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Adolfo Avella
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Strongly Correlated Systems

Experimental Techniques

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Editors

Strongly Correlated Systems

Experimental Techniques

With 117 Figures

 Springer

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Preface

This volume “Experimental Techniques for Strongly Correlated Systems”, together with the set “Methods and Techniques for Strongly Correlated Systems” it belongs to, builds upon the long-standing experience we have acquired in organizing the “Trainings Course in the Physics of Strongly Correlated Systems” in Vietri sul Mare (Salerno, Italy) since 1996 and our scientific working experience in the field. Running a school for advanced graduate students and junior postdocs, we have realized that this field of condensed matter and solid-state physics lacked in adequate textbooks and that the whole strongly correlated systems community would benefit from a systematic exposition of the field. The present volume consists of a series of monographs on the most relevant experimental techniques currently used to tackle the hoary problem of correlations. The authors have been selected, the major experts in the field have been consulted, among the most world-wide famous scientists who have invented or greatly helped improve/spread the specific technique in the community. Each chapter presents the method in a pedagogical way and contains at least one case study where the method has proved to give a substantial leap forward in the knowledge and a very rich bibliography. The book is mainly intended for neophytes, who will find in one single volume all the pieces of information necessary to choose and start learning an experimental technique. Also more experienced researchers would benefit from this volume as they would gain a deeper understanding of what any single technique can really tell them and what cannot. Accordingly, the accent is more on the ideas behind (origins, pros/cons, perspectives, ...) than on the technical details, which are left to the comprehensive bibliography.

We wish to thank all the authors of this volume as they all joined this editorial project with enthusiasm and provided the whole community with what we hope will become a relevant resource for any researcher in the field as a comprehensive and extended reference.

Salerno, Italy
June 2014

Adolfo Avella
Ferdinando Mancini

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Foreword

Hans R. Ott

1 Introduction

This volume is intended to give an overview of various important experimental methods and techniques for studying correlation and many-body effects in solids. Naturally, the content of the chapters concentrates on the modern, i.e., state-of-the-art situation of these aspects. In order to put these contributions in relation to the developments in studies of correlations in solids, the first section of this foreword aims at briefly reviewing the history of corresponding investigations, emphasizing the interplay between experiment and theory.

An early experimental or rather observational evidence for correlation effects among electrons in solids, but certainly not identified as such at the time, is the phenomenon of persistent magnetization in ferrous materials found in nature. A much more recent but in this context also early and then unexplained indication of the same was the discovery of superconductivity via experiments probing the electrical resistance of Mercury (Hg) at low temperatures in 1911 [1]. In 1933, simple experiments [2], again probing the temperature dependence of the electrical resistivity $\rho(T)$ of a metal, at this time Gold (Au), marked the beginning of a new direction in the slow development of understanding the role of electron correlations that was to bloom only much later. At these early times, electronic transport in metals was considered to be adequately described by the motion of free or quasifree electrons in the crystal lattice. Hence the observed increase of $\rho(T)$ with decreasing T at low temperatures was registered as a not understood anomaly which, eventually but much later, was shown to be due to transition-metal (TM) impurities in common metals such as Cu and Au [3]. The first theory-based link between magnetism and electronic conduction in solids was provided by Bloch [4].

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Yet another experimental fact concerning the electronic conduction in solids, namely the insulating behavior of NiO, initiated new ideas on how correlation effects among electrons are decisive for solids to turn out to be either metals, i.e., electrical conductors, or insulators. Following conventional wisdom, NiO is expected to be a metal and not an insulator as verified experimentally. In 1949, based on a comparison of the Heitler-London approach [5] with Bloch's [6] approximation in dealing with electronic states in solids, Mott [7] argued that the NiO puzzle was a result of correlation effects. Already in this first discussion of his ideas, known data on the magnetic susceptibility and the specific heat of transition-metal elements were used to support the conjectures.

Subsequently, experimental and theoretical investigations on the stability of magnetic moments and the occurrence of magnetic order in metals, launched a development of activities that continue to be a major part of contemporary condensed matter physics research. The behavior of magnetic moments in, and their influence on a metallic environment was first treated by considering a single magnetic moment as an impurity in an itinerant-electron system by Friedel [8], Blandin [9] and others around 1956. Experiments employing the still young experimental technique of nuclear magnetic resonance (NMR) provided information on the polarization of conduction electrons by the spins of more localized electrons on atoms of d-transition-metal elements [10]. Accompanying theoretical investigations [11–13] finally provided a scheme for describing the onset of magnetic order induced by the interaction between itinerant and more localized core electrons, the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.

Magnetization measurements probing the influence of magnetic moments on the normal state of metals, mainly by Matthias, Suhl, Clogston, and others [14, 15], revealed unexpected complications. This prompted Anderson to extend the then existing model by creating what is now known as the Anderson Hamiltonian [16], aiming at explaining why a magnetic moment due to localized electrons is stable in one metal but not in another. At the same time, with the same simple experiments, again Matthias and co-workers, noted detrimental effects of magnetic moments on the superconducting state of selected materials [17]. In this case it was Abrikosov and Gorkov [18] who provided an explanation by considering the particular correlated superconducting ground state put forward a few years earlier by Bardeen, Cooper, and Schrieffer (BCS) [19].

