PHOTOELECTRON SPECTROSCOPY AND AUGER ELECTRON SPECTROSCOPY
OF SOLIDS AND SURFACES

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ABSTRACT

High resolution photoelectron spectroscopic (PES) investigations of a wide range of solids are discussed as well as some related results from Auger Electron Spectroscopy (AES). Chapter I gives a brief introduction to PES. In Chapter II, the photoemission process is reviewed with the primary intent being in judging the reliability of a PES spectrum $I(E)$ in reflecting the electronic density of states $N(E)$ of solids. The effects of several modulations -- Final-State (Band-Structure) effects, Cross-Section (Transition Probability), and Relaxation (Screening) -- are discussed. Particular attention is given to understanding the role of many-electron interactions in PES to help in interpreting $I(E)$'s in terms of $N(E)$ and in using PES as a probe of many-electron interactions. Evidence of several many-electron effects -- core-level asymmetry, extra-atomic relaxation,

and electron correlation satellites -- is presented. A case in which the one-electron energy level picture essentially breaks down completely over a large portion of the periodic table, is examined. The connection between XPS, AES, and X-Ray Emission Spectroscopy (XES) as probes of the one-electron density of states is discussed.

Chapter III covers the experimental aspects of the PES and AES studies reported in this thesis. The various components of the ultra-high vacuum PES/AES system are described. Particular emphasis is given to the problem of sample preparation.

Chapter IV covers multiplet splitting phenomenon of core levels. The manganese levels in MnF_2 are examined in great detail to further the understanding of the multiplet splitting phenomenon to aid in its use as a diagnostic probe of unpaired spin distribution. The importance of intra-shell and inter-shell correlations is examined. The 2s and 3s levels of Mn in MnF_2 are demonstrated to be understood quantitatively. The results of these studies are applied to other transition metal compounds as well as transition metals and rare earth metals. Multiplet splitting as a diagnostic tool is discussed with examples from studies of rare earth intermetallics.

In chapter V, the density of states of the $A^{N_8-N}B^{8-N}$ are examined by means of high resolution valence band x-ray photoelectron spectra. Trends in these spectra are related to trends in chemical bonding in these materials. A quantitative spectroscopic scale of ionicity for $A^{N_8-N}B^{8-N}$ and $A^{N_{10-N}}B^{10-N}$ compounds is developed on the basis of splittings between the two most tightly bound valence bands

("the s-bands"). Further information about trends in ionicity is shown to be obtainable from differential extra-atomic relaxation shifts.

The valence band density of states for free-electron-like metals (Na, Mg, and Al), the 3d metals (Sc through Zn), the rare earth metals (La through Lu), and several alloys (8-NiAl, rare earth dialuminides, YbZn_2 , and CePd_3) are reported and discussed in chapter VI. The valence band density of states of several transition metal compounds are analyzed in chapter VII. For the 3d metal difluorides, it was shown that the F2p and metal 3d bands are decoupled. Alkali halide spectra were used to obtain the 3d partial density of states of the compounds. These 3d partial density of states were then used to evaluate recent Multiconfigurational Hartree-Fock (MCHF) calculations of Bagus and Viinikka on transition metal clusters (MF_6^{4+}). Several oxides which possess empty 3d shells were also studied and compared to theoretical results and XES results.

The application of PES to the study of surfaces and surface phenomena is discussed in Chapter VIII. The technique of using low electron take-off angles was employed to make PES a surface spectroscopic probe. Preliminary studies on Al and Ni films examined:

- 1) differences between the binding energies of surface and bulk atoms
- and 2) differences between bulk and surface density of states.

1. INTRODUCTION

A. Background

Photoelectron spectroscopy (PES) has rapidly emerged as one of the most important spectroscopic techniques for the characterization and investigation of the electronic structure of atoms, molecules, liquids, solids, and surfaces. The extremely rapid growth of this technique in the past decade has been due to the versatility of the PES technique and to the fact that PES is the most direct spectroscopic probe of the energy distribution of occupied electron states. Some of the basic features of PES are summarized in Fig. 1. The PES experiment simply consists of irradiating a sample with a nearly monoenergetic beam of photons of energy $h\nu$. Electrons within the irradiated sample volume, which have energy less than $h\nu$, are ejected into the vacuum via the photoelectric effect, where some property of the ejected electrons is analyzed. The photoelectric effect was discovered in 1887 by Hertz¹, and Einstein in 1905² explained the main features of the photoelectric effect with the hypothesis of quantized radiation. Shortly thereafter several experiments based on the photoelectric effect were attempted,³⁻⁵ nevertheless PES did not evolve as a viable spectroscopy of the electronic structure of materials until the late 1950's and early 1960's because of experimental difficulties.⁶⁻¹³ Extensive development of high resolution and high-transmission electron spectrometers for beta-ray spectroscopy by Kai Siegbahn and his collaborators at the Institute of Physics at

Uppsala was carried out and led to the development of PES in the X-ray Photoelectron Spectroscopy* (XPS) regime.⁷⁻¹⁰ These studies were carried out primarily using soft x-ray sources. At about the same time, pioneering work in PES employing photon sources in the ultra-violet range were being performed by D.W. Turner and his coworkers.¹¹ These studies were concerned with the ionization potentials of the outermost electrons in free atoms and molecules and utilized helium discharge lamps as the photon source. W. E. Spicer and his colleagues, first at RCA and then later at Stanford, used hydrogen lamps to study solids.¹² These early investigations led to the emergence of PES as a powerful tool for chemists and physicists with applications in many fields of chemistry, physics, and related sciences. Several excellent monographs summarize this early pioneering phase of PES.¹³⁻¹⁶ Since these early studies, PES has been extensively developed and applied to a wide variety of interesting and important problems, both fundamental and applied, as can be seen from the proceedings of several conferences devoted to this topic,¹⁷⁻²⁴ as well as several books²⁵⁻³² and review articles.³³

Due to the two distinct lines of development of the early investigations, PES has been arbitrarily divided into two branches on the basis of the energy of the incident photons used for excitation. Some of the more common photon sources are listed in Fig. 1 along with their energies. The low energy regime is now usually referred to as

* This was initially denoted by the name Electron Spectroscopy for Chemical Analysis (ESCA) by these workers. The technique has developed much wider application than the acronym ESCA implies, thus we will not employ the terminology ESCA.

Ultraviolet Photoelectron Spectroscopy (UPS)^{*} usually employs rare gas resonance lamps as photon sources with the most common source being HeI radiation ($h\nu = 21.21$ eV).³⁴ HeII radiation ($h\nu = 40.8$ eV) has become increasingly popular as techniques have been developed to optimize the condition of the He lamps for HeII radiation output. The high energy regime, which we will denote as X-ray Photoelectron Spectroscopy (XPS) utilizes characteristic x-ray lines as the excitation source. The most common XPS sources are the soft x-ray lines such as Mg K α ($h\nu = 1253.6$ eV) and Al K α ($h\nu = 1486.6$ eV). UPS and XPS each have advantages and disadvantages and in many respects are complimentary. UV sources possess narrow linewidths resulting in quite good resolution (~ 20 meV) and some of the resonance lines are very intense. However, because of the low energy of these photon sources, UPS is limited to only probing just the outermost electron energy levels of a specimen. On the other hand, XPS can probe more deeply bound levels and thus many core-levels are readily accessible for analysis. This allows for easy in situ chemical analysis of the specimen which is particularly valuable and necessary for the study of solids and surfaces because of the fairly high surface sensitivity (~ 5 atomic layers sampling depth). However, the resolution, which in this case is primarily determined by the linewidth of the source, is of the order of 1 eV for Mg K α and Al K α . Since chemical shifts of core levels and the separation of features in

^{*} In some of the earlier work, UPS was referred to as Molecular Photoelectron Spectroscopy (MPS). Both ESCA and MPS are terms which are applicable to both the high energy and low energy regimes and so will not be used in here for the sake of clarity. We will use the terms PES, XPS, or UPS depending on which is most appropriate.

molecular orbitals or valence bands are commonly of this order of magnitude or less, this can limit the usefulness of XPS studies. Narrower linewidths may be obtained by means of monochromatization albeit with a concomitant loss of intensity. Several schemes of monochromatization applicable to PES have been discussed by Gelius et al.³⁵ Resolution of 0.2 to 0.5 eV have thus been attained with the Al K α line by means of monochromatization.³⁵⁻³⁷

There is much current interest in developing photon sources of other energies, in particular in the region intermediate between the XPS and UPS regimes, where there are very few conventional laboratory sources. The reasons for desiring other sources, which will be discussed elsewhere in this thesis, include the variation of the photoionization cross-section $\sigma(h\nu)$ with energy. This is a quantity of fundamental theoretical interest because it is a stringent test for the quality of theoretical wavefunctions. Also the cross-section variation contains important practical information concerning the atomic orbital composition of molecular orbitals and valence bands. Secondly the mean free path of an electron, which determines the effective PES sampling depth, is a function of photon energy. Many sources of the elements in the region, $Z = 39$ to $Z = 47$ appear to be very promising. Studies employing YMC α have been able to obtain information about orbital symmetry of molecular orbitals in several molecules.³⁹ One of the most important developments in the last several years has been the availability of synchrotron radiation for the spectroscopy of solids and molecules. Synchrotron radiation

with proper monochromatization provides an intense source which is tunable over a wide range of photon energy.⁴⁰ Synchrotron radiation has already made valuable contributions to PES studies⁴¹ and has the promise of many more applications. While synchrotron radiation has blurred most of the artificial distinction between UPS and XPS, there is still an important reason for making a distinction in the case of solid-state studies. That is, separation based on whether final-state band structure effects are important or not. This depends on the momentum broadening of k_f and has been discussed in detail by Feibelman and Eastman.⁴² We will briefly return to this point in the next chapter.

