2) the quantity $\langle r_i^2 \rangle$ is the average radius of the motion of electron i. A comparison of the para- and diamagnetic susceptibilities shows the latter one to be usually much smaller. In fact, for most systems with open electronic shells the diamagnetic part is negligible. Only in cases where all electron shells are filled and the paramagnetic contribution (ideally) becomes zero, can a net diamagnetic susceptibility be observed (e.g. copper, noble-gases).

At this point of the development of a theory of magnetism there existed a beautifully simple model for the understanding of both para- and diamagnetism which seemed to be based on purely classical physics. The drawback came when in 1919 Miss van Leeuwen, a Ph.D. student of Niels Bohr, demonstrated that classical Boltzmann statistics applied rigorously to any dynamical system must lead to a zero susceptibility [14]. The proof of the theorem, which is also referred to by van Vleck [15], is most elucidating for the understanding of magnetism and is briefly reviewed here.

Unambiguously one can assume that any magnetic moment, which has to be related to an angular momentum of a charged particle, can be written as a linear function

$$m_z = \sum_{k=1}^{f} a_k \dot{q}_k \quad , \tag{1.3}$$

of the generalized velocities $q_1 ... q_f$. This assumption is particularly clear in Cartesian coordinates where the magnetic moment (e.g. m_z) is given as

$$m_z = \frac{1}{2c}\sum e_i \left(x_i \dot{y}_i - y_i \dot{x}_i \right) \quad , \tag{1.4}$$

and the linearity in the velocities is preserved under any transformation to another set of generalized coordinates. The magnetic moment in the direction of the applied field (which defines the z-direction) is then given by

$$M_z = CN \int \ldots \int \sum_{k=1}^{f} a_k \dot{q}_k \mathrm{e}^{-\mathcal{H}/k_\mathrm{B}T} \mathrm{d}q_1 \ldots \mathrm{d}q_f \mathrm{d}p_1 \ldots \mathrm{d}p_f \quad . \tag{1.5}$$

Since Hamilton's equations relate the velocities to the momenta via

$$\dot{q}_f = \frac{\partial \mathcal{H}}{\partial p_j} \quad , \quad \dot{p}_f = -\frac{\partial \mathcal{H}}{\partial q_j} \quad , \tag{1.6}$$

the integrand for a particular index j is merely

$$-k_\mathrm{B}T \frac{\partial \left(a_j \mathrm{e}^{-\mathcal{H}/k_\mathrm{B}T}\right)}{\partial p_j} \tag{1.7}$$

so that for this value j the integral in (1.5) becomes

$$-CNk_\mathrm{B}T \int \ldots \int \left[a_j \mathrm{e}^{-\mathcal{H}/k_\mathrm{B}T}\right]_{p_j=-\infty}^{p_j=+\infty} \mathrm{d}q_1 \ldots \mathrm{d}q_f \mathrm{d}p_1 \ldots \mathrm{d}p_{j-1} \mathrm{d}p_{j+1} \ldots \mathrm{d}p_f . \tag{1.8}$$

Ergodicity requires that the integration has to be carried out over the whole range of the phase space so that the value for p_j varies over $\pm\infty$. From the convexity property of the free energy (see Sect. A.) one deduces that the energy has to become infinite for infinite values of the coordinate p_j which makes the integrand zero for any particular coordinate p_j. This proof holds for any Hamiltonian $\mathcal{H}$ (also with an applied field) since no properties of $\mathcal{H}$ were required.

This result is not only the formal proof that classical mechanics cannot account for magnetism but it also asks for an explanation of why one is able to obtain the Langevin results, (1.1) and (1.2), from the same classical mechanics. The answer is both simple and complicated at once: To derive Langevin's formula one has already assumed that finite and constant magnetic moments are present. In the sense of the proof given above, this means that one has restricted the integration to particular parts of the phase space, or in other words, some relevant parts of the energy remain finite (even constant) while the coordinates go to infinity. While classical mechanics cannot give any reasoning for such a restriction, quantum mechanics can, e.g. by requiring quantized values for the angular momentum or finite occupation numbers. In this sense van Leeuwen's theorem not only proves the inability of classical mechanics to explain magnetism, but also calls for a different mechanics on the microscopic scale which justifies the requirements for the Langevin formulation.

Langevin's result (1.1) can of course be derived from first principles quantum mechanics where it is known under the name Langevin–Debye formula. In the chapter about the Weiss molecular field model (Chap. 6), it will be shown how the Langevin–Debye result (6.13) can be obtained. A more profound derivation together with an extensive discussion is given in the book by John van Vleck [15].

The first successful quantum mechanical theory of magnetism goes back to N. Bohr who, around 1913, developed what is now known as the old quantum mechanics. (The "new quantum mechanics" – starting about 1921 – was later pioneered by Heisenberg, Schrödinger, Born, and Dirac.) With Bohr's astonishingly simple theorem that the angular momentum is given by multiples of Planck's constant, he immediately solved all problems which classical statistics imposed on the physics of microscopic particles. Among these problems of classical physics one usually only refers to the electrodynamically forbidden stationary electron orbits, but there existed other unanswered questions which rely on the application of Maxwell–Boltzmann statistics. One of these problems is the distribution of atomic (or molecular) sizes, since if Maxwell–Boltzmann statistics applies, the distribution of atomic radii in an ensemble of atoms must vary from very small ones (even zero) to very large ones. In particular the behavior for very small radii resembles the problem of the black-body radiation where classical physics requires that the energy density goes to infinity for zero wavelength (Rayleigh–Jeans law). Since quantum mechanics can thus explain why some variables remain constant, as discussed by van Leeuwen, it can also account for magnetism.

The microscopic theory of ferromagnetism starts with Weiss [16] who in 1907 postulated his famous molecular field model. Although formulated before the advent of quantum mechanics, he already assumed discrete energy levels associated with respective values for magnetic moments (angular momenta). To explain spontaneous alignment of the elementary magnetic moments, he postulated the existence of an internal (molecular) field which should represent the then unknown interaction between these moments. Later this interaction was found to be the exchange interaction which again is of entirely quantum-mechanical origin.

With the advancing spectroscopic techniques, the explanation of atomic spectra required the introduction of a new quantum number. Landé [17] proposed that he could explain his g-factor by assuming that the atom contained a mysterious *Atomrumpf* whose magnetic moment is exactly half the value found for ordinary angular momenta. The actual idea that the electron has an internal degree of freedom is due to Uhlenbeck and Goudsmit [18]. Only with the spin did it become possible to understand the anomalous Zeeman effect (i.e. the non-linear splitting of spectral lines in a weak applied field). Although the spin was originally described in analogy to the other angular momenta its actual origin was discovered by Dirac on formulating the relativistic quantum mechanics [19].

With the knowledge of the four principle quantum numbers (angular l, magnetic m_l, spin s, and spin–magnetic m_s) and the two different ways of coupling these angular momenta in the non–relativistic (ll–coupling) and in