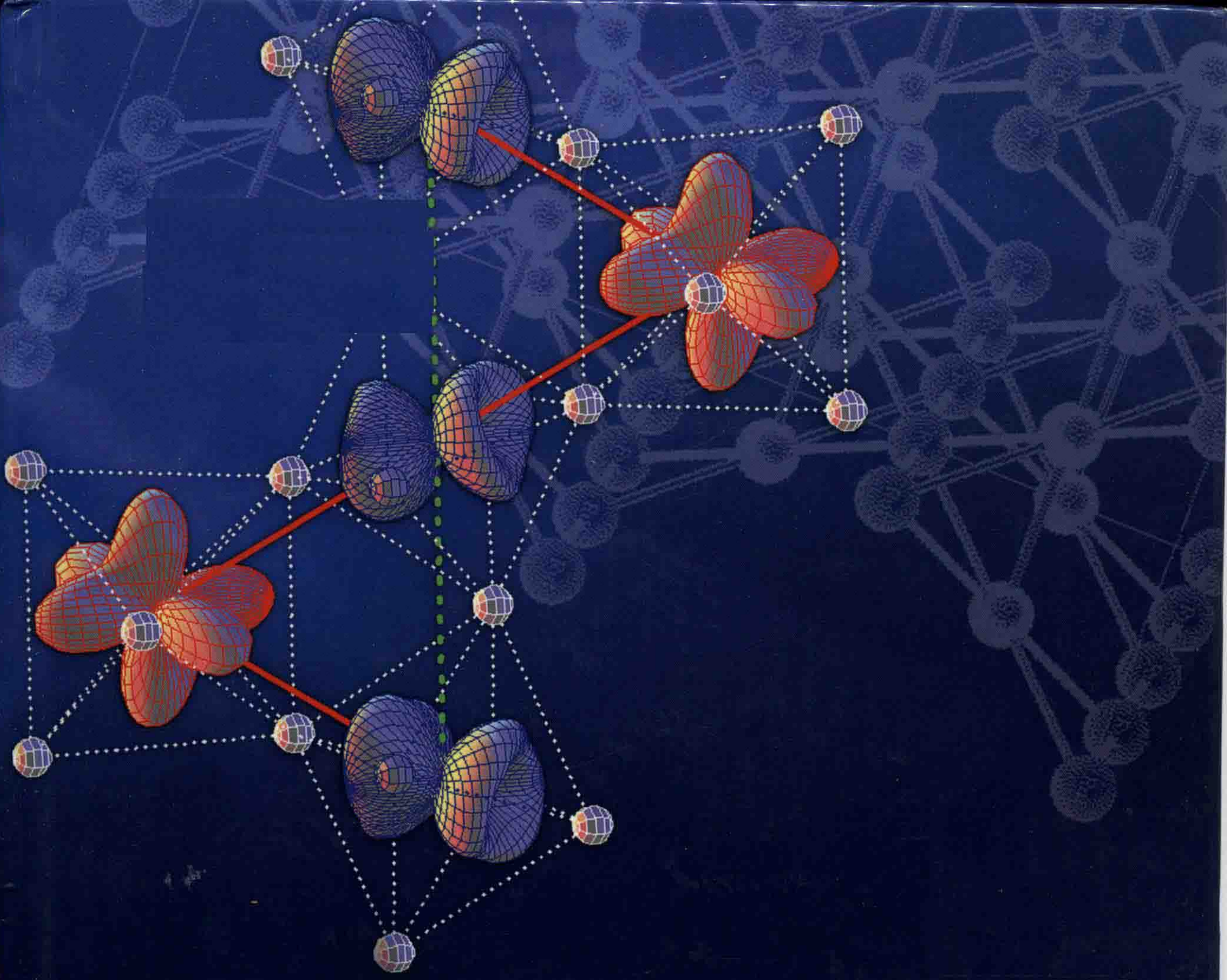
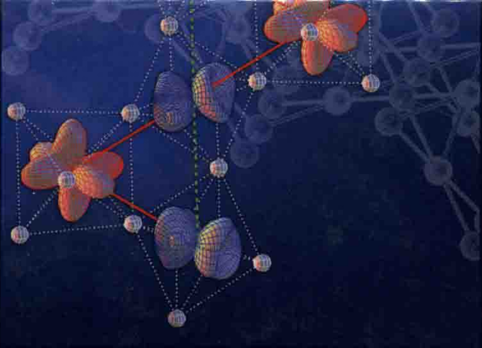


TRANSITION METAL COMPOUNDS

DANIEL I. KHOMSKII



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Describing all aspects of the physics of transition metal compounds, this book provides a comprehensive overview of this unique and diverse class of solids.