PES is extremely useful as a spectroscopic tool because it can be applied to matter in its various states and is sensitive to all the elements.* Gaseous free atoms and molecules have been commonly studied in many laboratories.^{14,15} Transient species⁴³ and vapors of metals^{44,45} are currently being studied by several groups. Recently the Uppsala group has demonstrated the feasibility of studying liquids.⁴⁶ It appears that much useful information will be obtained from studies of liquids such as the role of hydrogen bonding and that there will be many applications of PES to solution chemistry forthcoming. While the initial XPS experiments were performed on solids,¹³ experiments on solid samples were hindered by high surface sensitivity due to the relatively poor vacuum environments. In recent years the ready availability of ultra-high vacuum (UHV) technology has led to

* At XPS energies, the cross-section for hydrogen is extremely low (essentially zero), but all the other elements have levels which are easily detected.

much work being done on solid samples.⁴⁷ The various techniques used in preparing solid specimens in situ and under UHV conditions are discussed in Chapter III.

Returning to Figure 1, we see that the ejected electron flux may be analyzed as a function of several different parameters. Normally, one measures the ejected electron flux as a function of kinetic energy (or momentum) and obtains an intensity versus energy distribution $I(E)$. From the conservation of energy relation

$$h\nu = E_B + E_K \quad (1)$$

where E_K is the kinetic energy of the ejected electron, the binding energy E_B of the electron is obtained. For simplicity, in Eqn. 1 we ignore the problem of reference levels, which are especially important in obtaining accurate values of E_B from solids. For discussions of this point, see Refs. 13, 14 as well as C. S. Fadley, S. B. M. Hagström, M. P. Klein, and D. A. Shirley, J. Chem. Phys. **48**, 3779 (1968); A. F. Carley, R. W. Joyner, and M. W. Roberts, Chem. Phys. Letters **27**, 580 (1974); P. Ascarelli and G. Missoni, J. Electron Spectros. **5**, 417 (1974); and P. J. Estrup and J. J. Quinn, Surf. Sci. to be published. E_B is a quantity of fundamental interest and is a probe of the charge distribution and polarizability of the valence electron system.^{48,49} The measured $I(E)$ is often corrected for either inelastic background, discrete loss structure and/or instrumental response function, yielding an $I'(E)$ which is hoped to be related to the one electron density of states $N(E)$ [see Fig. 2] i.e., a one-electron eigenvalue spectrum. $I(E)$ or $I'(E)$ can never give $N(E)$ exactly because it is

modulated by cross-section effects as well as other effects such as many-electron interactions. These effects are discussed in Chapter II. It nevertheless has been very useful to use $I(E)$'s or $I'(E)$'s to obtain information about $N(E)$. Besides measuring $I(E)$ in a PES experiment, the angular distribution⁵⁰⁻⁵⁴ or spin polarization⁵⁵ of the ejected electrons may be measured. Other parameters which may be varied include the photon polarization⁵⁶ and angle of the incident photon. Recently the use of synchrotron radiation has introduced several variants such as photoemission yield,⁵⁷ partial yield (fixed final-state kinetic energy)⁵⁸ and partial yield (fixed initial-state energy)⁵⁹ spectroscopies.

Finally, it should be mentioned that there are several other closely related and complimentary experimental techniques. Auger electron spectroscopy (AES),^{60,61} based on the Auger effect, which like PES had very early roots but took a long time before the technique blossomed into a valuable spectroscopic probe.⁶⁰ Some use of AES will be made in this thesis. The Auger process starts with a system which already has an electron ejected. This initial electron is usually ejected via electron impact but may also be ejected by other charged particles such as protons or ions. The initial hole state may also be created by photon impact which is the case in our studies. The hole is then filled by a radiationless transition and another electron (the Auger electron) is ejected. Other techniques include Ion Neutralization Spectroscopy (INS),⁶² Penning Ionization Spectroscopy (PIS),⁶³⁻⁶⁶ Appearance Potential Spectroscopy,^{67,68} Soft-X-ray Spectroscopy,⁶⁹⁻⁷¹ Electron Impact Spectroscopy,⁷²⁻⁷⁴ (e, 2e)

Spectroscopy,⁷⁵ Electron Energy Loss Spectroscopy (ELS)^{76,77} Low Energy Electron Diffraction (LEED),⁷⁸ and Field Emission Energy Distributions (FEED).⁷⁹

B. Scope and Objectives

This thesis will deal with the use of PES, primarily XPS, to obtain information on the electronic structure of a wide variety of solids through the measurement of $I(E)$ curves. We will be mostly concerned with the bulk electronic structure of solids. Both valence-band and core-level spectra, as well as a few cases of photon excited AES, will be employed in these investigations to derive information on $N(E)$.

The organization of the thesis is as follows. A short review of the present understanding of the photoemission process is presented in Chapter II to develop a framework for the use of $I(E)$'s to obtain information about $N(E)$. In particular the effect of several modulations inherent in the measured $I(E)$'s, i.e., final-state band structure, cross-section, and relaxation, will be discussed. Some examples of the observation of many electron interactions in PES will be given, including a case (the 4p levels in the elements $Z \sim 48$ to $Z \sim 69$) where a large collective resonance and strong intra-shell correlation combine to essentially completely break down the simple one-electron interpretation of $I(E)$. Chapter III is concerned with some of the experimental aspects of these PES and AES studies. Particular emphasis is on sample preparation techniques, which are extremely important because of the high surface sensitivity of PES and AES. Chapters IV

through VII will cover the study of bulk electronic properties of solids. Multiplet splitting of core-levels is examined in Chapter IV. The Mn levels in MnF_2 are used as a detailed case study of multiplet splitting. These studies illustrate the importance of intra-shell electron correlations and quantitative verification of a Manne-Aberg-type sum rule. Also reported in this chapter will be core-level multiplet splittings in transition metals, rare earth metals, transition metal halides, and several alloys. The diagnostic use of multiplet splitting will be examined. Chapter V treats the application of PES to the study of the chemical bond in some crystalline semiconductors and insulators, $\text{A}_B^{\text{N}}8\text{-N}$ and $\text{A}_B^{\text{N}}10\text{-N}$ compounds. A spectroscopic scale of ionicity for these compounds is developed from the measured "s-band" splitting in the valence band density of states VB DOS. The densities of states of some metals (free-electron-like metals Na, Mg, and Al), the 3d metals (Sc-Zn), and the rare earth metals (La-Lu) and alloys are presented and discussed in Chapter VI. Chapter VII deals with the electronic structure of transition metal compounds. Results from the 3d halides and several transition metal oxides will be presented. Chapter VIII briefly discusses the potential applicability of PES to the study of the electronic structure of surfaces. A preliminary study of polycrystalline films of Al is presented. The differences between the core-level binding energies of atoms in the bulk and at the surface, as well as differences between bulk and surface densities of states are examined. Included in the Appendices are a compilation of binding energies of the solid elements ($Z < 36$) and LMM Auger energies of Sc-Zn. Also XPS studies

of the valence electronic structure of several layered compounds, chalcopyrite compounds, and amorphous binary semiconductors are reported.

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FIGURE CAPTIONS

Fig. 1. The principle features of Photoelectron Spectroscopy.

Fig. 2. A schematic comparison of the relationship between the one-electron density of states $N(E)$ of a material with the measured intensity versus energy distribution $I(E)$.

- a) A hypothetical $N(E)$ for a solid (left side). For simplicity surface states, conduction band density of states, possibility of multiplet splitting, etc., are ignored. The rightside shows the electrons which are ejected by photons of energy $h\nu$. In this example, $h\nu$ is energetic enough to eject electrons from all the energy levels except the $1s$ level. Note that the levels are broadened due to lifetime effects and the linewidth of the radiation.
- b) The measured $I(E)$ from a solid. Note the relative peak intensities are different than in $N(E)$ due to cross-section modulation, that the peaks are shifted due to relaxation and that the core levels have become asymmetric due to electron-hole interactions. Note also the background due to inelastically scattered electrons and the discrete peaks due to surface P_s and bulk plasmons P_B .