Not much later, in 1963, another model Hamiltonian, attempting to capture correlation effects among narrow-band d-electrons in transition metals (TM), was introduced and analyzed by Hubbard [20]. Although formally quite simple, rigorous solutions are difficult to obtain. The model and variations of it are, however, still very popular and, as mentioned below, often used in numerical investigations of correlated electron systems. Almost in parallel, an explanation of the above-mentioned experimental observation of the minimum in $\rho(T)$ was given by Kondo [21]. He argued that a single localized magnetic moment embedded in a metallic environment is shielded by oppositely oriented spins in a cloud of conduction electrons

in the neighborhood of the impurity. The resulting partial rearrangement of the excitation spectrum of the conduction electrons is then responsible for the observed increase of $\rho(T)$ with decreasing temperature below a material-specific temperature T_K , the Kondo temperature.

New aspects of electronic correlations in metals were soon discovered via experiments probing thermal, transport, and magnetic properties of rare-earth and actinide compounds. It was expected and confirmed that the corresponding 4f- and 5f-electrons are even more localized than the d-electrons in the above-mentioned d-transition metals and their compounds. As expected, Curie-Weiss type magnetic susceptibility data below room temperature indicated the presence of well localized, weakly interacting f-electron moments occupying regular lattice sites. A particularly intriguing result was the observation that a Curie-Weiss type magnetic susceptibility at elevated temperatures does not necessarily imply the onset of magnetic order at low temperatures [22]. In other cases, the established magnetic order was among moments, in magnitude much reduced below the values indicated by the Curie-Weiss effective moment at elevated temperatures [23]. A particular case in this respect is CeAl_3 with Ce^{3+} ions carrying a significant localized magnetic moment and occupying a regular crystalline sublattice. Results of measurements of the temperature dependences of the specific heat, the electrical resistivity and the magnetic susceptibility were interpreted as being due to conduction electrons with extremely large effective masses [24] or, equivalently, very low Fermi velocities v_F . In a first approximation, these features obviously imply that the involved itinerant electrons occupy energy states in very narrow bands and may be regarded as forming a very strongly renormalized Fermi liquid, a situation that was discussed in detail by Landau 20 years earlier [25]. In some sense, the magnetic degrees of freedom appear to be transferred to the subsystem of the itinerant electrons at low temperatures. The resulting anomalously large effective masses mimic the tendency to localization and the local ionic moments are substantially reduced. An interesting toy model describing the situation of order among much reduced moments or eventually no order at all was put forward by Doniach [26]. He suggested that a competition between different correlations, those of Kondo type and those of RKKY type, might cause this anomalous electronic many-body state. Not surprisingly and early indicated by results of thermal expansion [24] and elastic-constant measurements [27], the properties of these narrow-band electron systems are easily influenced by the application of external pressure. Subsequently and as also mentioned below, some spectacular transitions from magnetic order to superconductivity were discovered in later studies [28].

In view of the above-mentioned previously observed detrimental effect of magnetic moments in superconducting materials, the discovery of superconductivity [29] in these materials with narrow bands and strong electronic correlations, was really unexpected. Experimental data, mainly invoking thermal (specific heat) and spectroscopic (NMR) properties, soon prompted first claims of the identification of unconventional superconductivity in metallic solids [30].

Research on electronic correlations in solids received an unprecedented boost by the again completely unexpected discovery of superconductivity in a particular class of copper-oxide compounds with critical temperatures T_c between 30 and 40 K [31]. Efforts to enhance the critical temperature T_c in the same and various other cuprate materials were soon successful in raising the onset of superconductivity to above the boiling point of liquid nitrogen and finally to temperatures up to 134 K [32]. Considering the onset of superconductivity in such materials at all and the magnitude of T_c seemed to violate conventional wisdom to an extent that conjectures of unconventional superconductivity also in these cases, were to be expected. Experimental efforts employing a variety of methods probing the phase of the superconducting order parameter indeed confirmed the occurrence of nodes in the k -dependent energy gap of the electronic excitation spectrum in the superconducting state [33, 34]. In another experimental approach to directly verify such gap nodes, a new experimental method with a rapid development in technical perfection, namely angular-resolved photoemission spectroscopy (ARPES), encountered its first real success [35]. The increasing importance of this method was naturally based on the growing availability of intense light sources in the form of large electron synchrotrons. The mapping of $E(k)$ spectra of cuprate superconductors was widely used in many ARPES-based investigations, hoping that this type of information would help to understand the reasons for the instability of the electronic subsystem leading to superconductivity at unusually high temperatures in these compounds.

