Preface

The physics of condensed matter, that is liquid, solid, or amorphous materials, occupies something like 50% of physicists working in fundamental research, and the industrial opportunities in the engineering sciences are very important. The best known applications are in hi-tech, especially communications and information processing (semiconductors, magnetic data storage), but also medical imaging (superconductivity and magnetism). However, this discipline has also led to spectacular progress in the use of more commonplace materials employed in metallurgy (steels, special alloys, composites) or the construction industry (concretes).

By its very nature, condensed matter physics has a broad interface with other scientific disciplines relating to chemistry, biology, and mechanics. And this multidisciplinary aspect is growing steadily, through conceptual and instrumental developments which allow us to tackle ever more complex systems.

Before the advent of modern physics, it would have been difficult to understand the physics of electrons in solids, and this is the key feature of condensed matter physics. Since solids are collections of atoms, it is clear that the quantisation of atomic electron states must play a major role in their properties. The basic concepts of quantum mechanics and statistical physics are thus absolutely essential if we are to understand the macroscopic behaviour of electrons in solids.

Although a whole range of different atoms can be built up from protons, neutrons, and electrons, there is nevertheless a limit to what can be produced. On the other hand, atoms can be associated in infinitely many combinations to make up a solid. But from this apparent lawlessness, a range of original generic types of behaviour emerge, whose properties would be difficult to imagine on the basis of the individual atoms making up the solid. How is it that the electrons circulate freely in some solids (metals), and induce significant magnetic forces in others (magnets)? The great difficulty in predicting behaviour on an a priori basis is a characteristic of this discipline, whence the predominant role of observation.

This is therefore a useful point to specify the spirit of our own teaching, and hence of this textbook. In many countries, teaching traditions have always given pride of place to a formal, and essentially deductive, presentation of the physics, i.e., starting from formal hypotheses and leading up to observable consequences. This deductive approach leaves a purely a posteriori verificational role to observation, and hides the thinking that has gone into building up the models in the first place. Here we shall adopt the opposite approach, which begins with the fact that in science in general, and in solid state physics in particular, the qualitative understanding of a phenomenon is an important step which precedes the formulation of any theoretical development. We thus urge the reader to carry out a careful examination of the deeper significance of experimental observations,[1] in order to understand the need for specific models and carry out realistic approximations.

In this way we can also present the main physical effects without necessarily developing the whole theoretical formalism. This approach is indeed unavoidable, since it is impossible today to explain the properties of all solids within a single theoretical framework. Quite the contrary, in fact, since the main themes discussed in the book, viz., metals, superconductivity, and magnetism, are currently understood through radically different approximations. For this reason, many issues which now occupy researchers can be located precisely at the interface between these themes. The best example is undoubtedly high-temperature superconductivity, discovered in 1986, which involves all three phenomena at the same time!

Another aim of this book is to demonstrate the high level of interplay between fundamental scientific research and the development of modern technologies. Indeed, these physical phenomena underlie many developments that are set to revolutionise technology in the twenty-first century. We have thus decided not to restrict here to the fundamental physical concepts, but to go ahead and introduce those ideas that are essential for describing applications. Note that the nanotechnologies which are so much in the news these days seek to exploit the properties of very small objects, with length scales in the nanometer range. However, it would be hopeless to try to understand the characteristics of nanomaterials without a firm grasp of the properties of larger physical systems and the methods used to study them.

From the earliest times, humans have exploited the properties of materials they found in their natural surroundings, and many of these were solids. Of course, they did not have to wait for the arrival of modern science in order to find uses for them. The natural approach was always to take advantage of some observed behaviour, e.g., the exposed edge of a broken flint for cutting purposes, the ductility of metals for forging tools, or the good conduction of metals for making cooking pots, and so on. The recognition of these properties, even if they may today appeal to elaborate mathematical formulations, in no way requires an understanding of the fundamental underlying reasons. The mechanics of materials is almost always governed by macroscopic constitutive laws based on observation, whose microscopic origins are far from being fully understood. This in no way prevents their use. Magnetism is a case in point. The natural occurrence of rocks able to attract iron has been known since ancient times. The striking magnetic behaviour of iron has been ingeniously exploited in the compass to help explorers find their way. But while observation suffices for simple applications, it was only little by little that the chemical nature of the constitutive elements, the regular structure of crystals, and other microscopic features could eventually be identified.