<u>SOURCES</u>	<u>SAMPLES</u>	<u>ELECTRON ANALYZER</u>	<u>DETECT</u>
He I, 21.2 eV He II, 40.8 eV	Gases Liquids	Magnetic electrostatic	Energy distribution $I(E)$
Y M_{45} , 132.3 eV	Solids		Angular distribution $A(\theta)$
Mg $K\alpha$, 1253.6 eV Al $K\alpha$, 1486.6 eV			Electron spin polarization $P(\sigma)$
Synchrotron radiation, (10^{-4} eV $\lesssim h\nu \lesssim 10^4$ eV)			

XBL 755-3053

Fig. 1

Fig. 2

II. THE PHOTOEMISSION PROCESS

A. Introduction

In most PES measurements one obtains an Intensity versus Energy curve $I(E)$. The goal of these measurements is then to derive information about the one-electron density of states $N(E)$ from the experimental $I(E)$. The usefulness of PES as a probe of the electronic structure of materials depends on how well $N(E)$ is reflected in $I(E)$. Therefore it is extremely important to have a good understanding of the photoemission process before $I(E)$'s are used to provide information about $N(E)$'s. Thus the first part of this chapter will briefly review the current understanding of the photoemission process, in particular for the case of photoemission from solids. The various ways $N(E)$ is modulated in PES measurements will be discussed with an eye toward their implication for the physical interpretation which may be attached to the experimental results reported elsewhere in this thesis. These modulations include Final-State Modulation (Band-Structure Effects), Cross-Section Modulation (Matrix-Element Effect), and Relaxation Modulation (Final-State Screening Effect). To fully exploit the potential of PES, it is also essential to understand the role of many-electron effects in photoemission. The last sections of this chapter will present some experimental manifestations of many-electrons interactions observed in the course of our PES studies of solids. These many-electron effects include Extra-Atomic Relaxation

(Solid-State Binding Energy Shifts), Core-Level Asymmetries (Transient Singular Response to the sudden creation of a core hole), and Correlation Satellites ("Final-State Configuration Interaction").

B. Theoretical Aspects of the Photoemission Process

Despite the important role that the photoelectric effect played in the evolution of quantum theory, it is only recently that rigorous microscopic theories of the photoemission process in solids are being developed. The usual framework for the interpretation of photoemission from solids is the phenomenological, so-called "three-step model" which initially was extensively applied by W. E. Spicer and his co-workers.¹ This semi-classical approach partitions the photoemission process into a three-step process with each step being considered as independent. The first step is the absorption of a photon and the excitation of an electron from an occupied state to a higher-energy empty state. The second step involves the propagation of the electron to the surface of the solid and in the third step, the electron overcomes the surface barrier and escapes into the vacuum where it is then detected in a PES experiment. This partitioning into separate and independent steps is of course arbitrary and just a conceptual convenience. Nonetheless the three-step model has been very useful in interpreting $I(E)$'s in the past. More sophisticated approaches have been developed in recent years²⁻¹² and some have challenged the validity of the simple three-step picture of photoemission. However, Feibelman and Eastman¹¹ have analyzed the many-body formulation of photoemission developed by Caroli *et al.*¹⁰ and have demonstrated that

in lowest order (i.e., the independent-electron solid), this formulation can be converted to yield a Fermi's Golden Rule expression for the photoemission flux, which could be made to approximately correspond to (in the limit of weak electron damping) the semi-classical three-step model.

For our starting point we will then use the independent-electron model and the three-step model with our attention primarily focused on the first step (the excitation probability). The photoemission flux is then given as

$$I(E, hv) \propto \sum_{fi} d^3k T_f(E, \mathbf{k}) D_f(E, \mathbf{k}) \sigma(E, hv) \delta[E_f(\mathbf{k}) - E(\mathbf{k}) - hv] \times \delta[E_f(\mathbf{k}) - E] \quad (1)$$

where $D(E, \mathbf{k})$ and $T(E, \mathbf{k})$ are the probability of propagation to the surface and probability of transmission through the surface barrier, respectively, i.e., these are the probabilities associated with steps two and three.^{13,14} The next term in (1) is the cross-section or transition probability for photoionization $\sigma(E, hv)$ where $\sigma(E, hv) \propto |\langle \psi_f | P_{fi} | \psi_i \rangle|^2$ and P is the transition operator between the initial- and final-state (ψ_i and ψ_f). The first delta function imposes energy and momentum conservation and the second delta function selects out the final state. Ignoring terms which are approximately constant and inelastic scattering, $I(E, hv)$ is determined by both the initial- and final-state bands through $\mathbf{k}$ conserving transitions.¹⁸ This is known as the "UPS limit" or "Band-Structure Regime." Eastman has recently reviewed results in this regime,¹³ where one measures a joint density of states and observes binding energies of

peaks in $I(E, h\nu)$ change with changing $h\nu$. We may then rewrite (1) as

$$I(E, h\nu) \propto N_V(E) N_C(h\nu - E) \sigma(E, h\nu) \quad (2)$$

where $N_V(E)$ and $N_C(h\nu - E)$ are the densities of the occupied valence (initial) -- and unoccupied conduction (final) -- states respectively.

However, for the experiments which are reported here, we are interested in $I(E, h\nu)$ for the case where $h\nu \geq 1000$ eV. In this case we are in the "XPS limit" or "density of states" regime where the density of available final states is sufficiently dense that all initial states can be excited. A comprehensive discussion of these two limits and the criteria for these regimes is given by Feibelman and Eastman.¹¹ So in the XPS limit we are left with

$$I(E, h\nu) \propto N_V(E) \sigma(E, h\nu) \quad (3)$$

That is, in the independent-electron solid, the photoemission spectrum (in the XPS limit) reflects the occupied one-electron density of states modulated by the cross-section for photoemission.

Much work has been devoted to calculating the photoemission cross-section for atoms and molecules.²²⁻³² The matrix element simply depends on how well the deBroglie wavelength of the ejected photoelectron "matches" the curvature of the initial-state wave function.* Thus electrons in valence s, p, d, and f bands will have different cross sections because of their different radial wavefunctions.

* The deBroglie wavelength for an electron of energy 1486.6 eV is 0.32 Å, 132.3 eV is 1.07 Å, 40.8 eV is 1.92 Å and 21.2 eV is 2.66 Å. These correspond to electrons in valence orbitals excited by the various common photon sources.

This has been demonstrated for gases by Price et al.³³ and for solids by Eastman and Kuznietz³⁴ and by Cavell et al.³⁵ Gelius³⁶ developed a semi-empirical intensity model involving the use of "experimental" atomic orbital cross-sections which allowed information about the orbital symmetry of molecular orbitals to be obtained.³⁷ This approach is also applicable to solids as shown by McFeely, et al.³⁸ for diamond and graphite and by Prins³⁹ for oxyanions. Thus, although $\sigma(E, h\nu)$ modulates $N(E)$, it provides very important information, that is, the partial density of states. This is especially the case if one either has available several photon energies, such as with a synchrotron source,^{13,40,41} or multiple conventional sources,^{37,42} or if one has x-ray emission results available to compare PES results with.^{38,43} Another modulation, which is inherent in $I(E)$'s, must be mentioned at this point. This is final-state relaxation -- i.e., the response of the passive electrons towards the hole to screen the appearance of increased positive charge. This lowers measured binding energies of core-levels several eVs. This causes the well-known breakdown of Koopmans' theorem. We will discuss relaxation in a little more detail shortly, when we consider many-electron effects below, as relaxation is really a many-electron effect. It will just be noted here that peaks in VB DOS will tend to be shifted towards the top of the valence band. Ley et al.⁴⁴ have examined the effect of the degree of localization of the hole-state on relaxation in metals and shown it to be small.

We have only mentioned the radial effects on the cross-section but angular effects may also be important especially in studies of single crystals.⁴⁵

C. The Effects of Many Electron Interactions On I(E)

Up to this point, we have considered photoemission as a one-electron process but photoemission is manifestly a many-electron process. Nonetheless much of the language and interpretation of PES spectral features are discussed in terms of one-electron quantum numbers. This is justified since orbital theories of atoms and molecules and one-electron theories of solids have worked quite well at least in a semi-quantitative fashion. Many-body effects have in the past been primarily looked at either as minor perturbations on the one-electron spectral distribution or as the explanation of features in I(E) of unknown origins. We will present in this section several examples of many-electron interactions observed in the course of these studies.

1. Relaxation

Relaxation effects on binding energies have been recently reviewed by Martin and Shirley.⁴⁶ Hedin and Johansson,⁴⁷ in a theoretical investigation of ionization energies of inner core electrons, pointed out the effect of relaxation (which they termed polarization) and showed that experimental binding energies thus probes the charge density and polarizability of the valence electrons. A simple equivalent cores screening model was developed by Shirley to account for the effect of atomic and extra-atomic relaxation on core-level binding energies⁴⁸ and on Auger energies.⁴⁹ We will apply

the Shirley model first to the case of core-level binding energies in zinc metal and then to the case of Auger energies in solids demonstrating differential extra-atomic relaxation as well as comparing PES and AES energy shifts. There have been several other approaches to account for the relaxation energy.⁵⁰⁻⁵⁴

2. XPS Studies of Extra-Atomic Relaxation in Zinc Metal^{*}

a. Results

Figures 1-3 show, respectively, spectra of the 2s, 2p_{1/2}, 2p_{3/2} region, of the 3s, 3p_{1/2}, 3p_{3/2} region, and of the 3d-4s, 4p valence bands from clean zinc metal. Derived binding energies relative to E_F are set out in Table I.