Similar progresses in instrumentations of this and other experimental techniques provided new ways for investigating the influence of electronic correlations in solids. With respect to access narrow bands of electronic excitations, the energy resolution in photoemission methods was greatly improved and finally resulted in commercially available detectors for this purpose [36]. A similar but less rigorous development took place in using elastic and inelastic neutron diffraction. In particular, the method of small-angle neutron scattering [37], primarily used for studies of macromolecules and polymers, gained in importance for studies of (H, T) phase diagrams of superconductors [38]. In parallel to these improvements of the instrumentation at large-scale facilities, the methods employing scanning-tunneling techniques such as based on electron-tunneling (STM) and atomic-force microscopy (AFM) provided new ways of probing electronic and magnetic properties at a local, i.e., atomically resolved level [39].

It turned out that the electronic conductivity in these materials is the result of specifically doping initially insulating and magnetically ordering compounds. The aims to provide a theoretical basis for explaining the observations concerning the normal state of these substances led to a revival of the above-mentioned models of Mott and Hubbard and extensions thereof [40]. Yet another model, earlier devised by Anderson by reviving Paulings resonant-valence-bond concept [41], was considered as a possible approach to solve the problem. An early account of strong correlation and superconductivity is given in [42]. Some of these models implied the formation of a ground state that would not be consistent with the Fermi liquid type description of the metallic, i.e., $\partial\rho/\partial T > 0$, state and a number of the available experimental data seemed to support this view [43]. The anomalous electronic

properties of the normal state of cuprates encouraged detailed experiments investigating the electronic properties of TM oxides and related materials. An early review of the results of these efforts, concentrating on the phenomenon of externally controlled metal-insulator transitions was provided by Imada and co-workers [44].

Because of the very high upper critical fields H_{c2} of these cuprate superconductors, the low-temperature electronic structure of the normal state of these materials was, at the time, not accessible by employing the usual magneto-oscillatory effects on the resistivity and the magnetisation. The already mentioned progresses in ARPES experiments made it possible to investigate these features also at elevated temperatures above T_c , previously not accessible by conventional means [45]. Much more recently, improved sample quality and progress in the technical handling of high-field magnets and measuring devices made it possible to observe the long sought field-induced oscillatory features of transport coefficients [46]. New insights into the correlations in electronic subsystems, mainly in cuprates and other TM compounds close to metal-insulator transitions were achieved via measurements of optical properties and using advanced photoelectron spectroscopy techniques.

Inspired by earlier results and to some extent encouraged by the experimental results indicating the anomalous features of the normal state of the cuprate compounds and noting the perspectives of new aspects in the understanding of metallic conductivity, more detailed experimental investigations, mostly probing thermal, transport, and magnetic properties, were made on compounds featuring heavy electrons. Data from specific heat experiments at very low temperatures indicated significant deviations from the behavior expected for Fermi liquids [47]. Other studies revealed that the properties of this low-temperature electronic state can be significantly altered by changing externally controlled parameters, such as variations of the chemical composition, external pressure, or magnetic fields. Again, some of the results of the corresponding experiments indicated properties not compatible with Landau's original Fermi-liquid model; others suggested the occurrence of so-called quantum phase transitions (QPT) [48], a concept [49] with a bright future, as will be seen below.

Structural investigations of the cuprate superconductors, mostly by employing X-ray and neutron diffraction [50], revealed that the arrangement of atoms in the crystallographic unit cells may be viewed as a stacking of planes of atoms. It turned out that the essential physical properties of these compounds are determined by planes consisting of copper and oxygen atoms; additional planes, occupied by atoms of the other constituent chemical elements, are regarded as mostly inactive spacer blocks and charge reservoirs [51]. This insight triggered new and extensive efforts in synthesizing other similar oxide materials based on Cu and other TM elements with low-dimensional (low-D) structural subunits, such as planes, multileg ladders, and chains. These included both electrical conductors and insulators. Since the Cu and other TM ions, depending on their charge configuration, carry a definite electronic spin, the cited subunits may be regarded as spin chains, ladders, and planes. In special cases, the interactions between the low-D spin subunits in insulators turn out to be weak. For this reason, these particular materials were and

still are considered as assemblies of quasi-individual low-D objects, serving as model systems for testing rigorous theoretical predictions concerning the properties of ensembles of spins which accumulated over many years up to present.

With respect to theory, low-D spin arrangements have a long history, starting with Isings model of individual magnets on a chain in his contribution to the theory of ferromagnetism [52]. The more general approach of Heisenberg to consider the exchange phenomenon in the quantum-mechanical description of indistinguishable particles for the description of ferromagnetism was the next step [53]. It was taken up by Bloch who concluded that planar arrangements of magnetic moments would not support ferromagnetism [4]. Next it was Bethe who calculated the eigenfunctions and eigenvalues of a linear chain of atoms, each with a single valence electron and its spin [54]. With this method he aimed at establishing the magnetic and transport properties of such systems, also in higher dimensions.

