Photoelectron spectroscopy, new angle-resolved spectrometer and study of dilute alloys

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CHAPTER I

INTRODUCTION AND SCOPE

1. INTRODUCTION

This thesis is devoted to the photoelectron spectroscopy of solids and their surfaces. As in many spectroscopic techniques it involves the use of particles to probe the properties of matter. In a typical arrangement, under ultra-high vacuum conditions photons of well-defined energy, polarization and direction impinge on a sample. As a result of the impact, electrons (or photons) escape from the sample and can be analyzed according to their energy, direction and polarization and afterwards detected. Although the photoelectric effect already was discovered in the last century, it took until the late 1950's before it became appreciated as a technique for inferring the electronic structure of solids. In this application two distinct fields can be observed, the study of the valence electrons with low photon energies (UPS) and that of the inner core levels of the atom, the latter using high energy (~1000 eV) radiation (XPS).

Mainly through the work of Spicer et al. (1962) on silicon it was realized that the photoemission spectrum could be correlated with the band structure. And in the next step considerable effort was spent to distinguish between electronic transitions in which the electron wavevector $k$ is conserved (vertical or direct transitions) and those in which this is not the case (non-direct transitions). This controversy has remained until now in the interpretation of the spectra, although it has been realized that this is intimately related to the nature of the photoemission process itself, being a surface phenomenon.

On studying the valence band, in the early work the photon energy was limited at about 6 eV, but has later been extended to 12 eV using a hydrogen lamp separated by a LiF window from the vacuum chamber. With the rise of synchrotrons a wide spectrum of photon energies became available, although not for every ordinal mortal. The use however of rare gas resonance lamps,
possibly together with polarizers, has given the ordinary electron spectroscopist up to now relatively uncomplicated working conditions.

In a parallel development, it appears worthwhile to improve the energy resolution of the analyzers. Electrostatic deflection analyzers are now commonly used in the field, which offer in the lower energy range (≤ 1500 eV) good resolution and transmission and can easily be shielded from stray magnetic fields. The most preferred types are the cylindrical mirror and the hemispherical analyzer. Beside the energy resolution also the angular resolution proves to be important, as this offers the possibility of determining the electron wave vector k outside the solid which, together with the electron binding energy, provides the basis of determining the dispersion relation E(k). This was originally proposed by Kane (1964) and demonstrated by Gobeli et al. (1964). Angle-resolved photoemission now has become a major field in the area of photoelectron spectroscopy, not only for investigating the band structure of solids but also in the study of surface atoms and molecules. As a final parameter recently also the spin of the photoelectron becomes involved (spin-polarized photoemission), as was first demonstrated by Busch et al. (1971). This appears to be an important direction in the study of magnetic materials.

As photoelectron spectroscopy is bound to the surface region of the solid because of the small mean free path (< 50 Å) of the escaping electrons, it is in particular a surface sensitive technique. This aspect should be viewed as an advantage, as it offers the possibility of studying the specific phenomena related to the surface. One could think, for instance, of surface states and surface magnetism, surface segregation and reconstruction, and the study of surface layers and adsorbates. It should be mentioned that photoelectron spectroscopy does not stand alone in the study of bulk and surface properties. Also other techniques, which are often related, have shown to give important information like Auger spectroscopy, (surface) extended X-ray absorption fine-structure spectroscopy, electron loss spectroscopy, low electron energy diffraction, thermal (photon or electron) stimulated desorption spectroscopy, ion scattering spectroscopy, and recently, inverse photoemission (electrons in, photons out). All in all, from this a new branch of surface science has developed.