In the n = 2 shell, the three lines are well separated (Fig. 1). The 2s line is relatively wide, and its Lorentzian shape suggests lifetime broadening. The 2p lines are much narrower but still considerably wider, 2 eV full-width at half maximum (FWHM), than the instrumental resolution ~ 0.5 eV. Their width probably arises mainly from lifetime broadening (note particularly the Lorentzian-like "tail" on the low-E_B side of the 2p_{3/2} line in Fig. 1) and from final-state effects, which produce a marked asymmetry in both 2p lines.

Direct comparison of the 2s and 2p binding energies with theory is not possible. No theoretical values for core hole-state energies in zinc are available, and it is probably not feasible to calculate such energies directly at this time. However, it is possible to estimate atomic binding energies for these states by

^{*}Based on work done in collaboration with L. Ley, F. R. McFeely, R. A. Pollak, and D. A. Shirley and published in Phys. Rev. B 8, 2392 (1973).

using published calculations on copper and zinc and a somewhat involved argument. These energies are estimated in this way below and compared with our experimental values because of the relevance of this comparison to the discussion of extra-atomic relaxation that follows.

J. B. Mann⁵⁵ has given nonrelativistic Hartree-Fock orbital energies ϵ_{nr} for the elements. Rosen and Lindgren⁵⁶ gave relativistic optimized Hartree-Fock-Slater orbital energies ϵ_r and binding energies E_B for core levels in atomic copper. To estimate core-level binding energies in atomic zinc, we use the recipe

$$E_B(nl, Zn) \cong \epsilon_{nr}(nl, Zn)\epsilon_r(nl, Cu)/\epsilon_{nr}(nl, Cu) \\ + [E_B(nl, Cu) - \epsilon(nl, Cu)].$$

Here the second term is an atomic relaxation energy. The usual sign convention, in which for bound states $\epsilon < 0$ but $E_B > 0$, is used here. Weighted average energies for np states were used throughout, because ϵ_{nr} does not include spin-orbit splitting. Zinc core-level atomic binding energies estimated in this way are given in Table II, together with corresponding values of $E_B^V = E_B^F + \phi_{Zn}$, the vacuum-level referenced metallic zinc binding energies obtained by adding the work function ϕ_{Zn} to the experimental binding energies. The experimental (metal) binding energies are lower by 3-8 eV than the estimated atomic values.

The $2p_{1/2}$ - $2p_{3/2}$ spin-orbit splitting of 23.15 ± 0.05 eV is slightly smaller than the value 24.8 eV obtained by taking the difference between free-atom Hartree-Fock-Slater (HFS) energy eigenvalues.⁵⁷

Satellite or loss structure is associated with every core-level peak. For the broad (and weak) 2s peak no details are resolved, losses appearing as a higher background on the low-kinetic-energy (high- E_B) side. The other lines all show distinct satellites, peaking at ~ 12 -13 eV below the main line. The satellites associated with the 2p lines are the best characterized in this work, because of the high intensities and narrowness of these lines. Particularly for the $2p_{3/2}$ line, the broad satellite peak may be resolved into two or more components, at ~ 9 and 14 eV. We have not studied the satellite structure intensively, and it appears unlikely that a single, unique interpretation of this structure can be made solely on the basis of our data. It is not even clear to what extent the satellite structure is intrinsic and to what extent extrinsic to the localized hole state. Since the satellites appear to differ in form from one core line to another, they are probably at least partially intrinsic.

Most of the above comments about the $n = 2$ peaks apply also to the 3s and $3p_{1/2}$, $3p_{3/2}$ peaks. Experimental and estimated theoretical binding energies for these orbitals are also set out in Table II. The 3p spin-orbit splitting of 2.60 ± 0.02 eV is also somewhat lower than the HFS value⁵⁷ of 3.20 eV. In both the $n = 2$ and

$n = 3$ shells the $(2p_{1/2}/1p_{3/2})$ intensity ratio is 0.58 rather than the multiplicity ratio of 1/2.

Moving up to the valence-band spectrum (Fig. 3), we find a 3d band peak centered at 10.18 ± 0.10 eV below E_F . The 4s, 4p band is low and flat, and the Fermi edge is clearly visible, with a (signal)/(background) ratio of > 50 . Since the (3d)/(4s,4p) height ratio is also 50, the spectrum is conveniently plotted on a semi-logarithmic scale. Unfortunately none of the published theoretical band-structure calculations on zinc⁵⁹ were accompanied by density-of-states plots, so it is not clear whether the calculated 4s, 4p bands would be in more than qualitative agreement with Fig. 3. The previous experimental studies of zinc⁶⁰⁻⁶⁴ give results in only fair agreement among themselves. The ultraviolet-photoelectron-spectroscopy (UPS) studies^{62,64} and the newer soft-x-ray work⁶³ appear to have given very precise results on well-characterized materials. In the soft-x ray work the actual binding energy could not be determined directly, but the $3d \rightarrow 2p_{3/2}$ transition gave a peak energy of 1011.6 eV. Combining this with our $E_B^F(2p_{3/2}) = 1021.96 \pm 0.15$ eV from Table 1, we deduce $E_B^F(3d) = 10.36 \pm 0.15$ eV, in reasonably good agreement with our XPS result. The UPS values of 9.5⁶² and 9.46⁶⁴ are substantially lower, and the discrepancy appears to lie well outside of any reasonable estimates of experimental error. Further study will be needed to resolve this discrepancy. In the course of trying to explain it in terms of partial relaxation around a 3d-hole, we have examined carefully the available data on atomic and extra-atomic relaxation in conductors. The results of this work are discussed below.

b. Atomic Relaxation

To establish a basis for the discussion of extra-atomic relaxation toward a hole state, it is first necessary to consider atomic relaxation. That photoemission from deep-lying core states can be accompanied by complete relaxation is generally accepted, and core-level binding energies that include relaxation can be obtained by direct calculations of hole-state energies.⁵⁶ Recently a simple model⁴⁸ was used to estimate relaxation energies of deep core-hole states due to "outer-shell" relaxation, giving excellent agreement with experiment for rare gases. In this work, however, we are interested in the relaxation energies of orbitals like the 3d shell in zinc, which form closed shells but are not deep core states. Since these relaxation energies are small and we wish to obtain accurate values, we must examine the experimental evidence carefully.

First let us recall the meanings of the various energy parameters. The orbital energy ϵ from a Hartree-Fock calculation gives, by Koopmans' theorem,⁵⁸ (minus) the value of the binding energy E_B which the orbital would have if there were no relaxation. The actual binding energy can be obtained theoretically either by reducing the orbital energy in magnitude by a calculated relaxation energy E_R ,

$$E_B = -\epsilon - E_R \quad (4)$$

or from the direct calculation of the total energies of the initial and final states,

$$E_B = E_f - E_i \quad (5)$$

Hartree-Fock-Slater (HFS) calculations give one-electron eigenvalues that are neither true orbital energies nor binding energies. Thus Koopmans' theorem does not apply to HFS eigenvalues.⁵⁶ However, optimized HFS eigenvalues are essentially identical to Hartree-Fock orbital energies.⁵⁶ Thus, optimized HFS theory can be used to give binding energies via either of the above relations. Of course these theoretical estimates of E_B are still subject to the limitations of Hartree-Fock theory. Thus no allowance is made for electron correlation. There are, however, optical data available that establish the atomic binding energies of electrons in near-core levels for several elements. In Table III are listed the experimental binding energies taken from tabulated data,⁶⁵ the orbital energies,^{55,56} and binding energies from total energy differences,^{56,66} for both the outermost s orbital and the next most loosely bound (p or d) orbital for the five elements of configuration p^6s , $d^{10}s$, or $d^{10}s^2$ which we have been able to find the necessary data.

It is clear from Table III that the orbital energies ϵ are well in hand, with the two calculations^{55,56,66} showing good agreement in most cases. The relaxation energies are perhaps less well understood, with the theoretical values being somewhat too high in most cases. Of course the "experimental rearrangement" energy ΔE_B (expt) includes correlation effects, while the theoretical relaxation energy ΔE_B (theo) does not. Two features of Table III are of special relevance to the zinc photoemission problem. First, the rearrangement energies of near-core filled-shell states (p in p^6s , d in $d^{10}s$ or $d^{10}s^2$) are

positive (i.e., $E_B < |\epsilon|$), and typically ~ 3 eV for d shells, while for the outer s orbitals in these configurations they are small or even negative. Second, there is available from optical data a binding energy for the 3d orbital in atomic zinc.

c. Extra-atomic relaxation

In this section, we examine the evidence that binding energies of atomic core and quasicore levels are different in conductors than in free atoms. As shown below, the available data clearly establish that

$$\Delta E_B = E_B(\text{atom}) - E_B(\text{conductor}) \quad (6)$$

is always positive, as indicated earlier.⁴⁸ At the end of the section arguments are presented for interpreting ΔE_B as arising in large part from extra-atomic relaxation.