[1] To help things along, a number of questions have been interspersed throughout the book. The answers to these questions can be found at the end of the chapter in which they have been raised.

The levitation of a magnet by a superconductor provides one of the most amazing manifestations of superconductivity, a source of wonder to all that witness it for the first time, and especially to students who have just themselves synthesised the superconducting ceramic $YBa_2Cu_3O_7$. How can three insulating oxides Y_2O_3, CuO, and BaO react in the solid phase to generate a metallic material which becomes superconducting in liquid nitrogen? This illustrates the fact that, in complex systems, properties are very hard to predict from a straightforward understanding of the separate constituents. The richness of condensed matter physics lies in the experimental revelation of spectacular phenomena arising from complex systems, which leads us to seek rational explanations

Recent Trends in Condensed Matter Physics

The nineteenth and twentieth centuries witnessed a major change in condensed matter physics as developments in metallurgy, then in chemistry, produced more and more artificial materials. For its part, physics tends to investigate natural materials under artificial conditions, in order to characterise certain properties. Physicists try to understand why some materials conduct electricity (Ohm's law!), by studying simple elementary metals. Experimentation can discover novel constitutive laws. Superconductivity is a case in point. It was demonstrated for the first time in 1911 when investigating the properties of metals at very low temperatures. But the theory needed to understand the microscopic origins of the behaviour was not yet available.

The decisive step here was the advent of modern physics in the form of statistical physics and then quantum mechanics, which led to considerable progress. It was found that many types of behaviour are *macroscopic manifestations of microscopic quantum phenomena*. Examples are the quantum origins of magnetism and the relation between the optical properties of solids and the organisation of their electronic energy levels into energy bands, among many others. The process of discovery picked up momentum after the 1950s, with the large-scale expansion of scientific endeavour and the development of cross-disciplinary research: chemical substances provided a host of new types of behaviour for physicists. The rate of fundamental discoveries has held up over the past thirty years, with the quantum Hall effect, scanning tunneling microscopy, high-T_c superconductivity, fullerenes and graphene, experimental observations that led in each case to Nobel prizes for those involved.

In time, these new types of behaviour are put to use in applications. But here scientists no longer limit themselves to understanding, nor engineers to application. The two roles are moving closer and closer together. The discovery of semiconductors was the direct result of a hybrid approach, with applications (the diode and the transistor) following very quickly after the discovery of the new type of behaviour (the junction between two differently doped semiconductors). Likewise gas lasers, and subsequently solid-state lasers, were purely artificial constructions which started life as laboratory curiosities based on a sound understanding of the basic science. The time scales between the discovery of new phenomena and concrete applications are shrinking fast, but still remain rather long (20 years for lasers, and 50 for superconductors). Economic factors are clearly the key, but experience shows that *a deeply novel type of behaviour always leads in the end to some viable application*.

This discussion might suggest that solid-state physics is a purely utilitarian science, but this would be quite wrong. In order to understand a novel observation, sophisticated theoretical models are often required, and these problems are naturally more difficult to solve than those generated by simple systems that prove easier to formulate. The difficulty here comes from trying to understand the macroscopic properties of ever more complex systems. This still involves the use of sometimes simplistic models, but which may be very hard to solve formally. More and more sophisticated instruments are developed to probe the structure and properties of materials on the microscopic scale. One has to deal with problems in which the basic state of the physical system is far from being intuitive, such as superconductivity or the Kondo effect. But novel theoretical ideas and methods are also devised. The theory of the renormalisation group has revolutionised the study of phase transitions, and the notion of disorder has become a subject of theoretical physics. Minimisation methods can determine the energy minimum of a disordered magnetic system, such as a spin glass, but can be broadly generalised to study neural networks or optimisation of the travelling salesman problem.

