Chapter 1

Introduction

Between 1911 and 1986, superconductivity was strictly a low-temperature phenomenon. The highest critical temperature T_c for any superconductor was 23.2 K for Nb_3Ge. For any possible applications, the only useful refrigerants were liquid helium and liquid hydrogen. For much of this period, an understanding of the microscopic origin of superconductivity was lacking. Bardeen, Cooper, and Schrieffer published the BCS theory in 1957, and the more general Eliashberg theory soon followed. Theoretical predictions of the highest T_c one could hope for were not very useful for finding new materials with T_c above 23.2 K. In 1986, Bednorz and Müller discovered that La_2CuO_4 went superconducting when Ba substituted for some of the La. Later doping studies with Ca, Sr, and Ba showed that in this system T_c reached 38 K. Soon thereafter, Wu *et al.* found that suitably doped $YBa_2Cu_3O_7$ had a T_c of 92 K, well above the boiling point of liquid nitrogen. In the intervening years several other classes of high-temperature superconductors were found. All of these had several properties in common. All contained one or more planes of Cu and O atoms per unit cell, all had structures which were related to the cubic perovskite structure, and all were related to a "parent compound" which was antiferromagnetic and insulating. Doping this parent compound (in one of several ways) produced a metal which was superconducting and, for some optimum doping, T_c could be very high, usually above the boiling point of liquid nitrogen. For some doping ranges the material exhibited semiconducting behavior in the normal state, but was still superconducting at lower temperatures. Considering various doping schemes, over 300 cuprates have been studied in some fashion. Fewer than this have been

studied by any type of photoelectron spectroscopy, and only a handful to date have proven amenable to study by angle-resolved photemission.

After the discovery of the cuprate superconductors, two other classes of materials were discovered which would have attracted great attention as high-temperature superconductors were it not for the previous existence of the cuprate-based materials. $BaBiO_3$ is a perovskite-structured insulator. Obviously it contains no Cu and it is not magnetic. It also contains no two-dimensional planes of Ba or Bi and O atoms. It can be doped to produce a metal, and an optimum doping results in T_c values higher than that of Nb_3Ge. $Ba_{1-x}K_xBiO_3$ has a peak T_c of 30 K for $x = 0.4$. The fullerene or buckyball molecule, C_{60}, forms an insulating crystal with several crystal structures. C_{60} can be intercalated with alkali metals, e.g., K. At a composition of K_3C_{60} the material is metallic with a minimum in resistivity as a function of the C : K ratio, and this metal is superconducting. The highest T_c achieved to date is 33 K using two alkali metals to make Cs_2RbC_{60}.

In order to understand superconductivity at a microscopic level in a given material one needs an understanding of the electronic structure of the material, a microscopic mechanism for the coupling of electrons into pairs, and a scheme for forming a coherent condensate from a large number of such pairs. The BCS theory with extensions by Eliashberg and Bogoliubov provided the last of these. The BCS model used the electron–phonon interaction to form the Cooper pairs. The electronic structure was assumed to be simple, that of a gas of Landau quasi-particles, with no band structure effects. Thus in this model all metals should become superconducting at some, possibly very low, temperature. The electronic band structure and the actual phonon spectra were introduced later, but finding increases in T_c by examining electronic structures and phonon spectra to select new materials is far from a science. There were no predictions of a high T_c for a cuprate. Recently Emery and Kivelson reintroduced a picture in which T_c is limited not by the breaking of quasiparticle pairs, but by the loss of long-range phase order. Pairs may then exist above T_c. They suggested this picture is most likely to be valid for underdoped cuprates which are superconductors with very low superfluid densities. Although there were a number of results from several types of experiment on $YBa_2Cu_3O_{7-x}$ that could be explained by the occurrence of a pseudogap, such a pseudogap, presumably the same one, was found in recent photoemission studies of $Bi_2Sr_2CaCu_2O_{8-x}$. Since this pseudogap closely resembled in magnitude and symmetry the gap found in the superconducting phase, it may be attributed to pair formation above T_c.