X-ray photoemission and optical data

The Zn(3d) binding energy from this XPS work (Tables I and II) and the atomic binding energy from optical data (Table III) can be compared directly. Similar comparisons can be made for Cu(3d)⁶⁷ and for Cd(4d).⁶⁸ All three are summarized in Table IV. Recently the $4f_{7/2}$ binding energies in Pb and Bi have been measured.⁶⁹ These are also included in Table IV, together with our values for $E_B^F(4f_{7/2})$, for the metals. The metal binding energies are referred to the vacuum level by adding the work function to the binding energy referred to the Fermi level,

$$E_B^V = E_B^F + \phi. \quad (7)$$

Work functions⁷⁰ of 3.7 eV (Zn), 4.5 eV (Cu), 3.9 eV (Cd), 4.05 eV (Pb), and 4.3 eV (Bi) were used.

It is evident from Table IV that the d orbitals in these metals have Al_B^V values of about 3 eV.

X-ray photoemission and theoretical atomic core-level binding energies

For deeper core levels, optical data are no longer available. It is still possible in a few cases to compare measured core-level binding energies in the solid elements with the theoretical atomic core-level binding energies. In the course of other XPS studies on the elements we have obtained core-level binding energies for orbitals in carbon (as graphite), aluminum, and copper. In Table V these are compared with theoretical binding energies for the atoms, from published optimized HFS calculations.⁶⁶

Additional comparisons are available from the work of Siegbahn et al.⁶⁶ They gave experimental XPS binding energies E_B^V for core levels of a number of elements, accurate to ± 1 eV. Also given were optimized-HFS (OHFS) results for the atoms: orbital energies only in some cases and binding energies also in others. For those cases in which E_B^V (OHFS) was given, direct comparisons can be made. In other cases rearrangement energies (from OHFS calculations) have now been given by Gelius and Siegbahn.⁷¹ Table VI lists, for several elements, E_B^V and E_B (atomic, OHFS), from Refs. 66 and 71, for the $n = 2$ core levels. These were judged to give the most reliable comparisons. For 1s states the theory is less successful presumably because of quantum electrodynamic effects,⁵⁶ while the experimental values are

also less accurate in an absolute sense because of high energies and wide lines. The $n = 3$ data were excluded because multiplet splitting introduces uncertainties. Both the $n = 1$ and the $n = 3$ results are in general agreement with those in Table VI, however.

From Tables V and VI it is evident that ΔE_B is always positive. It varies considerably in magnitude, showing especially large values for graphite and for the heavy 3d transition-series metals, although it is small again for copper (Tables IV and V) and zinc (Tables II and IV).

Core-level binding energies for rare gas atoms embedded in metals

Siegbahn et al.⁶⁶ gave binding energies for core levels of rare-gas atoms embedded in metal foils, as well as for free rare-gas atoms.⁷² The former were given as E_B^V . The free-atom binding energies were in most cases larger than those of the embedded atoms by ~ 2.5 eV. In Table VII the average differences $(\Delta E_B)_{av}$ are listed for each of the four rare gases Ne, Ar, Kr, and Xe. Recently Citrin et al.⁷³ have repeated the measurements on rare-gas atoms embedded in metal foils. The differences ΔE_B between their results and the free-atom values⁷² are also set out in Table VII. We have also observed shifts of this kind for argon levels in connection with argon-ion bombardment procedures for cleaning metal surfaces. Our average result for the Ar $2p_{1/2}$, $2p_{3/2}$, and $3p$ levels is set out in Table VII. Again ΔE_B is always positive, ranging from 2.2 to 4 eV for these four rare gases.

The results of this section can be summarized as indicating that $\Delta E_B = E_B(\text{gas}) - E_B^V$ is always positive for atomic core levels, falling in a rather wide range of values up to ~ 15 eV. This shift cannot be assigned with certainty to any single effect, but we believe that extra-atomic relaxation is the dominant factor. This interpretation is supported by the rather good detailed agreement with experiment shown by an "extra-atomic relaxation" model derived below. There is, however, another effect that may also be important; namely, a change in the magnitude of the core level's orbital energy ϵ in the solid relative to that in the gas.⁷⁴ This change could apparently have either sign, depending on the details of the local bonding structure. It is difficult to estimate the magnitude of $\Delta\epsilon = [\epsilon(\text{solid}) - \epsilon(\text{atoms})]$, but we would expect it to be rather small for core levels, probably in the 1-2 eV range or less in most cases. It is difficult to see how $\Delta\epsilon$ would be substantially larger than this. If $\Delta\epsilon$ were very large for the 3d orbital in zinc, for example, very strong chemical bonds would have to be present. In fact, the cohesive energy of zinc is less than 1 eV.

We can gain some insight into the relative importance of $\Delta\epsilon$ and the relaxation energy in molecules by comparing the orbital energies of the carbon-1s electron in atomic carbon and in fluoromethanes. Two values that are available for $\epsilon(1s, \text{atomic carbon})$ are -308.5⁵⁵ and -310 eV⁶⁶. In methane itself carbon is negatively charged and there is a chemical shift of $\epsilon(C 1s)$ down to -305.2 eV. There is, however, a good correlation between $\epsilon(1s)$ and gross atomic charge. The values of $\epsilon(C 1s)$ in CH_3F and CH_2F_2 have been found by Gelius et al.⁷⁵

to be -307.96 and -313.88 eV, respectively, while their gross carbon atomic charges are -0.13 and +0.67. Interpolation to zero charge gives $\epsilon \cong -308.9$ eV, or about the same as in atomic carbon. Thus $\Delta\epsilon \sim 1$ eV or less in this case, while the total relaxation energy is ~ 15 eV.⁴⁸

While ϵ does not change appreciably from atoms to molecules, provided that chemical shifts are excluded, and probably doesn't change very much from atoms to metals (with which we are concerned in this work), it seems likely that ϵ might change appreciably from an ion to an ionic solid. In that case the strongly attractive ionic forces could hold the solid together while $|\epsilon|$ for each ion core orbital was decreased relative to the free ion by the confining effect of being held in the lattice. This would increase the local electron density, make the core orbital environment more repulsive, and decrease $|\epsilon|$. Even for ionic solids, however, this effect is strongly self-limiting. Binding-energy shifts from free atoms to solids appear on all core levels, and the same two-electron integrals that contribute to ϵ also contribute to the total energy. Thus that part of the negative shifts in E_B from atoms to solids that arises from $\Delta\epsilon$ will show up strongly in the total energy, raising it and making the solid unstable.

In summary, we believe that extra-atomic relaxation, rather than the $\Delta\epsilon$ effects, is dominant in the observed binding-energy shifts from atoms to metals. The $\Delta\epsilon$ effect, though probably small, is difficult to evaluate, and more work on it is clearly needed.

d. Screening model for semilocalized excitons

Extra-atomic relaxation in small molecules during core-state photoemission, by transfer of electronic charge through the chemical bonds, is well established.⁴⁸ Extra-atomic relaxation in solids has also been pointed out.⁴⁸ From the above discussion it now seems clear that extra-atomic relaxation is generally present during core-level photoemission from conducting solids. Indeed this should come as no surprise: It is simply a very direct experimental manifestation of "screening" of an excess charge -- the hole -- on an "impurity" by the itinerant electrons. Friedel suggested twenty years ago^{76,77} that screening of an impurity charge should be accomplished by the formation of an occupied semilocalized (exciton) state about the impurity via the dropping down of a conduction-band state below E_F at the impurity site. We assume that the outgoing photoelectron will interact repulsively with nascent valence band state as the latter forms adiabatically during photoemission. This would be in complete analogy with atomic relaxation of the valence orbitals during photoemission from core states.⁴⁸ Here, too, it would result in a lowering of the binding energy.

Hedin and Johansson⁴⁷ showed that the atomic binding energy E_B^i of an electron in an orbital $|i\rangle$ can be related to the orbital energy quite accurately by

$$E_B^i(\text{atomic}) = -\epsilon_i - 1/2 \langle i | V_p^a | i \rangle, \quad (8)$$

where V_p^a is an atomic "polarization potential" given by

$$V_p^a = V_a^* - V_a, \quad (9)$$

where V_a^* is the Hartree-Fock potential of the occupied passive orbitals in the (relaxed) final state of the atom and V_a is the Hartree-Fock potential in the initial ground state. Since we are interested in the case of an atom in a metal, the V_p term in a metal must include all passive orbitals that are occupied in the final state, rather than just those atomic orbitals occupied in the initial state. Thus we can write formally

$$E_B^i(\text{metal}) = -\epsilon_i - 1/2 \langle i | V_p^a | i \rangle - 1/2 \langle i | V_p^{ea} | i \rangle, \quad (10)$$

where V_p^{ea} includes all orbitals newly occupied in the final state. The exciton state is the only new occupied orbital. There must also be a newly unoccupied orbital on balance, but it is relatively diffused through the lattice and thus interacts with the hole much less strongly than does the new semilocalized state. Thus only the latter need be considered in a first estimate of $\langle i | V_p^{ea} | i \rangle$.