The style and choice of material in the following lectures on electrons in solids attempts to reflect this kind of approach, which characterises the discipline and which is not generally familiar to students. To achieve this, we have put the emphasis on two themes, namely magnetism and superconductivity, which are manifestations on the macroscopic scale of the quantum properties of solids, and which lead to many current or potential hi-tech applications. Although these same themes have up to now been the subject of detailed independent presentations, it seems judicious here, for historical reasons, to present them in tandem.

Magnetism and Superconductivity

How do magnetism and superconductivity fit in to the general context of condensed matter physics? The two disciplines are clearly distinct, in particular through their history, and have different consequences for technology. Magnetic materials have been known since ancient times, while superconductors were only discovered at the beginning of the twentieth century. The former have well known applications resulting from their behaviour, i.e., strong mutual attraction, and interaction with fields produced by electric currents. The latter also display novel types of behaviour, i.e., zero electrical resistance and diamagnetism, but which are only manifested *under currently unfavourable economic conditions*, viz., low temperatures. Everything would tend to distinguish the industrial impact of these two sciences.

But if one considers their most basic manifestations, the analogy between the magnetic fields produced by currents or by magnets has been common knowledge since the nineteenth century. Even before the end of the 1930s, quantum mechanics had shown that the electronic moments of atoms, like the persistent currents in superconductors, are quantum phenomena. It was soon understood that they result indirectly from electrostatic interactions between electrons. The two scientific disciplines witnessed several novel developments, rewarded by Nobel prizes: Bloch–Purcell–Pound, Mössbauer, Néel, Mott–Anderson–Van Vleck in one, and Bardeen–Cooper–Schrieffer, Josephson–Giaver in the other. Common scientific applications were developed, such as superconducting solenoids used in nuclear magnetic resonance (NMR) in chemistry, physics, and biology, but also instrumentation based on superconductors for work on magnetism (SQUIDs). But there was still no common scientific textbook discussing both disciplines, and lecture courses remained quite separate, reserved for a few hundred specialists. Magnetism is interesting for scientists because it can be used to study more general problems through specific high-performance experimental tools (neutrons, NMR, Mössbauer), while remaining susceptible to simplified and well tested theoretical formulation. In this way, many problems of statistical thermodynamics, such as phase transitions, low-dimensional systems, disorder, spin glasses, and so on, found elegant solutions.

At the beginning of the 1980s, industry had little time for superconductivity, but the applications of magnetism were many and varied. The electrical industrial revolution was made possible thanks to the magnetic materials used in electrical generators and motors. The magnetic recording industry alone represents an annual turnover that can be measured in multiples of 100 million US dollars. But superconductivity has come into the limelight through its association with NMR in *magnetic resonanance imaging* (MRI), bringing together the two disciplines in the first application to affect the general public. But these results were not enough to lead to generalised applications. (At the time, P.G. de Gennes, an original contributor to both fields and future Nobel prizewinner, claimed that these were sciences of the past!)

However, the discovery of high-temperature superconductors in 1986, with the attribution of the Nobel prize to Bednorz and Müller, gave hope for applications in the twenty-first century. Until then, theoreticians working on superconductivity had thought that the critical temperature T_c of superconductivity would not be able to go above 30 K. And yet here was an example of superconductivity with $T_c \approx 150$ K, in systems expected rather to exhibit novel magnetic properties. Understanding this kind of superconductivity has proved to be a tremendous challenge for science. These new superconductors incidentally allow us now to exhibit and popularize the basic superconducting phenomena in simple demonstrations as that depicted in the image of page vii, or using toy levitating trains.

Regarding magnetism, new high magnetisation ferromagnetic materials have been discovered. Magnetic data storage gained little benefit from scientific developments in the 1970s, since increases in data storage density were achieved rather through improved mechanics and accuracy of read heads. But more recently, a new read method has been devised, based on a magnetic phenomenon known as giant magnetoresistance, which has allowed a considerable step forward in this domain. This too was rewarded by the Nobel prize, attributed to A. Fert and P. Grünberg in 2007. This has initiated the novel field known as *spintronics*, which exploits the electron spin in electronic devices, and has also given hope of new applications. It involves new materials and is currently the subject of considerable interest in research centers.