General aspects of phase transitions in low-D systems were first discussed by Onsager [55]. He considered a 2D model which exhibits an order–disorder transition. Later, Griffiths [56] as well as Mermin and Wagner [57] discussed the possibility of magnetic order in low-dimensional systems. Based on earlier work of Bloch [58], the features of low-D electronic systems were also studied, first by Tomonaga [59] and later by Luttinger [60]. From still later work by Haldane [61] and Affleck [62] it was concluded that the above-mentioned Fermi-liquid model, describing the electronic properties of common metals so well, was not applicable in treating 1D conductors. These authors saw a more suitable treatment with a concept that they termed Luttinger-liquid model, the 1D equivalent of the Fermi-liquid model. It turns out that quite generally the physical properties of low-D systems are characteristically different from those usually observed in common 3D objects. The 1D physics is strongly influenced by quantum effects, defects, and fluctuations which are usually masked in standard 3D materials. For unraveling these effects, systems with chains (1D) of spins with $S = 1/2$ and antiferromagnetic couplings are the most favorable choice. The low-energy excitations were shown to be objects carrying a spin $S = 1/2$ and the spectrum of these Fermions, termed spinons, turns out to be gapless [63]. A rather unexpected theoretical result was Haldanes conjecture that the excitation spectrum of the same type of chains but with $S = 1$ ought to exhibit a gap [64]. Follow-up studies by Affleck and co-workers [65] demonstrated that the theoretical reasoning for explaining this difference is far from trivial. Later, a very fruitful development originated in interpreting the low-energy excitations of low-D spin systems as particles. To see this it is useful to note that in the considered spin systems, spin dimers with a singlet ground state and $S = 1$ excitations to a triplet excited state may form. Apart from regarding the above-mentioned spinons as Fermions, an analogy between these $S = 1$ excitations termed triplons and Bosons was established [66]. As a consequence, a Bose-Einstein condensation (BEC) of such excitations in the form of magnetic order was predicted to occur under the influence of an external magnetic field [67]. It also turned out that some of these systems are show cases for studying the properties of a Luttinger liquid [68].

First experiments for testing some of the theoretical predictions were made with TM bronzes and some organic compounds, both of which exhibit considerable anisotropies in electronic conduction. Early results are reviewed in [69]. Soon it was found that some of the low-D organic compounds exhibit a variety of ground states from insulating and magnetically ordered to metallic and superconducting; varying by applications of external pressure and/or magnetic field. An up-to-date review can be found in [70]. Later, the research interests began to focus on materials containing the mentioned weakly coupled low-D spin systems in an electrically insulating environment. The physics of these spin systems is often assumed to be captured by relatively simple Hamiltonians of the Heisenberg type; complications are to be expected from the unavoidable anisotropies and spin-orbit coupling. The interactions in each individual spin chain are based on the exchange phenomenon. Naturally, they depend on the bond strength and directions between the atomic sites. Therefore, they may be varied by applying external pressure and introducing selected defects. Likewise, the application of external magnetic fields which softens the above-mentioned triplon excitations is expected to induce phase transitions. This offers new opportunities for studies of the physical behavior of these systems if links between the theoretical concepts and really existing materials can be made. Many new compounds with spin-carrying cations (Cu, V, Ni) were synthesized. Based on first structural and magnetic characterisations, some of them were indeed identified to serve as model compounds for experimental tests under varying external conditions as outlined above. Both bulk and microscopic experimental probes, such as magnetization measurements as well as neutron-scattering and NMR techniques are being used to identify the magnetic properties of these systems. A good part of corresponding efforts and the achieved results up to 2003 are summarized in [71]. More recent results, mainly in connection with the BEC phenomenon in quantum magnets are presented and discussed in [72]. The model Hamiltonians offer a playground for analytical as well as numerical studies of the influence of correlations in solids; the current status of both these activities is documented in detail in two other, recently published volumes of this series [73, 74].

As mentioned at the beginning, the third volume of this series is devoted to reviewing current experimental methods and techniques that play an essential role in contemporary studies of correlation effects in solids. Below, brief summaries of the content of each chapter are given.

2 Nuclear Magnetic Resonance

As mentioned in the introduction, nuclear magnetic resonance (NMR) experiments were already employed in early studies of correlation effects in metals. A highlight was the experimental confirmation of the NMR-related coherence effect in superconductors as predicted by the BCS theory.

In the first section, Nicholas Curro covers the basic theoretical background of the method. It includes the density-matrix approach, the introduction of the concept of the rotating frame and Bloch's equations. The latter defines two important parameters representing the characteristic times of the decay of the transverse magnetization (T_2) and of the recovery of the longitudinal equilibrium magnetization (T_1). A section on pulse techniques explains the principles of the free induction decay and the spin-echo technique, including some practical technical details concerning the detection of the response signals and briefly recalling the role of spin-lattice relaxation.

Since many probed nuclei possess spins $I_n > 1/2$, quadrupolar effects due to the interaction between the nuclear quadrupole moments and the local electric potential at the site of the nucleus, complicate the response and hence the spectra. The corresponding section summarizes the essentials of these complications and the resulting spectra and their dependence on the angle between the magnetic field orientation and the principal axes of the crystalline lattice. The case where the external magnetic field is set to zero, i.e., the nuclear quadrupole resonance (NQR), is also briefly addressed.