At the time of this writing the data base of the *High-T_c Update* newsletter at the Ames Laboratory has over 60 500 entries. There are at least two journals whose entire contents are devoted to superconductivity, mostly in cuprates in the past few years, *Journal of Superconductivity* and *Physica C*. The mechanism

for superconductivity in the cuprates is still not known, or if one of the several mechanisms already proposed is correct, it is not yet widely accepted as correct. It is not yet known how best to describe the normal state of the cuprates. Are they Fermi liquids or not, and if not, how are they different? Should we approach the electronic structure of the normal state with conventional band theory, modified to take better account of correlation effects or is a highly correlated many-body model a better, or even necessary, starting point? What is the excitation spectrum in the superconducting state? Is there evidence for pairing above T_c? Can cuprate superconductivity be described by the BCS model with phonon coupling or some other coupling mechanism giving the Cooper pairs? What is the symmetry of the pairs? What is so special about Cu and O? Is the correct model for cuprate superconductivity the same for electron doping as for hole doping? Does superconductivity in doped $BaBiO_3$ have any connection with superconductivity in the cuprates? What is the role of the newly discovered stripe phases? Photoelectron spectroscopy can address these questions and provide insight which can aid in answering them, but it rarely gives a direct answer. It is an excited-state spectroscopy, and the connection between the observed spectrum and the ground-state properties is usually not a direct one, especially when the non-interacting- or independent-electron model is not accurate. Even for simple metals like Na, photoelectron spectra show departures from predictions of the independent-particle model. Often the reasons for such departures are known and spectra that agree with experiment can be calculated. Comparable understanding of the photoelectron spectra of high-T_c superconductors is still lacking.

Photoelectron spectroscopy (often called photoemission spectroscopy, although the photon is not emitted) has been employed increasingly since about 1970 to obtain electronic structure information. In the most common experimental setup a beam of monochromatic radiation illuminates the surface of a sample in vacuum and the kinetic energy spectrum of the emitted electrons is measured. The electrons analyzed may be most of those emitted (angle-integrated mode) or only those in a small solid angle that may be varied (angle-resolved mode). Using ultraviolet or soft x-ray photons, angle-integrated photoelectron spectra bear a resemblance to a density of states, and by varying the photon energy some information about the nature of the electronic wave functions can be gained. If the analysis of the photoelectron kinetic energies is done with angle resolution as well, and the sample is a single crystal, electron momentum information becomes available and one can map the energy bands. One result of this type of study is an experimental Fermi surface. With soft x-ray photons one can also excite core levels. Their binding energies, line shapes, and the occurrence of satellite lines give information on local bonding. All these spectroscopies have given considerable detailed information on a wide variety of materials. However, this information is not obtained readily. Because all the electrons in a

solid may respond to the photohole, the spectrum may deviate from that expected from a one-electron model, e.g., band structure, by a small or large amount. A well-known example is the photoelectron spectrum of the 4f electrons in Ce. There is approximately one 4f electron per atom in Ce metal, but the photoelectron spectrum has two peaks reliably associated with the 4f initial state. A rather elaborate many-electron model is needed to understand this result, but with it one learns a great deal about the ground state of Ce metal. Similar, but less obvious, problems arise with so-called band mapping.

Naturally, in the early days of the cuprate superconductors many scientists with photoelectron spectrometers made measurements on the best samples of the time. These were sintered ceramics containing many small crystallites of the desired material, and perhaps small amounts of another phase or of unreacted starting materials. X-ray diffraction was used to select samples that were primarily of one phase. Fresh surfaces were obtained by fracturing or scraping *in situ*. Early efforts were centered on questions of Cu valence and on which atoms the holes produced by doping resided. Data were sample dependent, and rarely did the spectra show the Fermi edge characteristic of a metal, even though the samples exhibited bulk metallic conductivity and were superconducting upon cooling. The fracture may have taken place on grain boundaries where a minority phase may have precipitated, and the spectra may have been dominated by this minority phase. The fresh surfaces may have reacted with molecules in the ambient, or impurity atoms may have diffused from the bulk so rapidly that they reached equilibrium before photoelectron spectroscopic studies of surface stability were begun. A common problem in the early data was the occurrence of a satellite peak around 8–12 eV in the valence-band spectra, a peak now known not to be intrinsic to clean surfaces of those high-T_c materials frequently studied.

As single crystals became available in sizes suitable for ultraviolet and soft x-ray photoelectron spectroscopy, the quality of the data improved rapidly. Samples freshly cleaved in ultrahigh vacuum at low temperature were stable for many hours at low temperature. The photoelectron spectra showed the expected Fermi edge, and angle-resolved photoemission mapped a few bands, including the important ones near the Fermi level. Improvements in instrumental resolution and in crystal quality led to much more informative data, especially on $Bi_2Sr_2CaCu_2O_8$ and, to a lesser extent, on $YBa_2Cu_3O_7$. In the former, the Fermi surface was mapped, bands just below it were mapped, photohole lifetimes were determined, although at energies too far below the Fermi energy to allow theoretical work to be applicable, and the opening of a gap below T_c was observed. The anisotropy of the gap in the basal plane was revealed later when yet better crystals became available. The effects of electron doping on the electronic structure were also studied in Nd_2CuO_4.

