Summary

Many of the physical and chemical properties of solids and solid surfaces are determined by the behaviour of the outer electrons of the constituent atoms. Electrical conductivity, magnetism, optical properties and chemical reactivity are a few examples for which the valence and conduction electrons play a crucial role. One of the most fascinating class of solids is that of transition metals and their compounds. While these elements are classified into the same group in the periodic table, they and their compounds show a quite wide variety of properties. Sometimes the properties could be quite contradictory. To mention the most spectacular: CuO in an antiferromagnetic insulator, while CuO based perovskites like La_{1.85}Sr_{0.15}CuO_4, YBa_2Cu_3O_7 and Bi_2CaSr_2Cu_2O_8 are superconductors with exceptionally high critical temperatures. Many transition metals and their compounds are active as heterogeneous catalysts for various chemical reactions, indicating the existence on surfaces of various intricate forms of bonding with intermediate species in the reactions. Also in many biological systems, transition metals and their complexes are indispensable. Understanding of the variety of these properties has to start with some understanding of the electronic structure of these materials. A combined experimental and theoretical study of this structure will be required.

The electronic structure of various forms of bonding between oxygen and the noble metals copper and silver are studied in this thesis. In terms of material choice, CuO, Cu_2O and also oxygen adsorbed on the Cu(110) surface are of direct interest as models for the high-T_c copper oxide superconductors. Ag_2O is useful in studying the possible substitution of copper by silver in these high T_c's and the recently claimed superconductivity of silver oxide perovskites. Ag_2O and oxygen adsorbed on the Ag(110) surface serve also as model systems for epoxidation processes catalyzed by silver.

From a more fundamental point of view, the material choice could provide more insight in the influence of electron-electron correlation on the electronic structure of transition metal compounds. It is known that in going from the left to the right in the periodic table, the intra-atomic Coulomb interaction increases and, in the 3d transition
whether or not $d-d$ correlation effects will show up in the electronic structure of Cu compounds can now be studied as a function of filling of the Cu 3$d$ band. In a full band system like Cu$_2$O ($\text{Cu}^+, d^{10}$) one would expect band-structure theory to work. For CuO on the other hand, where the 3$d$ shell is open ($\text{Cu}^{2+}, d^9$), one might expect correlation effects to occur and a consequent breakdown of the band-structure theory because it is based on a one-electron approximation. A further reduction of the bandfilling leads into the class of high $T_c$ copper oxide superconductors, where now interesting questions arise concerning the character of the holes, the low lying excitations and the quasi particles. In a sense, going from Cu$_2$O to CuO and to the high $T_c$'s can be considered as performing various degrees of hole doping. Going on the other hand to a metal-adsorbate system like the oxygen covered Cu(110) surface, where Cu-O chains are formed, one would expect to increase the Cu 3$d$ bandfilling with respect to Cu$_2$O, thereby validating more firmly the application of a one-electron theory.

In changing from Cu-O compounds to analogous Ag-O compounds, one reduces the $d-d$ Coulomb interaction $U$, thereby keeping the formal chemical valency the same and increasing the on-site d binding energy slightly. The interesting point shows up now that the full band systems Ag$_2$O and Ag(110)-p2x1-O have the same crystal or surface structures as Cu$_2$O and Cu(110)-p2x1-O respectively, whereas the system with reduced bandfilling, AgO, has a quite different crystal structure and magnetic properties than CuO. Does the large difference in correlation energy, which is only effective if the $d$ shell is open, plays a decisive role?

The relationship between the various types of Cu-O and Ag-O compounds is illustrated in figure 1.6 on page 15.

The question now arises how to describe the electronic structure of these solids and solid surfaces. Can ab-initio band-structure calculations provide reliable results? If not, what types of model Hamiltonians are to be used? Can one suffice to use one type of model Hamiltonian, where the differences in the electronic structure for the Cu(110)-p2x1-O, Cu$_2$O, CuO and high-$T_c$ copper oxide systems are reflected only in differences in bandfilling and/or in translational symmetry. To be more specific, to what extent are the one-particle and two-particle parameters in the model Hamiltonian transferable from one system to the other? The same questions also apply for the Ag-O compounds. In addition, what is the relationship between surface geometric structure and surface electronic structure for Cu(110)-p2x1-O and Ag(110)-p2x1-O?