The usually dominating interaction in correlated electron systems is the hyperfine coupling between the spins of the probed nuclei and the spins of electrons in the local environment. In metals the latter includes conduction electrons and localized electrons on ions occupying neighboring lattice sites; in insulators the so-called transferred hyperfine interaction couples to spins of localized electrons. These interactions lead to resonance shifts which are summarized under the term Knight shifts. While simple and usually temperature independent in simple metals, these shifts are more complex in cases where different hyperfine couplings contribute to the total shift or correlation effects influence the local susceptibilities. These interactions not only influence the position of the corresponding resonance but also affect the dynamics of the above-mentioned spin-lattice relaxation process.

The last section is devoted to a case study of field-induced magnetism in superconducting CeCoIn_5 , demonstrating the power of NMR-based methods in studies of the strongly correlated electron system in this compound. It is demonstrated that the available microscopic information may correct seemingly solid interpretations of data obtained from measurements of bulk thermal properties. The NMR data reveal a static antiferromagnetic order in the superconducting phase close to H_{c2} at $T \ll T_c$. Although coexistence of antiferromagnetic order and superconductivity has been observed before in several cases, the phenomenon in CeCoIn_5 is most likely of different nature and still awaits a sound theoretical interpretation.

3 Angle-Resolved Photoemission

Before the authors, Riccardo Comin and Andrea Damascelli, address the technical aspects of angle-resolved photoemission (ARPES) experiments, they offer an overview on correlation-dominated materials in the form of d-electron transition-

metal oxides (TMOs). In view of correlation effects the chosen classification scheme of these systems includes (i) Mott-Hubbard insulators, (ii) charge-transfer insulators and (iii) relativistic Mott insulators. As usual, this choice is based on the relative magnitudes of the on-site Coulomb repulsion U , the band width W and the spin-orbit interaction λ .

Angle-resolved photoelectron spectroscopy is the experimental dream tool for those interested in exploring the electronic structure of materials. Its application requires the availability of both intense photon sources which are provided by, e.g., electron synchrotrons, and detectors with sufficient energy and angular resolution for harvesting the escaping photoelectron as a function of their energy and momentum. A section of the chapter is devoted to discuss technical aspects of state-of-the-art photoemission with respect to both radiation sources and electron detectors and their current performance parameters. Also briefly addressed are specific aspects of the geometrical configuration of the incoming light beam and the detector in ARPES experiments.

Starting with the basics, the authors first explain the kinematics of photoemission and continue by summarizing the essentials of the three-step model and the sudden approximation which they use to model the photoemission process. As the interpretation of the collected photoelectron spectra requires solid theoretical guidelines, the authors discuss the routinely employed Green's function formalism to obtain the one-particle spectral function $A(\omega, k)$ which is directly probed by ARPES. For extracting quantitative information from the spectra, matrix element effects and the influence of the unavoidable limited resolutions and the extrinsic background have to be considered.

The discussion of rather generic aspects of photoemission experiments is followed by a longer section emphasizing the physics of correlations probed by ARPES. It starts with describing spectral functions of small many-body systems such as molecules, in this case H_2 . Considering solids, electron-phonon correlations and the corresponding quasiparticle, the polaron, are described first and illustrated with existing results. Naturally, the electronic structure of Cu oxides is a primary example for illustrating correlation effects in solids and corresponding work and results are summarized under the heading: doping controlled coherence. For temperature-controlled coherence manganese oxide (Mn-O) compounds are chosen as examples. A particular feature of the ARPES technique, namely to exploit the dependence of matrix elements that determine the spectral intensity on the light polarization, is exemplified in a discussion of relevant work on cobaltates where contributions of different electron bands to the spectra need to be unraveled. Further subsections deal with the influence of relativistic effects due to enhanced spin-orbit coupling in 4d and 5d electron TMO materials, including a novel type of insulating state due to correlations in an Ir oxide material, termed relativistic Mott insulator.

4 Spectroscopic Imaging Scanning-Tunneling Microscopy (SI-STM)

This chapter, co-authored by 8 contributors affiliated with various institutions, concentrates on efforts to visualize the electronic structure and its symmetry of a particular compound series of cuprate superconductors with scanning-tunneling microscopy in the spectroscopic imaging mode. First, a brief and rather general review of the low-temperature phase diagram and related electronic structures of hole-doped cuprate superconductors summarizes the principal features reported in the literature. The two distinct energy scales, Δ_0 and Δ_1 , related to two distinct phases, are introduced. While the first is clearly identified as being related to excitations across the gap that forms upon the onset of the superconducting state, the cause and significance of the second, characterizing the so-called pseudogap phase, is judged to be still rather obscure. The investigated system is based on the parent compound $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. The doping parameter δ is chosen such that the system is in the underdoped regime where both the superconducting and the pseudogap phase can be probed.