The superconducting gap or order parameter in cuprate superconductors is about 25 meV or less, depending on crystallographic direction. It was measured by photoemission spectroscopy using photons with an energy of about 20 eV, which eject photoelectrons of about 15 eV kinetic energy. In the first such measurement the photon bandpass was about 20 meV and the electron energy analyzer resolution also 20 meV. Additional energy broadening can be introduced by the combined effect of band dispersion and finite angle resolution. Neglecting the latter, the overall resolution was about 28 meV, so the accuracy of the gap measurement was not very great. It was first determined from the difference in two spectral edges about 20 meV apart, each measured with 28 meV resolution. Normally one would try to measure a 20 meV excitation using a probe with an energy of the order of 20 meV, i.e., by an infrared absorption or reflection measurement, or a tunneling study. Low-energy electron energy-loss spectroscopy and Raman spectroscopy would also be promising because of the high resolution in such experiments, although the probing particle is more energetic. Such measurements were, in fact, carried out, both on early samples and crystals of increasing quality. The infrared measurements showed a number of gap-like features, but continuing work has cast doubt on the early interpretation, and it not clear yet that gap information can be extracted. The early tunneling and electron energy-loss spectra similarly were controversial. The photoelectron studies on $Bi_2Sr_2CaCu_2O_8$ in 1989–90 gave the first widely accepted data on the electronic structure of a high-T_c material. At the time of this writing, there are comparable data only on one other family of high-T_c materials, $YBa_2Cu_3O_7$, but a gap in the superconducting phase was not measured reliably by photoelectron spectroscopy for many years. Recent (1997) results from two groups show the presence of a gap and suggest its symmetry. Crystals, or at least the cleaved surfaces of crystals, of Tl- and Hg-based high-T_c cuprates are not yet of good enough quality to have yielded useful photoelectron spectra.

One of the results of the application of photoelectron spectroscopy to the cuprates is that we have learned that we may not yet know how to interpret such spectra. Insulators or large-band-gap semiconductors had not been studied much, partly because of the effects of surface charging during the measurements and partly because metals and semiconductors simply attracted more interest. Thus the role of correlation effects on the spectra, especially valence-band spectra, were not sufficiently studied. Since the surge of interest in the cuprates began, other oxides have become important to study, in particular, the manganates. These oxides resemble the cuprates in many ways. Although they are not superconducting, they exhibit very large magnetoresistance effects, the so-called "giant" and colossal" magnetoresistance.

Photoelectron spectroscopy can yield information useful in technology as well as fundamental electronic structure information. The loss of oxygen to the

vacuum and its recovery from overlayers, the reactions with adsorbed water vapor and with overlayers of metals, potentially useful as electrical contacts, have been studied. Multilayer films containing alternate layers of high T_c-superconductors have been produced and the interfaces studied by photoelectron spectroscopy.

In the following chapters, we describe photoelectron spectroscopy and its instrumentation, and results from studies on high-T_c superconductors, preceded by some examples of photoelectron spectroscopy on some simpler systems. Photoelectron spectroscopy is described in considerable detail, for in trying to gain a better understanding of the electronic structure of high-T_c superconductors by photoelectron spectroscopy it is important to know what approximations are being made in its interpretation and what aspects of the interpretation of spectra are controversial or even inadequately studied. An example of the latter is the background of "inelastically scattered" electrons. We begin the description of photoemission with the three-step model which is known not to be suitable in most cases. We do this because it is a way to introduce many concepts that are themselves of considerable validity. An example is the treatment of inelastic scattering. We follow this with a description of the correct one-step model. Although it is correct, it is difficult to apply in many cases without approximations. For example, it should be used to calculate the inelastic scattering effects in the photoelectron spectrum, but this is often done in an approximate or empirical way, taking ideas from the three-step model. The chapter on photoemission is not intended to give compete coverage of the subject, for we include only techniques and phenomena that have been used on high-temperature superconductors, omitting any discussion of gas-phase photoemission, adsorbates, overlayers, and several other topics. We discuss instrumentation primarily as it impacts on issues of resolution and other limitations on the spectra. It is important to know why improvements in instrumentation are not easy to achieve. Since it makes little sense to study the results of photoelectron spectroscopy in isolation, we describe briefly several other related electron and photon spectroscopies that give similar or complementary information, although the discussion will be in less detail than that for photoelectron spectroscopy.

