Photoemission in Solids I

General Principles

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Preface

This book is devoted to the phenomenon of photoemission in solids or, more specifically, to photoelectron spectroscopy as applied to the investigation of the electronic structure of solids. The phenomenon is simple: a sample is placed in vacuum and irradiated with monochromatic (or as monochromatic as possible) photons of sufficient energy to excite electrons into unbound states. Electrons are then emitted into vacuum carrying information about the states they came from (or, more accurately, about the state *left behind*). This information can be extracted by investigating the properties of the outcoming electrons (velocity distribution, angle of emission, polarization). Photoelectron spectroscopy yields information sometimes similar and sometimes complementary to that obtained with other spectroscopic techniques such as photon absorption and scattering, characteristic electron energy losses, and x-ray fluorescence.

The potential of photoelectron spectroscopy for investigating electronic levels was recognized by H. Robinson and by M. de Broglie shortly after the discovery of the phenomenon of photoemission by H. Hertz and its interpretation by A. Einstein. However, due to the inadequacies of the available equipment, this method was soon overshadowed by developments in the field of x-ray absorption and emission spectroscopy. Commercial interest in the development of photocathodes and theoretical progress in the understanding of electronic states in solids produced new fundamental interest in photoelectron spectroscopy during the late 1950's. This interest was paralleled by an unprecedented development in experimental techniques, including ultrahigh vacuum technology, photon sources, spectrometers, and detectors. This development has continued to the present day as the number of commercially available spectrometers multiplies, spurred, in part, by practical applications of the method such as chemical analysis and the investigation of catalytic processes.

Photoelectron spectroscopy can be and has been used to study almost any kind of solids: metals, semiconductors, insulators, magnetic materials, glasses, etc. The purpose of the present book is to give the foundations and specific examples of these applications while covering as wide a range of topics of current interest as possible. We have, however, deliberately omitted a complete discussion of surface effects (except for semiconductors) and adsorbed surface layers because of the recent availability of other monographs. Two different methods of photoelectron spectroscopy have coexisted since their inception. One of them uses as photon sources gas discharge lamps (usually uv, hence ultraviolet photoelectron spectroscopy or UPS), the other, x-ray tubes (XPS).

In the past few years many experimental systems have been built with both x-rays and uv capabilities. Also, the dividing line between UPS and XPS has disappeared as synchrotron radiation has become more popular as a photon source.

This Topics volume is designed along the following guidelines. The tutorial Chapter 1 discusses the general principles and capabilities of the method in the perspective of other related spectroscopic techniques such as x-ray fluorescence, Auger spectroscopy, characteristic energy losses, etc. The current experimental techniques are reviewed. An extensive discussion of the theory and experimental determinations of the work function is given, a subject which is not treated in the rest of the work. Chapter 2 presents the formal, first principles theory of photoemission and follows the assumptions required to break it up into the current phenomenological models, such as the three-step model. One of these steps is the photoexcitation of a valence or core electron. The simplest model of this process, and one which usually applies to core electrons, is the photoionization of atoms. Chapter 3 treats the theory of partial photoionization cross sections of atoms. Chapter 4 discusses a number of phenomena which go beyond the one-electron picture of atoms and solids, such as relaxation, configuration interaction, and inelastic processes. One of these processes, the simultaneous excitation of a large number of electrons near the Fermi energy which accompanies photoemission from core levels in a metal, is treated in detail in Chapter 5. Finally, Chapter 6 contains a discussion of the increasingly popular method of angular resolved photoemission. A table of binding energies of core electrons in atoms completes the volume.

There will be a companion volume (Topics in Applied Physics, Vol. 27) which is devoted to case studies dealing with semiconductors, transition metals, rare earths, organic compounds, synchroton radiation, and simple metals. The complete Contents of Volume 27 is included at the end of this book.

The editors have profited enormously from the experience and help of their colleagues at the Max-Planck-Institut für Festkörperforschung, the University of California, Berkeley, and the Deutsches Elektronen-Synchrotron DESY. There is no need to mention their names explicitly since they appear profusely throughout the references to the various chapters. Thanks are also due to all of the contributors for keeping the deadlines and for their willingness and patience in following the editors' suggestions.

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