Magnetism and superconductivity thus raise novel problems of a fundamental nature, but also in relation to materials and their applications, and they are now commonly encountered together in the most recent developments. The same materials can be made magnetic or superconducting with the help of minimal chemical adjustments. The instruments used to investigate them are similar, and often even the same. This coexistence can only be strengthened by the advent of nanotechnology, and the trend has reached a point at which it seems essential to bring the two subjects together into a single lecture course for students of science, whether they intend to go into research or engineering. The basic level of knowledge required by the engineer is clearly going to increase in the decades to come!

A Brief Guide to the Course

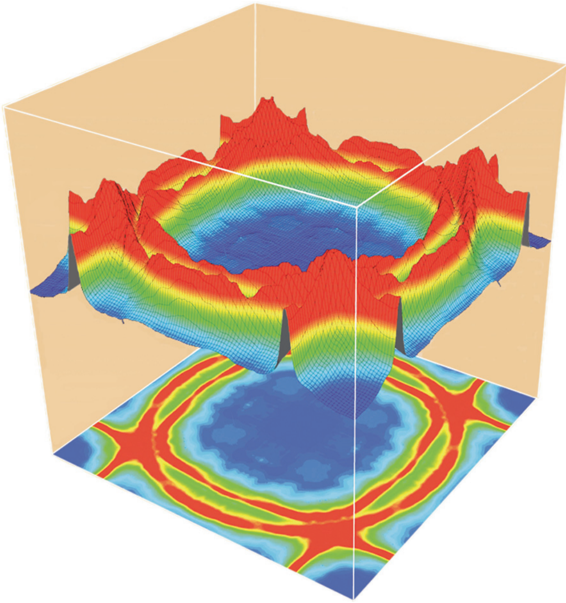
Why are electrons free to move in some solids, namely metals, but localised in others, namely insulators? To tackle this problem, we shall focus mainly on crystalline solids. The existence of a three-dimensional periodicity in these solids allows one to establish simple rules for the electron energy levels. We shall determine these basic rules using the *independent electron approximation*, i.e., considering only the Coulomb potential of the ions and accounting for the Coulomb repulsion of the electrons through only an average value. In this way, we find that the electron energy levels are distributed over allowed energy bands separated by forbidden bands, or bandgaps. This is shown in Chap. 1 for the simple case of a linear chain of atoms. To deal with 3D solids, some notions of crystallography are introduced in Chap. 2. We can then calculate the energy band structure using some simple approximations. Several experimental methods for determining the characteristics of the band structure are described in Chap. 3. The data displayed in page xiii exemplifies the most efficient technique, constantly improved since the 1990's, with the development of new synchrotrons. This energy level structure is the key to understanding the difference between metal and insulator, and introducing the notion of semiconductor. The physical parameters constraining the conductivity of metals are discussed in Chap. 4. These first chapters of the book already allow some simple applications of methods developed in quantum mechanics and statistical physics. They provide the basis for a subsequent understanding of semiconductors. The specificities of the band structure and transport properties of graphene, for which A. Geim and K. Novoselov have been awarded the 2010 Nobel prize, are highlighted as well.

The results of the first four chapters must be reconsidered *if interactions between the electrons can no longer be neglected*. But this is exactly what happens in superconductors and magnetic solids. Understanding the consequences of these interactions between electrons for the physical properties of the resulting solids is a central problem in our field. It goes well beyond the framework of an undergraduate course, which is the level aimed at here, but we feel it important to provide some kind of overview in the case of simple magnetic and superconducting materials.

Students have already acquired some understanding of phenomena related to magnetism. We have thus chosen to begin with superconductivity as the less familiar of the two disciplines. This should allow a gradual assimilation of the ideas, for we shall then refer back to them on many occasions in the rest of the course. A full discussion of the superconductivity of simple metals, which is now well understood, must be left to the doctoral level. For the present purposes, we shall stick to a limited description based on a historical and experimental presentation. This deliberate choice is used to place the student in the same conditions as those which led to our present understanding of this phenomenon. This is all the more important in that we shall then be able to illustrate an approach that is not altogether natural for students coming from a school education system. In any case, in the specific case of superconductivity, it would be optimistic to carry out a full theoretical presentation without first putting across the subtleties of the physical behaviour of superconductors.