Before discussing the photoelectron spectroscopy of high-temperature superconductors we describe our current understanding of the photoelectron spectroscopy and the electronic structure of some simpler materials: Na, Cu, Ni, NiO, Cu_2O, and CuO. NiO and CuO are not really simple, but they bear some resemblance to cuprates. Our understanding of the differences between the measured photoelectron spectra and those expected on the basis of the independent-electron model are quite well understood for these materials, while they are not yet as well understood for the cuprates. We precede all these with a survey of the properties of the high-T_c superconductors that are relevant for photoemission

studies. These include the crystal structure and the calculated electronic structures, but almost none of the other physical properties, for which many reviews exist. The central part of the book, Chapters 6–9, is an exposition of the studies of the electronic structure of the two classes of high-T_c materials mentioned above as the only ones for which adequate single crystals have been available. There has been much more work here than one might at first think, for there have been numerous studies of the effects of doping on the electronic structure, as well as the changes seen in cooling below T_c. Moreover, within one class there are several compounds with different numbers of CuO_2 planes per unit cell. Our emphasis is on valence-band studies carried out by angle-resolved photoelectron spectroscopy, but we also discuss less exhaustively the results from core-level spectroscopy. Connections are made with the results of other spectroscopies.

There has been an enormous amount of theoretical work on cuprates, ranging from discussions of speculative ideas to extensive numerical calculations. There is not yet widespread agreement on the type of normal state that exists in the cuprates nor on the pairing mechanism. Any theoretical model must account for the photoelectron spectra as well as experimental results by many other techniques. Disagreement with photoelectron spectra may not mean the model is wrong, for it may well be that we still have things to learn about how to interpret photoelectron spectra in systems in which correlation is important. We mention a number of theoretical papers, but have made no attempt to compare systematically photoelectron spectra from cuprates with several of the microscopic models for which such spectra have been calculated. Nearly all published calculated spectra bear some resemblance to experimental spectra!

Except in this introduction, we have tried to give many references to the literature. However, despite searches of data bases and old-fashioned library searches, we are sure to have missed a number of papers on photoelectron spectroscopy of high-T_c materials. We certainly have missed a number of papers on x-ray induced photoelectron spectroscopy (XPS) on cuprates. We deliberately omitted a number of papers published before 1990, admittedly an arbitrarary date. Many of these papers reported results on polycrystalline samples of unknown or demonstrably poor quality. Although some of the results in these papers may be useful, it is not easy to know which results are comparable with those found on better samples.

A very large number of papers has appeared in conference proceedings. These papers can be found readily in literature searches when the proceedings are published as special issues of journals, but not when they appear as books. Some published conference papers appear again in a journal, not always in an expanded form, and we may not reference both. We have not tried to carry out a thorough referencing of all work on areas not central to this book, e.g., crystal structures

or all of the photoelectron spectroscopy ever carried out on one of our examples, Cu. Instead we content ourselves with a few references to provide an entry to the literature. In the two chapters dealing with photoemission theory and experimental techniques, we have given many references to original papers and reviews, but we have not attempted to be encyclopedic, nor have we traced references back to find the first publication on a particular topic. General references on superconductivity are Tinkham (1996), Kuper (1968), de Gennes (1966), Rose-Innes and Rhoderick (1969), Poole *et al.* (1995), Waldram (1996), and Schrieffer (1964), while general references on the cuprates are books by Burns (1992), Cyrot and Pavuna (1992), Lynn (1990), Plakida (1995), a review by Brenig (1995), and a series of books of reviews edited by Ginsberg (1989, 1990, 1992, 1994, 1996). There are also many conference proceedings in book form or as special issues of journals. In addition, there are the journals devoted to superconductivity, e.g., *Physica C* and the *Journal of Superconductivity*. The majority of the papers in them deal with cuprates.