Beginning with the basic concepts of the physics of strongly correlated electron systems, the structure of transition metal ions, and the behavior of transition metal ions in crystals, it goes on to cover more advanced topics such as metal–insulator transitions, orbital ordering, and novel phenomena such as multiferroics, systems with oxygen holes, and high-T_c superconductivity.

Each chapter concludes with a summary of key facts and concepts, presenting all the most important information in a consistent and concise manner. Set within a modern conceptual framework, and providing a complete treatment of the fundamental factors and mechanisms that determine the properties of transition metal compounds, this is an invaluable resource for graduate students, researchers, and industrial practitioners in solid-state physics and chemistry, materials science, and inorganic chemistry.

Daniel I. Khomskii is a Professor at the University of Köln, Germany, where his research interests focus on metal–insulator transitions, magnetism, orbital ordering, and superconductivity.

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Introduction

Transition metal (TM) compounds present a unique class of solids. The physics of these materials is extremely rich. There are among them good metals and strong, large-gap insulators, and also systems with metal–insulator transitions. Their magnetic properties are also very diverse; actually, most strong magnets are transition metal (or rare earth) compounds. They display a lot of interesting phenomena, such as multiferroicity or colossal magnetoresistance. Last but not least, high-T_c superconductors also belong to this class.

Transition metal compounds are manifestly the main area of interest and the basis for a large field of physical phenomena: the physics of systems with strong electron correlations. Many novel ideas, such as Mott insulators, were first suggested and developed in application to transition metal compounds.

From a practical point of view, the magnetic properties of these materials have been considered and used for a long time, but more recently their electronic behavior came to the forefront. The ideas of spintronics, magnetoelectricity and multiferroicity, and high-T_c superconductivity form a very rich and fruitful field of research, promising (and already having) important applications.

There are many aspects of the physics of transition metal compounds. Some of these are of a fundamental nature – the very description of their electronic structure is different from the standard approach based on the conventional band theory and applicable to standard metals such as Na or Al, or insulators or semiconductors such as Ge or Si. Furthermore, transition metal compounds also possess many specific and unusual features, largely related to the details of the structure of the atoms or ions that form these compounds. These features have to be taken into account if we want to make our description realistic. Many interesting and diverse phenomena in transition metal compounds are based directly on the specific features of the corresponding atoms or ions. A book devoted to this class of materials has to deal with both of these aspects; it should describe the conceptual problems in the description of systems in which electron–electron interactions (or strong electron correlations) largely determine the very type of states we are dealing with, but it should also combine this with the specific details of particular types of transition metal ions, etc.

The aim of this book is to give a coherent general description of the main aspects of the physics of transition metal compounds. By these, I have in mind solids made up on the basis of transition metal elements. A large and separate field of molecular systems and chemical compounds containing transition metals belongs rather to inorganic chemistry, and is left out of this book. These topics are covered, for example, in Cotton *et al.* (1995) or Bersuker (2010). Nevertheless, many notions which first appeared and are crucial in this field are also very important for solids, and these are discussed to a certain extent in the present book. However, the main focus is indeed on the aspects of the physics of transition metal solids, both conceptual and general, and those specific for particular classes of materials and phenomena. A more general treatment of the theoretical aspects of solids in general can be found in many books, in particular in Khomskii (2010), which I will refer to relatively often. This and the present book can be considered in tandem.

I hope to cover the main aspects of this whole field. Of course, the field of transition metal compounds is actually enormous, and if one goes into all the details, every particular subfield would require a separate book three times bigger than the present volume. Therefore, I have chosen to concentrate on the basic notions and ideas, trying to explain them as qualitatively as possible, sometimes leaving out many technical details. I hope that this style will make this book accessible and useful to a broad audience: both specialists in the physics of transition metal compounds as well as people working in inorganic chemistry and material sciences. I also hope that it will be useful both for more senior and beginning scientists and for graduate students specializing in these fields. One can find more detailed treatments of some specific problems in the literature cited.

This book originated from a set of lectures, usually in the form of short "crash courses" on the physics of transition metal compounds, which I have given during the last 10 years at several places: Cologne, Grenoble, Loughborough, and Korea. These were usually lectures for both senior and younger researchers and also for graduate students specializing or interested in various aspects of the physics of transition metal compounds; the audiences came from physics, inorganic chemistry, and material science departments. Thus I hope that this book may be useful for such audiences, in particular as an advanced textbook.

The general approach taken in this book determines some of its specific features. Thus I prefer to illustrate the main notions by schematic figures, very rarely using real experimental data – rather, presenting such data in a schematic form and stressing the main conceptual features. Of course, this field of research is largely an experimental one. However, sometimes the real experimental data for a particular compound show not only the generic features, but also some specific details which mask or obscure the main effect we want to discuss.