The technique is based on measuring the voltage dependence of the tunneling current $\partial I/\partial T$ as a function of the tunneling site and the energy of the tunneling electrons. The authors prefer to describe the theoretical background of the method rather than its technical realization. For the latter, they refer to information existing in the literature. Probably led by previous experience, some of the most serious and in practice often overlooked systematic errors that may occur in such investigations are described and some guidance of how to avoid or at least minimize them is given. The next section is devoted to describing how magnetic and nonmagnetic impurity atoms can serve as indicators for the pairing mechanism and/or symmetry in superconductors. It is pointed out that the corresponding spectra change appreciably upon varying the degree of doping. The doping itself introduces electronic disorder at the nanoscale. The influence of these defects on spectra, especially related to the pseudogap phase are discussed. Information on quasiparticle scattering can be obtained from Bogoliubov-quasiparticle interference imaging. In particular, the evolution of the electronic structure in k -space in the form of Fermi arcs with varying degree of doping can be studied. This type of experiments is believed to clarify whether the pseudogap phase may be regarded as a state of incoherent d-wave superconductivity. In the strongly underdoped regime, the experimental results reveal ungapped Fermi arcs, a gap of a phase-incoherent superconductor and local symmetry-breaking excitations that are the same in the superconducting and pseudogap regime. The final two sections deal with observing symmetry-broken electronic states in the pseudogap regime. The simultaneous observation of two different broken symmetries in the form of nematic and smectic fluctuations allows to study their interactions. In spite of all this new information on local details of the electronic structure, the relation between the pseudogap phase and the superconducting phase are admitted to be not yet understood. There is no doubt, however, that the two phenomena are linked in some way. This type of

studies also reveals a characteristic difference between the electronic structures in the under and overdoped regime, respectively. The question of what is causing this transition is also still unanswered.

5 Point-Contact Spectroscopy

Although physically and technically quite different, point-contact spectroscopy (PCS) has at least one similarity with the above-mentioned STM technique. Both methods basically involve a transfer of electronic quasiparticles from one electrode to another. As it is explained in the introduction of this chapter, PCS is an extension of early experiments which employed point contacts for locally studying electron trajectories in a metal which is exposed to an external magnetic field.

In this chapter, Guy Deutscher concentrates on the use of PCS between a sharply pointed normal electrode and a laterally extended superconducting electrode. In the introduction he emphasizes the pros and cons of the method with respect to electron-tunneling methods, including scanning-tunneling techniques. Concerning the physical realization of PC, its concept invented by Sharvin and the parameters that govern the electronic transport through such a contact are discussed. The dominating factor is the Sharvin resistance which depends on the lateral extension d of the contact and the electron mean-free path in the electrode. Although simple in concept, various sources of complications in real contacts have to be considered. These include scattering effects if the mean-free path is smaller or similar in length as the contact diameter, which may lead to a local heating of the contact. Similar heating effects due to exceeding critical velocities determined by parameters of the probed superconductor may falsify the observed properties. At any rate, the most reliable results using PCS are obtained at low temperatures. An important parameter is the effective transparency coefficient of the contact, crucial in the determination of the contact size. A short review of practical realizations of PCs is presented in the next section. The controlled fabrication of a contact of desired quality is still a major problem. In so-called break junctions, both electrodes are of the same material, thus eliminating the usually unknown mismatch of the Fermi velocities between both sides of the junction.

The interpretation of PCS data on conventional superconductors is usually based on the theory of Blonder, Tinkham and Klapwijk (BTK) and a short overview on this approach is given in the next section and various aspects that have to be considered in practice are discussed. Next it is explained how extensions of the BTK theory in connection with the phase sensitivity can be used to establish the order parameter symmetry, an important aspect in connection with studies of unconventional superconductors for which the gap configuration exhibits nodes.

The well-known quasiparticle reflection effects at the contact interface, in particular the Andreev-Saint James reflections under special circumstances, are the topic of the next section. In it, the importance of retardation effects which open the possibility to evaluate the effective masses of quasiparticles in metals with very

strong correlations, is emphasized. In order to demonstrate how this approach can be used in the fitting procedure of conductance data, typical examples of superconductors with different causes of mass enhancement are discussed in detail. These include Nb, MgB₂, high- T_c Copper-oxide, and Fe-pnictide superconductors as well as intermetallics with moderate and strong enhancements of the quasiparticles' masses. It is concluded that effective masses due to strong correlations established in this way are in very good agreement with values that have been obtained from data that were acquired with other experimental techniques. Quite remarkably, the method also allows for a relatively easy access to determine the electron-phonon mass enhancement in conventional superconductors.

A brief account on some PCS data obtained with contacts between an inhomogeneously magnetic material and a conventional superconductor is given in the short final section.

6 Quantum Oscillation Measurements

Studies of the electronic structure of metals via measurements employing the de Haas-van Alphen (dHvA) effect and other magneto-oscillatory techniques had their first high in the 1960s and early 1970s of the last century. With the growing interest in metals with strongly correlated electrons, the corresponding methods experienced a revival and new experimental data revealed detailed insights into the behavior of such systems which are not accessible by other means.