Chapter 5 is thus devoted to the existence of persistent currents, the exclusion of magnetic induction in a superconductor, and the resulting quantisation of the magnetic flux. Chapter 6 studies the thermodynamic properties of superconductors, and the notions of coherence length and mixed phase that follow. Finally, in Chap. 7, we describe the experiments that help us to understand the microscopic origins of superconductivity, and analyse the Cooper calculation which lays the foundation for a full understanding.

In Chap. 8, we briefly discuss the origins of atomic magnetism and the exchange interactions responsible for ferromagnetism and antiferromagnetism. The idea of magnetic anisotropy which explains the existence of magnetic domains and domain walls in ferromagnetic materials is essential for understanding applications of magnetism (Chap. 9). In Chap. 10, we present experimental methods used to characterise the magnetic properties of materials. These reveal a methodological link between magnetism and superconductivity. In both cases, the need to understand physical properties and meet technological requirements has encouraged the development of methods for observing magnetism on microscopic, and even nanoscopic scales. Magnetic resonance detection is introduced in Chap. 11, and leads to a discussion of nuclear magnetic resonance and the importance of hyperfine methods for studying magnetism and superconductivity on the atomic scale. Finally, in Chap. 12, we discuss the elementary excitations (spin waves) in a ferromagnetic material, and also the basic theory of thermodynamic properties close to a phase transition (Landau and Ginzburg–Landau theories).



Experimental observation of the electronic states of Sr_2RuO_4 obtained by Angular Resolved Photoemision Spectroscopy (ARPES), a technique that takes benefit from the intense monochromatic light beams produced by synchrotrons. This technique has been intensively developed since the 1990s in particular for the study of high temperature superconductors.

Sr_2RuO_4 is a layered compound whose metallic behaviour is due to RuO_2 planes interleaved with insulating SrO planes. The Ru atoms form a square lattice with oxygen inserted between them. The single crystal sample has been cleaved and exhibits a flat RuO_2 plane. Irradiation by a monochromatic light of sufficient energy emits photoelectrons (this is the photoelectric effect for which A. Einstein has been awarded a Nobel prize). The study of the photoelectron intensity as a function of the emission angle allows one to map out the energy distribution of the electronic levels as a function of their in plane wave vector (k_x, k_y). The projected curves represent the Fermi surface (see question 3.6 in Chapter 3). Image courtesy of A. Damascelli, from experimental results by Damascelli, A., Lu, D.H., Shen, K.M., Armitage, N.P., Ronning, F., Feng, D.L., Kim, C., Shen, Z.-X., Kimura, T., Tokura, Y., Mao, Z.Q., Maeno, Y., Phys. Rev. Lett. **85**, 5194 (2000)

A Guided Choice of Problems

Over the years this lecture course on the physics of electrons in solids has been taught at the Ecole polytechnique (Palaiseau, France), its organisers have produced a significant number of written tests. We have often been led to propose themes focussing on experimental observations, which encourage students to reflect on their physical meaning.

In Chapter 13, we have included those problems which illustrate novel physical effects that are not discussed in detail in the lectures. Indeed, it seemed important to complement the basic ideas discussed in the book with a presentation of the more important aspects of solid-state physics which could not be taught during the year in the limited time available for lectures and supervisions. The aim here is not therefore a mere test of understanding acquired by studying the main course. Students who have independently acquired an understanding of the basic ideas of solid-state physics will be able to use the subjects here to glimpse some of the very active ongoing research themes, illustrated by modern experimental methods.