Formally we can write the Coulomb interaction between the exciton state $|E\rangle$ and the hole state $|i\rangle$ as

$$\langle i | V_{ea}^* | i \rangle = J(iE) - 1/2K(iE), \quad (11)$$

where J and K are Coulomb and exchange integrals, respectively, in standard Hartree-Fock notation. Now Friedel's theory gives us the quantitative Friedel sum rule

$$Z = \frac{2}{\pi} \sum_L (2L+1) \eta_L \quad (12)$$

which states that an impurity of charge Z relative to the lattice atoms will have its charge screened by net positive phase shifts in the conduction-electron partial-L waves. This does not indicate directly how to calculate J and K , because the wave function of the exciton state is not known. It is, however, expected that this state will be composed mainly of L waves corresponding to the symmetry of the lowest unbound states in the conduction band; e.g., the p wave in zinc, the d wave in iron, or the s (and p) wave in sodium. Furthermore, the wave function $|E\rangle$ of the exciton state, while oscillatory, will of course resemble an atomic wave function at the impurity ion core. We could therefore take

$$\begin{aligned} |E, Zn\rangle &\sim |Zn4p\rangle, & |E, Fe\rangle &\sim |Fe3d\rangle, \\ |E, Na\rangle &\sim |Na3s\rangle, \end{aligned}$$

etc., for the purpose of roughly estimating $\langle i|V_p^{ea}|i\rangle$ for these metals.

Two more steps are necessary to facilitate a simple estimate of $\langle i|V_p^{ea}|i\rangle$. First, we note that there is no exciton state before photoemission; thus

$$\langle i|V_p^{ea}|i\rangle = \langle i|V_{ea}^*|i\rangle. \quad (13)$$

Second this hole-state integral would be tedious to calculate, since a Hartree-Fock hole-state calculation would first be necessary. It may, however, be quite accurately estimated using the "equivalent cores" approximation⁴⁸ in which an ion core with atomic number Z and

a core hole is replaced by an ion core of atomic number $Z + 1$ and no hole; thus

$$\langle i, Z | V_p^{ea} | i, Z \rangle = \langle i, Z | V_E^* | i, Z \rangle \cong \langle i, Z+1 | V_E | i, Z+1 \rangle \quad (14)$$

and

$$\begin{aligned} |E, Zn\rangle &\sim |Ga4p\rangle, \quad |E, Fe\rangle \sim |Co3d\rangle, \\ |E, Na\rangle &\sim |Mg3s\rangle. \end{aligned} \quad (15)$$

With all these approximations we can now estimate for the 3d binding energy in zinc, for example,

$$\begin{aligned} E_B^V(3d, \text{metallic Zn}) &\cong E_B(3d, \text{atomic Zn}) \\ &\quad - 1/2[F^O(3d, 4p) - 1/15 G^1(3d, 4p) \\ &\quad - 3/70 G^3(3d, 4p)]_{\text{gallium}}. \end{aligned} \quad (16)$$

This gives $E_B^V(3d, \text{metallic Zn}) \cong 17.3 - 4.8 = 12.5$ eV, in fairly good agreement with the experimental value $E_B^V = 13.9$ eV. In fact this approach tends to overestimate ΔE_B , because the atomic 4p state on which it is based should be more localized than the exciton state.

Similar estimates ΔE_B have been made for all of the elements considered in this paper. The equations that were used to estimate the extra-atomic relaxation energies for the ns core levels are

$$1/2 \langle ns | V_p^{ea} | ns \rangle_Z \cong 1/2[F^O(ns, ms) - 1/2 G^O(ns, ms)]_{Z+1}$$

or

$$1/2[F^O(ns, mp) - 1/6 G^1(ns, mp)]_{Z+1} \quad (17)$$

or

$$1/2[F^O(ns, md) - 1/10 G^2(ms, md)]_{Z+1}$$

where the quantity chosen on the right-hand side depends on whether the exciton state is best approximated by an s, p, or d orbital. The coefficients of G^1 were obtained from standard multiplet theory.⁷⁸ The corresponding equations for p orbitals are obtained in the same way. They are

$$\begin{aligned} 1/2 < np | V_p^{en} | np >_Z &\cong 1/2 [F^O(np,ms) - 1/6 G^1(np,ms)]_{Z+1} \\ \text{or} \quad 1/2 [F^O(np,mp) - 1/6 G^O(np,mp) - 1/15 G^2(np,mp)]_{Z+1} &\quad (18) \\ \text{or} \quad 1/2 [F^O(np,md) - 1/15 G^1(np,md) - 3/70 G^3(np,md)]_{Z+1} & \end{aligned}$$

The only combinations that we actually used for d and f orbitals were

$$\begin{aligned} 1/2 < nd | V_p^{ea} | nd >_Z &\cong 1/2 [F^O(nd,ms) - 1/10 G^2(nd,ms)]_{Z+1} \\ \text{or} \quad 1/2 [F^O(nd,mp) - 1/15 G^1(nd,mp) - 3/70 G^3(nd,mp)]_{Z+1} &\quad (19) \\ \text{and} \quad 1/2 < nf | V_p^{ea} | nf >_Z &= 1/2 [F^O(nf,mp) - 3/70 G^2(nf,mp) \\ &\quad - 2/63 G^4(nf,mp)]_{Z+1} . \end{aligned}$$

The results of these calculations are given and compared with experiment in Table VIII. For brevity only one value is given for each lattice, excepting copper and zinc, for which several accurate values are available. Average experimental values are also quoted for brevity. Thus for most of the 3d transition metals, for example, only the average value

$$< \Delta E_B >_{av} = 1/2 [\Delta E_B(3s) + \Delta E_B(3p)] \quad (20)$$

is listed in Table VIII. Figure 4 is a plot of the experimental values of ΔE_B against values calculated on the above model. It shows

that the two quantities are correlated. It also shows that ΔE_B (theo) $>$ ΔE_B (expt) on the average, which is expected because this model is based on the highly localized atomic states. It must therefore overestimate ΔE_B somewhat. The scatter of the points in Fig. 4 could, we believe, arise largely from experimental error arising particularly from chemical shifts due to surface oxidation. Of course, inadequacies in the model may also create scatter.

The correlation in Fig. 4 is encouraging, but more dramatic evidence for the validity of this model can be obtained by studying trends. In Fig. 5 experimental and theoretical shifts are plotted against atomic number for the 3d series and for the rare-gas impurity series. The trends agree well in both series. Of special note is the sharp break in ΔE_B between Ni and Cu. This occurs because in Ni [atomic configuration (d^8s^2)] there are d states immediately above E_F . The screening of a hole-state charge on the "impurity" is thus achieved mainly by the d wave. The exciton state is thus d like, and it interacts relatively strongly with the hole state [e.g., $F^0(2s,3d)$ is large]. By contrast, in Cu (atomic configuration $3d^{10}4s$) the d band is filled and screening must occur mostly via the s and p waves. The atomic approximation to the exciton state thus involves integrals such as $F^0(2s,4s)$, which are smaller. It would be difficult to reproduce this dramatic break in ΔE_B at the top of the 3d series without explicitly considering atomic properties.

c. Conclusions

Two major conclusions can be drawn from this work: First, relaxation effects are important in zinc, even for the 3d band. The question, "do the 3d bands lie below the bottom of the 4s, 4p bands?" is too simply stated. When its phraseology is refined, it has two answers. If one adds, "...in the photoemission spectrum?" the answer is "No. see Figure 3." If one adds instead, "...in the initial state?" the answer is "Almost certainly yes, see sections on atomic and extra-atomic relaxation." From Tables III and IV it seems evident that atomic relaxation of the Zn(3d) orbitals amounts to about 4 eV and extra-atomic relaxation to about 3.4 eV. The binding energy $E_B(3d)$ is thus less than the orbital energy (Koopmans' theorem) estimates by 7.4 eV. Extra-atomic relaxation accompanying photoemission from the 4s, 4p bands is probably about the same size or a little smaller [i.e., $F^O(3d,4p)$] while atomic relaxation is smaller or even negative (Table III). Hence we would expect the 3d peak in the XPS spectrum to move ~ 5 eV closer to E_F relative to the 4s, 4p bands than their relative positions in a self-consistent Hartree-Fock calculation. Since most band-structure calculations are less rigorous than this, it is not clear where they "should" place the 3d bands in the initial state; probably higher. However the true d-band position would seem from this work to be at $\sim E_F - 15$ eV in the initial state. This result would thus be in rough agreement with the calculation by Mattheiss,⁵⁹ which placed the 3d bands at ~ 17 eV below E_F . The large relaxation energy of

the 3d bands in zinc carries implications for the photoemission spectrum of 3d transition-series metals. It seems possible that relaxation could distort the valence-band spectrum of nickel, for example. This might account for significant differences between the XPS spectrum and the density of states. Future interpretation of photoemission spectra should be made with relaxation in mind.

The second major conclusion from this work is that semilocalized exciton states accompanying photoemission have been identified through their effects on core-level binding energies in conductors. An approximate theoretical model was developed and used to estimate the extra-atomic relaxation energy accompanying the formation of these states. The model overestimates the effect somewhat, as expected, but it reproduces experimental trends very well. It appears to provide a first step toward a quantitative understanding of extra-atomic relaxation in metals.