This also relates to the references. Where possible, I have tried to refer not so much to original publications (although of course there are many such references too) but to books or review articles, whenever they exist. I apologize in advance to many of my colleagues whose important papers are not mentioned in this book.

As the material of different chapters often covers quite different fields and is to some extent independent, and I anticipate that some readers will not read the whole book but may skip some parts. Therefore in several places, to preserve the continuity of discussion, I repeat some of the material discussed in more detail in other chapters. This is done in very few places, but I think it justified as it makes each chapter more self-contained.

One more specific feature of the book is determined by its scope and style. I decided to conclude each chapter with a short summary or "digest," presenting in a few pages the main notions and material discussed. The aim is two- or even threefold. The short summaries should remind readers of the main ideas of the corresponding chapters, and help to "enforce" their understanding so that at least the main ideas settle in. Also, these short digests could be used at a first reading so that the reader can immediately see which problems are discussed in the respective chapters and then decide whether he or she needs to study a particular chapter in more detail, or maybe postpone it until later. Thus, for example, the chapter on multiferroics may be interesting for people working in this and related fields, but less so for those specializing in high-T_c superconductivity. These short summaries would give such people at least the opportunity to understand quickly "what it is all about," even in fields far from their own narrow interests.

In effect, these "digests" collected together would form something like a "book within a book," giving in a small volume a qualitative presentation of this whole field. I hope such a "book within a book" will be useful for a broad audience, both for younger people just starting to study and work in the field of transition metal compounds as well as for more mature scientists who could quickly refresh their memory on some topics of both general and more specific character.

A few more words regarding the general scheme and layout of the presentation. As I already mentioned above, in dealing with transition compounds the main physical effects are connected with strong electron correlations. This gives rise to such fundamental notions as electron localization, Mott insulators, etc. The usual starting point in discussing these questions is the simplest case of electrons in a nondegenerate band, with one electron per site ($n = 1$), and with strong electron interaction $U/t \gg 1$, where U is the on-site Coulomb ("Hubbard") repulsion and t is an electron hopping. With this example one can illustrate some key notions mentioned above. However, to make the description more realistic, one has to include many details such as intra-atomic characteristics, orbital structure, spin–orbit interaction, etc. Then, one can gradually relax the restrictions imposed at the beginning, such as integer electron occupation (e.g., one electron per site) or the condition of strong interaction.

The layout of the book more or less follows this scheme. Chapter 1 discusses the basic phenomena, using the example of the simple nondegenerate Hubbard model. Then, in Chapters 2–8, various specific features are gradually included such as the atomic structure of the corresponding elements, modifications occurring when atoms or ions are in a crystal, effects connected with orbital structure including orbital degeneracy, etc. This treatment still deals predominantly with strongly correlated electrons with integer occupation of d-levels, although already in some places the restrictions are relaxed and we treat, for example, charge ordering which mainly takes place for other filling of d-levels. The main effects connected with lifting this restriction, and the treatment of systems with doping and arbitrary band filling, are considered in Chapter 9. Finally, in Chapter 10 we lift the final "constraint" of strong electron correlations, $U \gg t$, and consider the general case of variable U/t, in particular paying attention to the extremely interesting phenomenon of metal–insulator or Mott transitions, which occur in this situation. Finally, in Chapter 11, which stands somewhat apart, we briefly discuss the main properties of another class of solids with strong electron correlations – those made not on the basis of transition metals, but of the $4f$ and $5f$ compounds (rare earths and actinides). Many interesting phenomena in these materials, such as the Kondo effect, are seen in one form or another also in transition metal compounds, and the main physics of these compounds is also similar, although they also have some special features. I think it makes sense for completeness to discuss these materials and phenomena in the present book, as they have close relations to the phenomena observed in transition metal compounds.

In conclusion, I am grateful to many of my coworkers and colleagues, whose contributions and discussions over many years contributed significantly to my understanding of this very large field. I am especially grateful to L. Bulaevskii, K. Kugel, I. Mazin, T. Mizokawa, M. Mostovoy, G. Sawatzky, S. Streltsov, Hao Tjeng, and Hua Wu.

Contents

1

Localized and itinerant electrons in solids

The main topic of this book is the physics of solids containing transition elements: $3d$ – Ti, V, Cr, Mn, . . . ; $4d$ – Nb, Ru, . . . ; $5d$ – Ta, Ir, Pt, . . . These materials show extremely diverse properties. There are among them metals and insulators; some show metal–insulator transitions, sometimes with a jump of conductivity by many orders of magnitude. Many of these materials are magnetic: practically all strong magnets belong to this class (or contain rare earth ions, the physics of which is in many respects similar to that of transition metal compounds). And last but not least, superconductors with the highest critical temperature also belong to this group (high-T_c cuprates, with T_c reaching ~ 150 K, or the recently discovered iron-based (e.g., FeAs-type) superconductors with critical temperature reaching 50–60 K).