After describing some of the advantages but also limits of employing this type of probing the electronic structure in comparison with other experimental methods, Stephen Julian gives a brief but fairly complete account of the theoretical basis of the dHvA effect, starting from the Landau quantization and a derivation of the Onsager relation for a cylindrical Fermi surface (FS) which relates the frequencies of the observed quantum oscillations with, in this case only one, extremal cross-sections of the FS. What follows are descriptions of various aspects that have to be considered when interpreting the recorded data. First, the influence of temperature and scattering on the amplitude of the quantum oscillations is discussed. It is recalled that while band-structure calculations employing the local density approximation (LDA) are adequate to predict the topology of FS, they usually underestimate the correlation effects which, to a large extent, determine the effective masses of the electronic quasiparticles. Julian's discussion of the influence of many-body effects on the Landau levels is original and clear. The resulting amplitude damping factors due to nonzero temperature and quasiparticle scattering at impurities can be used to obtain information on the effective mass and the mean-free path of the quasiparticles. The spin damping factor arises from the magnetic field-induced splitting of the FS into a spin-up and a spin-down part. It turns out that probing these split parts in strongly correlated systems reveals different amplitudes for each part. This difference can be traced back to spin dependent effective masses reflecting the electron-electron interactions. Mapping 3D Fermi surfaces requires

measurements of the angular dependence of the oscillations by varying the angle between the crystal orientation with respect to the direction of the applied magnetic field. Julian's description of how this is done in principle, is followed by a brief presentation of the Lifshitz-Kosevitch equation which governs the oscillatory magnetisation of common metals. Julian ends this section with number of comments on how this basic equation needs to be modified if strong correlations have to be taken into account.

Very helpful for prospective users is the section in which it is explained how measurements of the dHvA effect can actually be done. It includes the description and possible realization of measurements involving either the field modulation technique or using torque magnetometry. Briefly mentioned are measurements of all the other physical properties that are affected by the Landau quantisation of the energy levels of the itinerant quasiparticles, and therefore exhibit magneto-oscillatory behaviour. The section ends with a comparison of DC- versus pulsed-field applications and a short discussion on the information that can be gained from a detailed analysis of the dHvA signals.

These preparatory parts are complemented with an extensive case study on the compound Sr_2RuO_4 whose electronic subsystem is clearly influenced by strong correlation effects and exhibits unconventional superconductivity. It is shown that the topology and size of the Fermi surface obtained from the dHvA data is in very good agreement with those predicted by band-structure calculations. It is pointed out, however, that the dHvA analysis provides much more details concerning the form of the different FS parts as well as, from the temperature dependence of the oscillation amplitudes, the effective masses and their anisotropies. Finally, it is shown how the parameters obtained from the dHvA investigations can be tested with respect to their compatibility with measured bulk properties. It turns out that the correct, often not straightforward, analyses of the data and their combination provide very satisfactory results in this respect. This confirms that experimental methods under the heading of this chapter are particularly well suited to enhance the understanding of correlation effects in metals.

7 Pressure Probes

External pressure, often relatively moderate in magnitude, has been shown to be one of the versatile control parameters for studies of physical properties of materials that are dominated by correlation effects. Many examples of pressure-induced quantum phase transitions (QPT) are described in the literature. It is therefore quite natural that one chapter in this series, authored by Michael Nicklas, is devoted to an overview of currently employed methods for pressure generation and of experimental techniques to perform measurements of different physical properties under impeding conditions, including very low temperatures.

Pressure generation is the first topic that is addressed. First, two types of pressure cells are considered and described in some detail; piston-cylinder type and opposed

anvil type. The performance of these cells with respect to achieved pressures depends on the choice of materials for the different components of the cells. In many cases, very low magnetic susceptibilities of the chosen materials are required, which usually limits their mechanical strength. With piston-cylinder cells, pressures of 3–4 GPa have been achieved. For higher pressures, anvil-type cells are required; the highest static pressures, up to 30 GPa are achieved with diamond anvils. Other forms of pressure cells, including the indenter-type configuration, and solutions for contacting samples inside the cell with electrical leads are briefly discussed at the end of the same section.

The distribution of pressure within the cell's sample volume, i.e., hydrostatic or anisotropic, depends on the choice of the pressure-transmitting medium. Once the pressure is generated, its value needs to be measured independently under the conditions of the primary measurement, often at low temperatures. These two aspects are discussed in a subsequent section.

Very informative is the next section where it is shown that a wealth of different physical properties can in principle be measured under external pressure, although often only with difficulties and by taking into account a number of complications. For obvious reasons, thermal properties, where measuring constant small temperature differences is an important part of the experiment, are notoriously difficult to determine with accuracies that are achieved under ambient conditions. Nevertheless, possible ways to resolve the experimental difficulties for measurements of thermal conductivity, thermopower, specific heat and thermal expansion are discussed. Equally difficult are experiments probing magnetostriction. More feasible are measurements where monitoring an induction signal with a simple coil is the essential part of the experiment. This is the case for measurements of magnetic susceptibilities, magnetizations and de Haas-van Alphen oscillations, as well as resonance experiments such as NMR and ESR. Also experiments involving particle beams at large facilities, such as muon spin rotation/resonance and neutron scattering are routinely done for probing samples under pressure. For optical experiments where access of visible light to and from the sample is required, the use of diamond anvil cells is inevitable.

The chapter ends with a presentation of examples where pressure tuning of metals with strong electron correlations leads to phase transitions of various kinds. Well documented are the examples of 122 Ce compounds such as CeCu_2Si_2 , CeCu_2Ge_2 and other CeTM_2Si_2 compounds as well as CeIn_3 . For all of them, antiferromagnetic and superconducting phases are the competing ground states. More recent are the observations of pressure-induced phase changes in compounds of the type CeTMIn_5 .