3. Comparison of binding energy shifts and auger shifts and evidence of differential extra-atomic relaxation in Auger energies in compounds*

a. Introduction

X-ray photoemission (XPS) measurements yield core-electron binding energies; i.e., the energies of processes of the form

where M may be an atom, molecule, or solid, and M_1^+ denotes a final

* Based on work done in collaboration with I. Ley, F. R. McFeely, R. A. Pollak, and D. A. Shirley and published in Phys. Rev. B 9, 381 (1974).

state in which an electron has been removed from orbital i . We denote the binding energy for this process by $E(i)$. Shifts in $E(i)$ are well known: these are usually regarded as arising from chemical effects, most often oxidation in the ground state (M in this case).⁷⁹ We shall denote these shifts as $\delta E(i)$.

Auger processes, which have the form

also yield electrons of well-defined kinetic energy that often appear as peaks in XPS spectra. These Auger peaks originate from the formation of holes in the core j level through the photoelectric effect, followed by the $jk1$ Auger process. Thus the Auger kinetic energy $E(jk1)$ is independent of the incident x-ray energy. Shifts in the Auger energy, denoted by $\delta E(jk1)$, are also known.

In this paper we shall derive the relationship between $\delta E(jk1)$ and $\delta E(i)$, with $i = j, k, l$. To do so we must consider total binding energies rather than just shifts. Both atomic and extra-atomic relaxation energy terms in $E(i)$ ⁴⁸ and $E(jk1)$ ^{49,67} are found to play roles in these energies. Our conclusions about the relation of $\delta E(jk1)$ and $\delta E(i)$ are very similar to those reached by Wagner and Biloen,⁵² who used a somewhat different approach.

This section has three main objectives: to analyze the way in which Auger energies can be predicted from binding-energy data, to discuss derived values of extra-atomic relaxation energies in metals, and to present and analyze data showing differences between Auger

and PES shifts in Na and Zn metals and compounds. A general discussion of the contributions to $E(jkl)$ in solids is given first.

b. Theoretical background

Auger Energies and One-Electron Binding Energies

The Auger transition (jkl) can be broken up into three steps:

The energies of the last two processes can be subtracted from the first energy to give $E(jkl)$. The energies of steps (23a) and (23b) are simple one-electron binding energies $E(j)$ and $E(k)$, which can be used directly. The binding energy in step (23c) must be modified, however, to account for the effects on $E(l)$ of electronic relaxation in step (23b) and of two-hole coupling in the final state. As discussed earlier,^{49,67} these two effects yield an energy $E(l)^*$ for step (23c) of the form

$$E(l)^* = E(l) + F(kl;X) - R(kl) \quad (24)$$

in which $F(kl;X)$ is the interaction energy between the k and l holes in the final state X and $R(kl)$ is the relaxation energy. The Auger energy is then given as

$$\begin{aligned} E(jkl;X) &= E(j) - E(k) - E(l)^* \\ &= E(j) - E(k) - E(l) - F(kl;X) + R(kl) . \end{aligned} \quad (25)$$

We note at this point that the choice of reference energy level for $E(jkl)$ and $E(i)$ has no effect on the validity of Eq. (25); if a consistent energy (e.g., the Fermi energy) is chosen for both the Auger and binding energies, then any error of variation in this reference energy will cancel on the two sides of Eq. (25).

The $F(kl;X)$ term is readily calculable^{49,67} using standard multiplet coupling theory and tabulated Slater integrals.⁵⁵ The relaxation term $R(kl)$ can be estimated rather well in some cases,^{49,67} while in others the estimation of R is less straightforward. To discuss this problem, we first write R as the sum of an atomic relaxation energy R_a , arising mainly from the collapse of other electronic orbitals of the host atom toward the k hole in step (23b), plus an extra-atomic relaxation⁶⁷ term R_e ,

$$R = R_a + R_e. \quad (26)$$

Let us consider R_a first. There are two important contributions to R_a : outer-shell relaxation and intrashell relaxation.⁴⁹ Their relative magnitudes vary with the relative numbers of electrons outside the "final" shell (e.g., the L shell in KLL Auger processes) and in that shell. Thus for a KLL transition in a heavy element it is quite satisfactory to consider only outer-shell relaxation and the "equivalent-core" method gives good results.⁴⁹ For neon, on the other hand, intrashell relaxation alone is present. In fact, for the cases discussed below (the NaKLL and ZnLMM transitions) the intrashell effect is dominant. As was pointed out earlier,⁶⁷ the intrashell relaxation energy can be estimated as twice the dynamic intrashell relaxation energy E_R (intrashell),

$$R_a \text{ (intrashell)} \cong 2E_R \text{ (intrashell)} \quad (27)$$

Calculations of E_R are available from optimized Hartree-Fock-Slater calculations on hole states.⁸¹ We note that these values of E_R are useful for our purposes irrespective of whether the hole-state calculations predict binding energies accurately, because the latter question is affected by correlation effects which are omitted in the Hartree-Fock formalism.

Extra-atomic relaxation R_e occurs through a flow of electronic charge toward the host atom during step (23b). It has the effect of making the initial-state environment in step (23c) more repulsive, and of lowering the binding energy $E(1)^*$. R_e is expected to be largest for metals, in which electrons from the valence band can screen the k-hole charge locally, by being drawn down out of the conduction band into a localized state c drawn down out of the conduction band.^{67,80} In the limit of completely local screening, the screening charge can be regarded as occupying the first unfilled atomic orbital above the Fermi energy E_F , and R_e is then given by the two-electron interaction between this orbital and the 1 orbital,

$$R_e \cong F(1,c)_k \equiv F^0(1,c) + \dots, \quad (28)$$

where c denotes the conduction-band state, k indicates that this term arises because of the k hole, and the terms beyond F^0 (which is always by far the dominant term) are appropriate Slater (Coulomb and exchange) integrals. Thus the Auger energy in a metal is given by an expression of the form

$$E(jkl;X) = E(j) - E(k) - E(l) - F(kl;X) + 2E_R(l) + F(l,c)_k \quad (29)$$

Again we note that all four quantities $E(jkl)$, $E(i)$ ($i = j,k,l$) must be taken relative to the same reference energy.

In an application to the $1_{3^M}45^M_{45}$ Auger spectra of Cu and Zn, Eq. (29) gave very good results.⁶⁷ The predicted kinetic energies relative to E_F of the $1D$ lines were 921.1 eV in Cu and 993.2 eV in Zn, while experiment gave 918.0(2) and 991.8(2), respectively. This good agreement provided strong evidence for localized screening, because extra-atomic relaxation terms $F(l,c)$ of 9.6 eV (Cu) and 11.0 eV (Zn) were involved in the theoretical estimates. We were then led to inquire how effectively screening by extra-atomic relaxation can occur in nonmetals. If the R_e term is smaller in salts, for example, then one would expect significant shifts in the Auger line to lower kinetic energies from metals to salts. Such an Auger shift would arise not from chemical shifts per se, which would affect the $E(i)$ terms, but rather from the R term. Of course Auger shifts between two substances have meaning only if the lines are referred to meaningful reference energies. The Fermi energy does not qualify in this case, but the vacuum level does, for the same reason that holds for PES shifts. In the following discussion we shall show that the core-level photoemission lines can serve as a reference, and we shall also develop methods for isolating the extra-atomic relaxation energy by using optical data.

Use of optical data on free atoms

As an alternative to using Eq. (29) to predict Auger energies in metals, we can derive Auger energies for free atoms $E^A(jkl)$ from optical data,⁶⁵ usually in combination with x-ray energies⁸² and/or calculated atomic binding energies.^{81,66} First let us estimate $E^A(jkl)$ from free-atom one-electron binding energies $E^A(i)$. By going through a three-step process similar to Eqs.(23) for free atoms it is easy to derive the relation

$$E^A(jkl;X) = E^A(j) - E^A(k) - E^A(l) - F(kl;X) + 2E_R(l) , \quad (30)$$

which differs in form from Eq. (29) only in having no extra-atomic relaxation term. To apply these results to the $(L_3M_{45}M_{45};^1D)$ Auger transition in atomic copper, for example, we can use the data collected in Table IX to find

$$E^A(L_3M_{45}M_{45};^1D)_{Cu} = 903.9 \text{ eV} ,$$

for atomic copper.