In chapter 2, 3 and 4 the electronic structure of Cu$_2$O and CuO are studied and compared in view of electron correlation effects and high-$T_c$ superconductivity. The differences as revealed by various forms of electron spectroscopies are interpreted in terms.
of differences in the Cu 3d bandfilling. It is demonstrated that the results for Cu$_2$O agree well with band theory, whereas those for CuO show strong deviations due to correlation effects. From a comparison between cluster model calculations and photoemission (one-electron removal) experiments on CuO and Auger (two-electron removal) experiments on Cu$_2$O, consistent estimates can be made for the magnitude of one-particle and two-particle parameters in model Hamiltonians often used in describing the electronic structure of the high T$_c$'s. It is shown that CuO and the insulating high T$_c$'s are charge transfer insulators, for which the first ionization states have a localized singlet character. It is also found that the interatomic copper-oxygen Coulomb interaction $U_{pd}$ is smaller than approximately 1.5 eV, thereby suggesting that theories concerning paring mechanisms in high T$_c$ superconductivity, which rely $U_{pd}$ of 3 eV or more, are questionable.

In chapter 5 the electronic structure of Ag$_2$O is investigated using a combination of model calculations and electron spectroscopy experiments. An oxygen-radical source is developed in order to make well defined Ag$_2$O under ultra-high vacuum compatible conditions. The electronic structure of Ag$_2$O and Cu$_2$O are compared in view of high T$_c$ superconductivity and in view of the differences in stability and in presence of local moments between AgO and CuO. Substitution of copper by silver in the CuO$_2$ planes in the insulating high T$_c$ copper oxide superconductors will result in substitution of Cu$^{2+}$ by Ag$^+$ together with hole doping in the oxygen band. The study on Ag$_2$O also reveals that the existence of sub-surface oxygen in and on silver surfaces in catalytic epoxidation processes is possible but should not be accompanied with valence band photoemission spectra showing structure between 8 and 13 eV binding energies.

In chapter 6 and 7 a method is developed for calculating the electronic structure of clean and adsorbate covered metal surfaces. The relationship between the surface electronic structure and surface geometric structure is investigated. In chapter 6 the clean and oxygen covered Cu(110) surface is studied to check the method. From a comparison between the calculated valence and conduction bands with the measured angle-resolved photoemission and inverse photoemission spectra it is suggested that the observed p2x1 superstructure for the oxygen adsorption on the copper surface is due to a buckled-row reconstruction and not due to a missing-row reconstruction. The in photoemission “missing” band of Cu 3d anti-bonding character has been found, thereby establishing that correlation effects in the electronic structure of the Cu-O chains are negligible. In addition, the detailed information about the copper-oxygen bonds in terms of one-particle parameters are consistent with those found in Cu$_2$O and CuO, which is of importance for the high T$_c$'s. In chapter 7 the clean and oxygen covered Ag(110)
surface is studied by angle resolved photoemission, in view of the role of oxygen atoms in and on the silver surface in epoxidation reactions like those of ethylene and methanol. Calculations are performed in order to explain the spectra and to make suggestions for the possible p2x1 surface reconstructions.

Chapter 8 and 9 have a more experimental character. In chapter 8 the electronic structure of MgO is studied using angle-resolved ultraviolet photoelectron spectroscopy. A floodgun is developed in managing the usually catastrophic charging effects when measuring large bandgap insulators. MgO might serve as comparison material for other rocksalt transition metal oxides for which the angle-resolved spectra are complicated to interpret due to correlation effects. MgO is also useful for future research on the electronic structure of transition metal and transition metal oxide overlayers. The experimental results are in accordance with ab-initio bandstructure calculations. Chapter 9 finally, deals with the propagation of high energy electrons in solids. The anisotropy of inelastic scattering processes as suggested from this study might be of importance for the analysis of forward scattering and electron diffraction phenomena observed in angle-resolved X-ray photoemission and Auger electron experiments.