Direct manifestations of electronic band structure in the optical response of solids are examined in Problem 2: *Reflectance of Aluminium* and Problem 5: *Optical Response of Monovalent Metals*. The total energy of the electronic band states can affect the crystal structure of certain alloys (see the Hume–Rothery rules of Problem 4: *Electronic Energy and Stability of Alloys*) or induce a Peierls transition, which corresponds to a doubling of the unit cell and a metal–insulator transition in 1D compounds (Problem 6: *One-Dimensional TTF-TCNQ Compounds*).

We have illustrated the specific band structures of certain metals that are important for their superconducting properties, such as the high-T_c cuprate $YBa_2Cu_3O_7$ (Problem 3: *Band Structure of* $YBa_2Cu_3O_7$), the so-called A15 compounds, such as V_3Si in which the vanadium atoms are arranged in chains (Problem 14: *Electronic Structure and Superconductivity of* V_3Si), or the new superconducting compound MgB_2, whose highly 2D electronic structure is similar to that of graphene and graphite (Problem 16: *Magnesium Diboride: A New Superconductor?*).

Since semiconductor technology is often the subject of specific lecture courses, as is the case at the Ecole polytechnique, the discussion here simply reviews the relevance of the band structure for their electronic transport properties. The classic cyclotron resonance experiments are used to determine the effective masses of electrons and holes (Problem 8: *Cyclotron Resonance*). The notion of transition from a Mott insulator to a metal is introduced in such systems by examining the structure of donor electron levels introduced by substituting P in Si. This transition results from competition between Coulomb repulsion at an atomic site, which favours electron localisation, and the tendency of electrons to delocalise due to hopping integrals between neighbouring sites. This competition can explain the insulator–metal transition observed in Si when it is strongly doped with phosphorus (Problem 7: *Insulator–Metal Transition*).

The notion of atomic vibrations and their quantisation in terms of phonons is barely touched upon in the main course chapters. Further considerations can be found in Problem 9: *Phonons in Solids*, where their effects on the heat capacity of solids and the resistivity of pure metals are exemplified. Their consequences for X-ray diffraction diagrams are also studied in Problem 1: *Debye–Waller Factor*.

Many problems here are devoted to a deeper investigation of the novel properties associated with superconductivity. For example, one can study the effect of flux quantisation on the thermodynamic properties of superconductors (Little–Parks experiment discussed in Problem 10: *Thermodynamics of a Thin Superconducting Cylinder*) and the direct or alternating Josephson effect in zero field (Problem 11: *Direct and Alternating Josephson Effects in Zero Magnetic Field*). The existence of mixed states in a Josephson junction (Problem 12: *Josephson Junction in a Magnetic Field*), and the irreversibility of magnetisation curves induced by interactions between vortices and the surface of a type II superconductor (Problem 13: *Magnetisation of a Type II Superconductor*) provide a better understanding of the physics of vortices. The observation of these mixed states by scanning tunnelling microscopy (Problem 15: *Superconductivity of* $NbSe_2$) provides a window on the excited states of superconductors and the fine structure of the superconducting gap in compounds like $NbSe_2$ or MgB_2 (Problem 16: *Magnesium Diboride: A New Superconductor?*).

The aspects of magnetism dealt with here are the antiferromagnetism of undoped cuprates (Problem 17: *Electronic Properties of* La_2CuO_4) and the magnetic properties of antiferromagnetic materials in the molecular field approximation (Problem 18: *Properties of an Antiferromagnetic Solid*). Finally, the importance of the magnetism of thin films is illustrated by the use of magneto-optical methods to show how they decompose into domains (Problem 19: *Magnetism of Thin Films and Magneto-Optic Applications*), and an investigation of surface effects for the magnetic anisotropy of thin films (Problem 20: *Magnetism of a Thin Film*).

It is hoped that the reader's curiosity will be stimulated by the problem approach to these exciting physical phenomena and the considerable reflection required to explain the experimental observations discussed here. This problem set should allow the reader to glimpse the rich rewards of the scientific method, which relentlessly confronts observation with theoretical models.

Orsay, October 2010 *Henri Alloul*

http://www.springer.com/978-3-642-13564-4

Introduction to the Physics of Electrons in Solids
Alloul, H.
2011, XXVI, 618 p., Hardcover
ISBN: 978-3-642-13564-4