8 Neutron Scattering

As Igor Zaliznyak and John Tranquada point out, magnetic phenomena in solids are the result of correlation effects and different varieties of neutron-scattering techniques are the experimental tool of choice for investigating magnetic correlations in

condensed matter. In the introduction, they mention a few pros and cons for using these methods and they provide useful references to existing literature that cover the topic in more detail.

They continue with describing the basic properties of the neutron as a particle and briefly summarize the use of different energy scales for practical purposes. Using neutrons for scattering experiments of course requires that they are available in sufficient quantities and the authors offer a brief account on existing reactor-based and spallation-type neutron sources, including their performance characteristics.

Next they discuss the two fundamental scattering processes of neutrons in matter, namely the nuclear and the magnetic scattering which both are exploited in different scattering techniques. They then explain the notions of the scattering lengths and cross-sections relevant in neutron-scattering experiments. Subsequently, two subsections deal with nuclear scattering in more detail. The authors distinguish between nuclear scattering in condensed matter per se and in condensed matter in crystalline form. For the first case, they present the energy versus momentum dispersion curve of superfluid ^4He as a prime example of the usefulness of neutrons for studying elementary excitations in quantum-dominated systems. In the section on nuclear scattering in crystalline matter, aspects of experimentally establishing atomic order and the energy-momentum relations of lattice excitations are briefly discussed.

The context of correlations in solids the magnetic interactions of neutrons with magnetic moments due to electron's spins and orbital motion are of primary interest. First the authors stress the importance of the detailed-balance constraint and the fluctuation-dissipation theorem in interpreting corresponding neutron-scattering experiments. Static magnetization can be accessed by elastic neutron scattering while information on its motion may be obtained from inelastic scattering. The subsequent sections deal with magnetic Bragg peaks indicating magnetic order, the magnetic form factor and spin correlations, spin waves and anisotropy effects.

The content of the sections explaining the theoretical background for performing and analyzing neutron-scattering experiments prepare for a brief review of results on structural and magnetic properties of cuprate superconductors obtained by employing neutron-scattering techniques in the concluding section of the chapter.

9 Muon Spin Relaxation (μSR) Studies

In the first section of this chapter, Yasutomo Uemura briefly describes the particle-physics history of muons and their importance in the experimental verification of parity violation in weak interactions. He continues by explaining the very basic principles of $\mu^+\text{SR}$ experiments, based on implanting positively charged muons μ^+ into a specimen and monitoring the time evolution of their spin polarization via observing the ejection direction of the positrons that result from the decay of the muons. Also mentioned are the most versatile external-field configurations that are

employed for extracting different informations on the internal field distributions at the sites adopted by the muons at the time of their decay into positrons.

In the second section, the role of μ^+ SR in investigations of magnetic phase diagrams of unconventional superconductors is described. Examples of the interplay between magnetic order and superconductivity are presented for different families of superconductors, such as heavy-fermion and Cu–O compounds, organic materials, and fullerides as well as Fe-based chalcogenides.

Since μ^+ SR is a very sensitive probe for detecting small internal magnetic fields, it has been employed in searches for time-reversal-symmetry (TRS)-breaking phases in unconventional superconductors. Following the early cases of corresponding evidence in U-based heavy-fermion superconductors, other materials were investigated in this respect. The phenomenon of TRS has been reported to occur in the superconducting state of Sr_2RuO_4 and filled skutterudites. The corresponding evidence for TRS is much less convincing, however, in data obtained from studies of cuprate superconductors in the pseudogap regime.

Early experiments to determine the penetration depth λ of magnetic fields of cuprate superconductors were made by employing the μ SR technique. Section IV is a summary of such efforts to provide evidence for unconventional pairing in the superconducting state of cuprate superconductors by measuring the temperature dependence of λ and comparing it with corresponding theoretical predictions. Based on the fact that the value of λ at low temperatures is related to the pair density n_s , it was established that the critical temperature T_c of cuprate superconductors is, quite generally, controlled by n_s such that T_c varies linearly with n_s . Section V describes how from n_s , an effective Fermi energy in the excitation spectrum can be extracted and be compared with trends in the variation of T_c in cuprate- and other types of superconductors.

The following sections VI, VII, and VIII cover a wide range of efforts, not necessarily based on μ SR experiments, to establish correlations between different key parameters that might determine the critical temperature of superconductors. In particular, efforts to clarify the interrelation between antiferromagnetic order and superconductivity, often competing phases in unconventional superconductors, are described and illustrated. Phase boundaries and the physical properties in their vicinity are discussed. The last section is a brief outlook into the future with some ideas for future investigations of unconventional superconductors, including a comprehensive understanding of the driving mechanisms that induce these unusual condensates of charge carriers.

10 Optical Properties

This chapter, authored by Dirk van der Marel, offers a step-by-step introduction to the field of optical conductivity of correlated electrons. He focusses on the theoretical background for treating many-body effects influencing the optical