Chapter 2

Structure and electronic structure of cuprates

Photoemission studies generally give information on the electronic structure of a material, not the geometrical structure, although some surface structural information can be obtained by photoelectron spectroscopy. Knowledge of the crystal structures of the high-T_c materials is important in photoemission studies in several ways. First, crystal structures are required to determine the crystal potential for the calculation of the electronic structures. Even if a simple model of the crystal is being used, as in cluster calculations, the model should resemble part of the full crystal structure. Second, angle-resolved photoemission provides information in reciprocal space: energies as a function of angle or wave vector. The Bravais lattice of the crystal determines the Brillouin zone, hence the "space" in which theory and experiment often are compared. Third, the amount and nature of the anisotropy of the crystal structure, although difficult to quantify, are helpful in determining the anisotropy one might expect in physical properties, including photoelectron spectra. Orienting single crystals for angle-resolved photoemission studies also requires some structural knowledge. Fourth, there is an important experimental consideration. Most photoelectron spectroscopy is carried out on clean surfaces produced by cleaving in ultrahigh vacuum. It often is crucial to know what the cleavage surface is. Core-level photoelectron spectroscopy can help identify the atomic character of a cleaved surface, but knowledge of the crystal structure is needed and some idea of interplanar bonding is helpful. Fortunately, a structure determination is usually one of the first studies made on any new material. In the case of the cuprates, however, this has not been straightforward. Not only are the structures sensitive to composition, but as

time has passed, increasingly subtle modifications of previously determined structures have been found.

All the cuprates to be discussed have sheets of Cu and O atoms in the ratio of 1:2 in a square, or nearly square, array (Fig. 2.1). The sheets are either planar or slightly puckered. Such sheets may be separated from each other by several sheets containing atoms of oxygen and another metal, or there may be n CuO_2 sheets adjacent to each other, these n sheets being separated from the nearest pair of n similar sheets by several of the layers of metal and oxygen atoms. Some of the high-T_c cuprates have one or more chains of Cu and O atoms in the ratio 1:1 running parallel to one axis of the squares of the CuO_2 planes. This is shown schematically in Fig. 2.2.

In Section 2.1 we consider in some detail the crystal structures of the two "families" of high-T_c materials on which photoelectron studies of the valence band have been successful. There have been extensive studies of the crystal struc-

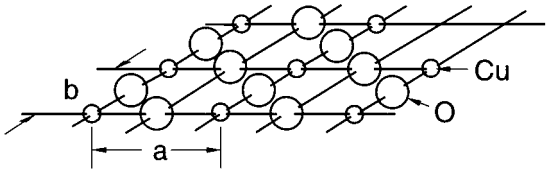

Fig. 2.1 Schematic CuO_2 plane. (Burns, 1992)

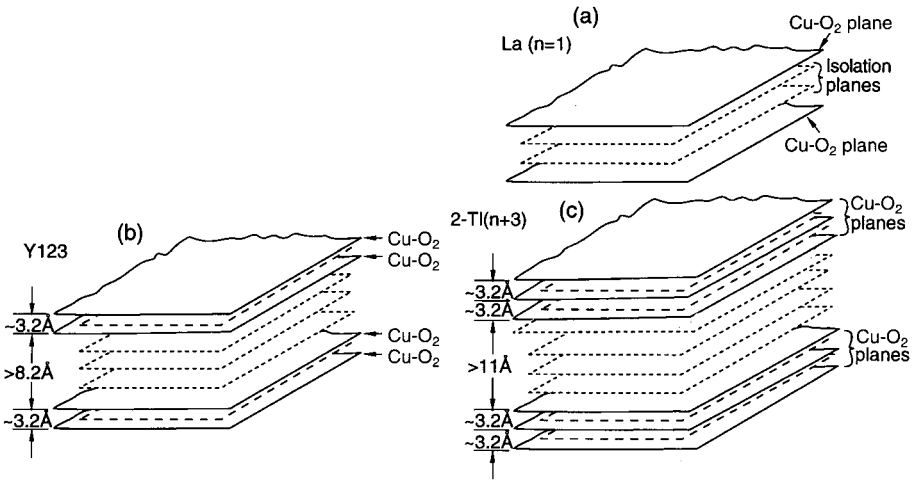

Fig. 2.2 Schematic stacking of CuO_2 planes (solid) with planes of other atoms, isolation planes (short dashes) separating them. (a) Single CuO_2 planes as in La_2CuO_4. (b) "Double" CuO_2 planes as in $YBa_2Cu_3O_7$. (There is an Y plane in between the pair, shown by longer dashes.) (c) "Triple" CuO_2 planes as in $Tl_2Ba_2Ca_2Cu_3O_{10}$. (There is a Ca plane in between each CuO_2 plane, shown by longer dashes.) (Burns, 1992)