The main factor determining the diversity of behavior of these materials is the fact that their electrons may have two conceptually quite different states: they may be either localized at corresponding ions or delocalized, itinerant, similar to those in simple metals such as Na (and, of course, their state may be something in between). When dealing with localized electrons, we have to use all the notions of atomic physics, and for itinerant electrons the conventional band theory may be a good starting point.

This division in fact goes back to the first half of the 20th century. In the early stages of the development of quantum mechanics one used to treat in detail the electrons in atoms, with different aspects of atomic structure, shell model, atomic quantum numbers, etc. All these details are indeed important for transition metal compounds as well, and we will discuss these problems in the main body of the book. However at the beginning, in this introductory chapter, we will treat the simplest case, ignoring these complications and paying most attention to the competition between localized and itinerant states of electrons in solids.

1.1 Itinerant electrons, band theory

The "fate" of atomic electrons when individual atoms form a concentrated system – a solid – was treated in the first half of the last century, and it led to a very successful picture known as band theory; see, for example, Mott and Jones (1958), Ashcroft and Mermin (1976), Kittel (2004a), and many other textbooks on solid-state physics. In this theory

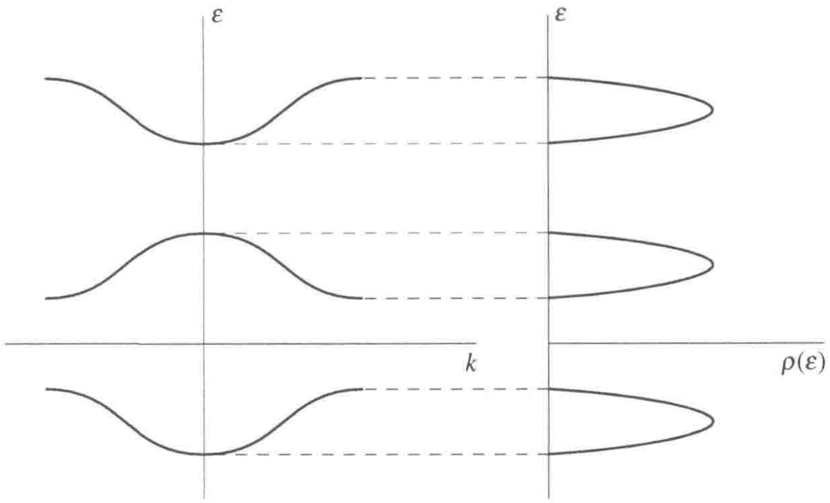

Figure 1.1 Schematic form of the energy spectrum $\varepsilon(k)$ and the density of states $\rho(\varepsilon)$ of free electrons in a crystal.

one considers the motion of noninteracting electrons on the background of a periodic lattice of ions. The spectrum of an electron in the periodic potential consists of allowed energy bands with forbidden states – energy gaps – between them; see the schematic picture of Fig. 1.1, where we show the energy bands $\varepsilon_i(k)$ and the corresponding density of states $\rho(\varepsilon)$.

If there are N atoms in a crystal, each band contains N k-points; for example in the one-dimensional case $k_n = 2\pi n/N$, $n = -\frac{1}{2}N, \dots, +\frac{1}{2}N$, so that in the continuous limit $-\pi \leqslant k < \pi$ (here and below in most cases we will take the lattice constant $a = 1$). The values $-\pi \leqslant k \leqslant \pi$ form the (first) Brillouin zone. For a system with N sites each band contains N energy levels and, according to the Pauli principle, one can put two electrons with spins ↑ and ↓ on each level, so that each band has room for $2N$ electrons.

In this scheme the electrons occupy the lowest energy levels, and if the number of electrons N_{el} is less than $2N$, that is the electron density $n = N_{\mathrm{el}}/N < 2$, the electrons would occupy the lowest energy band only partially, up to a certain maximal momentum k_{F} and energy ε_{F} (Fig. 1.2) and the system would be a metal. k_{F} and ε_{F} are correspondingly the Fermi momentum and Fermi energy.

In the one-dimensional (1d) case we would have two Fermi points $\pm k_{\mathrm{F}}$. In two-dimensional (2d) and three-dimensional (3d) systems the electrons occupy the states $\varepsilon(k) \leqslant \varepsilon_{\mathrm{F}}$, and the boundary of these occupied states forms the Fermi surface. There may exist several energy bands, which may intersect, and the corresponding Fermi surface of metals may in general be very complicated.

If, in the simplest case of one nondegenerate band of Fig. 1.1, we had $N_{\mathrm{el}} = 2N$, the electrons would fully occupy this first band and the system would be insulating, with an energy gap separating the completely full valence band and the empty conduction