The core level spectra as obtained with X-ray excitation have been
extensively used for chemical analysis. This application is originally worked out by Siegbahn and coworkers (1965). More recently the technique is shown to offer in addition valuable information about the valence bands of transition metals and their compounds. Although UPS can give more direct information about the valence electrons because of a better energy and angular resolution, the interpretation of the spectra in terms of the occupation of the valence bands is often hampered because the band shape is difficult to describe. Moreover the existence of fairly large Coulomb repulsions invalidates an interpretation which proceeds in the one-electron approximation, as is often done. This is not a problem if the valence band is initially completely filled, like in Cu or CuCl, since then the final states reached in a photoelectron experiment can be described with one-hole states which do not involve the Coulomb repulsions, and one expects a good correspondence between the results of the one-electron theory and the spectra. If on the contrary the initial state already contains holes, the final state should be described in a many-hole picture which involves the hole-hole repulsions. In Ni for instance the initial state consists mainly of atomic $d^{10}$ and $d^9$ states, and photoemission from the valence band will end up in $d^9$ and $d^8$ states, and in energy, the $d^9$ final states are separated by the effective Coulomb repulsion $U$ plus the one-electron binding energy from the $d^9$ final states. As this energy splitting is of the order of the $d^9$ band width, it is clear that a distinction between the $d^9$ and $d^8$ final states in the spectrum is impossible and one expects the one-electron picture to fail to reproduce the experimental spectrum. A nice example of this is found in the study of the valence band of Ni and Cu. The angle-resolved photoemission spectra from Cu correlate quite well with the one-electron theory, however for Ni this is not the case. Improved band structure calculations including correlation are shown to give good correspondence. Information about the effect of correlation on the valence band occupation is, indirectly, given in an XPS experiment. It is noted that the correlation energy can be obtained from a combination of XPS and Auger spectroscopy (Antonides 1977). Upon core ionization the effective nuclear charge is increased, which increases the binding energies of the valence electrons by the attractive core hole-valence electron Coulomb interaction $q$. For instance, for a Ni atom the creation of a Cu impurity atom, results in a threshold line with $d^{10}$ configuration. But by the sudden switching on of the core hole potential the system may be found in excited
states, in which valence electrons are excited above the Fermi-level. This
gives rise to satellite peaks in the spectrum, which correspond to $d^9$, $d^8$
etc. final state configurations. As the groundstate of the system is sharply
defined, the splitting of the satellite peaks is determined by the final state
energies, in XPS terminology: we measure the eigenstates of the $N$-1 electron
system, where $N$ is the total number of electrons.

The splitting between the satellites is determined by $Q$ and $U$. Whether
or not the corresponding final state configurations are observed, depends
on the existence of such configurations in the groundstate (no core hole) and
this is determined by correlation in the groundstate. As a result an
analysis of the satellite intensities may give us information on the valence
band occupation. As is often the case, in the study along these lines it is
found that at first instance one learns a lot about the origin of satellite
structure, and less about the ultimate goal of the research.

The created core-hole in XPS decays for the lighter elements mainly
via the Auger process, in which it gets filled and an outer-shell
electron leaves the atom (Auger electron). In the study of valence bands,
the Auger process in which one ends up with two holes in the valence band is
interesting. In the presence of strong correlation, the energy of this final
state is increased with $U$ relative to uncorrelated two-hole states. If $U > 2$
(atomic limit), where $W$ is the one-electron bandwidth, sharp bound states are
found with atomic character which is reflected in their multiplet splitting.
If this condition is not fulfilled the spectrum becomes complicated.

Another aspect is the decay of the two-hole final state. The narrow
lines in the atomic limit indicate slow decay. When studying impurities,
where $U > 2W$, it appears that the lines can become appreciably broadened.
This can give qualitative information about the interaction of the impurity
states with the host band states.

2. SCOPE

In this work examples of the various aspects of photoelectron
spectroscopy are given. The investigation was started with the development of
an angle-resolved spectrometer and this has taken most of the time of the
research. Therefore the first chapters deal with angle-resolved ultra-violet
photoelectron spectroscopy. To indicate the possibilities and pitfalls of
the technique, in chapter II the theory is briefly reviewed. Our main intere...