Returning to our general notation, we note that the Auger process, like photoemission, is one in which one electron is lost. Thus the Auger energy in a solid could be compared directly to that in an atom only if the former were referred to the vacuum level. If it is referred to the Fermi level, $E^F(jkl)$, a correction for the work function ϕ must be made. The two Auger energies also differ by the total Auger extra-atomic relaxation, which we shall denote by $R_e(TA)$. Thus

$$E^F(jkl) = E^A(jkl) + e\phi + R_e(TA) . \quad (31)$$

For the copper ($L_{3^4}M_{45^4}M_{45^4}^1D$) case we have $E^F = 918.0$, while $\phi = 4.5$ eV.⁸⁵ Combining these with Eqs. (30) and (31), we find

$$R_e(TA) = 9.6 \text{ V}.$$

By coincidence this has the same value as the theoretical estimate of $F(1,c)_k$. To understand this we note that atomic binding energies were used in Eq. (31), while Eq. (29) was based on binding energies in the metals. We may relate the two, and also derive a method for estimating $R_e(TA)$ theoretically, by going once again through a three-step sequence as in Eq. (23), but this time relating the energy of each step in the metal to that in the free atom. This gives

$$E^F(j) = E^A(j) - e\phi - 1/2 F(jc), \quad (32a)$$

$$E^F(k) = E^A(k) - e\phi - 1/2 F(kc), \quad (32b)$$

$$E^F(1)^* = E^A(1)^* - e\phi - F(1c)_k - 1/2 F(1c). \quad (32c)$$

Here $1/2 F(ic)$ is the amount by which the binding energy of the i th orbital is lowered in the metal through dynamic extra-atomic relaxation⁴⁹ of the conduction band. Combining Eqs. (32) to form Auger energies, we find

$$\begin{aligned} E^F(jk1) &= E^A(jk1) + e\phi + F(1c)_k \\ &+ 1/2[F(1c) + F(kc) - F(jc)]. \end{aligned} \quad (33)$$

Thus the total Auger extra-atomic relaxation is given by

$$R_e(TA) = F(1c)_k + 1/2[F(1c) + F(kc) - F(jc)], \quad (34)$$

from Eqs. (31) and (33). Since $F(1c)_k$ and the three quantities $F(ic)$ ($i = j, k, 1$) are all of approximately the same size

(as will be shown below for the case of copper), $R_e(TA)$ is about 1.5 times as large as $F(1c)_k$.

Specializing now to the copper $(L_3M_{45}M_{45};^1D)$ Auger transition, we substitute L_3 for j , etc., in Eq. (34), expand the $F(1c)$ in terms of Slater integrals, invoke the equivalent-cores approximation, and use Mann's values⁵⁵ for these integrals. In this case $k = 1$; thus $F(1c)_k = F(kc)$, but $F(kc) \neq F(1c)$, since in $F(kc)$ a conduction electron (which we assume to be 4s) is screening a single hole, so that Slater integrals in zinc are appropriate, whereas in $F(1c)$ the conduction electron (which we take as 4p) is screening a second hole and gallium is the equivalent core. Thus

$$F(jc) \cong [F^0(2p,4s) - 1/6 G^1(2p,4s)]_{Zn} = 11.7 \text{ eV},$$

$$F(kc) = F(1c)_k \cong [F^0(3d,4s) - 1/10 G^2(3d,4s)]_{Zn} \\ = 11.0 \text{ eV},$$

$$F(1c) \cong [F^0(3d,4p) - 1/15 G^1(3d,4p) \\ - 3/70 G^3(3d,4p)]_{Ga} = 9.6 \text{ eV}.$$

Thus from Eq. (34), we have

$$R_e(TA, CuL_3M_{45}M_{45};^1D) = 15.5 \text{ eV}.$$

This estimate exceeds the "experimental" value of 9.6 eV given above, presumably because the screening charge is not as localized as this approach assumes. This estimate (15.5 eV) together with $\phi = 4.5$ eV and the free-atom estimate for $E^A(L_3M_{45}M_{45};^1D)$ leads to an estimated Auger energy for the 1D line in metallic copper of

$$E^F(L_3M_{15}M_{45}, {}^1D) \cong 923.9 \text{ eV} ,$$

or 6 eV larger than the experimental value of 918 eV.

Another approach that also employs optical data is based on the use of the one- and two-hole states in free atoms that correspond to the initial and final states in the Auger transition. Denoting these by $E^A(j)$ and $E^A(kl)$, we have $E^A(jkl) = E^A(j) - E^A(kl)$, and this quantity can go directly into Eq. (31), giving

$$E^F(jkl) = E^A(j) - E^A(kl) + e\phi + R_c(TA) . \quad (35)$$

In the copper example above $E^A(j)$ is the $\text{Cu}^+(2p_{3/2})$ hole state at 940.1 eV (Table IX), while the appropriate 1D final state lies at the weighted mean energy of the $3d^8({}^1D)4s$; ${}^2D_{3/2}$ and $3d^8({}^1D)4s$; ${}^2D_{5/2}$ states in Cu III; i.e., at 37.72 eV above the ground state of Cu I.

Thus we estimate

$$E^A(L_3M_{45}M_{45}; {}^1D) = 902.4 \text{ eV} ,$$

using this approach. From Eq. (35), the experimental value

$E^F = 918.0 \text{ eV}$, and $e\phi = 4.5 \text{ eV}$, we find

$$R_c(TA) = 11.1 \text{ eV}$$

in better agreement with the theoretical estimate of 15.5 eV. This "two-hole" estimate of $R_c(TA)$ is preferred because it uses more optical data and fewer assumptions than does the "one-hole" method based on Eq. (30).

Careful bookkeeping is required at several points in discussing extra-atomic relaxation energies for Auger transitions in metals. Only two simple concepts are involved, however. First, as a charge q is removed from an atom, a screening charge q moves in, reducing the binding energy by the dynamic relaxation energy $R_e = 1/2 q^2/r_{eff}$ classically, where r_{eff} is an effective screening radius. In quantum-mechanical language, n electrons are removed, $q = n|e|$, and $R_e = 1/2 n^2 F$, where F is a linear combination of Slater integrals in the limit of localized screening. Second, if the Auger energy is estimated by summing over one-electron binding energies, then an additional static relaxation term must be added [e.g., in Eq. (23c)]. This amounts to $R_e = F$, or e^2/r_{eff} classically.

When one-electron binding energies in metals $E^F(i)$ are used to estimate $E^F(jkl)$, as in Eq. (29), the dynamic screening effects are included in the $E(i)$. Thus only the static term remains, and $R_e = F$.

If one-electron atomic binding energies $E^A(i)$ are used, each must be reduced by $1/2 F$ to account dynamic extra-atomic relaxation in the metal. Because these binding energies appear in the combination $E(j) - E(k) - E(l)$, two of the $1/2 F$ terms will cancel, leaving a net dynamic term $1/2 F$ to be added to the static term F , giving the total Auger extra-atomic relaxation energy $R_e(TA) = 3/2 F$.

If one- and two-hole atomic states (j) and (kl) are used, there is no static term. The dynamic terms by which $E(j)$ and $E(kl)$ must be corrected are $1/2 F$ and $2 F$, respectively, for $n = 1$ and 2 . The net correction is therefore $3/2 F$, as above.

In summary, we have explored three ways to derive the energy associated with extra-atomic relaxation of Auger transitions in solids. They are based on comparison of experimental Auger energies with (i) one-electron binding energies in solids⁶⁷ [Eq. (29): this gives $F(1,c)$]; (ii) one-electron binding energies in atoms [Eq. (31): giving $R_e(TA)$]; (iii) initial and final Auger states in atoms [Eq. (35): giving $R_e(TA)$]. Both $F(1,c)$ and $R_e(TA)$ can be estimated theoretically on the equivalent-cores model, as described previously⁶⁷ and above. Results for the $(L_{23}M_{45}M_{45};^1D)$ transition in Cu, derived above, are collected in Table X.

These results further substantiate the earlier observation of extra-atomic relaxation accompanying Auger transitions in metals,⁶⁷ as well as showing how atomic optical data can be used to isolate $R_e(TA)$. Since the 3d hole states now appear to be essentially localized and the screening at least semilocalized in copper, it would be valuable to determine the extent to which this is true in the transition metals, which have open 3d shells. We address this question below.

Hole-state localization and d-wave screening in transition metals

In a recent analysis of the effect of extra-atomic relaxation on the binding energies of core electrons in transition metals, striking evidence was found for d-wave screening through Ni and s,p-wave screening for Cu and Zn.⁸⁰ The quantity $\delta E(i) = E^A(i) - E^F(i) - e\phi$, which should be $1/2 F(i,c)$ according to Eq. (32b), rises to 12-13 eV for Co and Ni, then drops to 3-4 eV in Cu and Zn. This is expected

because the d band fills between Ni and Cu. The experimental $\delta E(i)$ were only about 2/3 as large for the transition metals as the theoretical estimates of $1/2 F(i,c)$ based on atomic integrals, suggesting the screening is not completely localized (or to be more precise, that the conduction-band d state doing the screening is less localized than an atomic 3d function). In this case there was no doubt that the hole state was localized, because it was in the $n = 2$ shell. The results are reproduced, for comparison purposes, in Fig. 6(a).

Let us next consider an Auger transition in which the final state is certainly localized; the $L_3 M_{23} M_{23}$ transition. Data are incomplete and of variable quality for this transition, but we have derived tentative values of $R_e(TA)$ from available data, using the relation

$$R_e(TA) \cong E^F(L_3 M_{23} M_{23}) - E^A(L_3) + 2 E^A(M_{23}) + F^O(3p, 3p) - e\phi - 2 E_R(3p), \quad (36)$$

which follows from Eqs. (30) and (31), if final-state multiplet splitting is neglected and $F(kl;X)$ is approximated as $F^O(kl)$. Auger energies were taken from the compilation of Haynes.⁸⁴ Even at this level of approximation, several of the data needed in Eq. (36) are not very reliably known, and we have serious reservations about the accuracy with which we have estimated $R_e(TA)$. The values of the parameters that we used are given in Table XI. Also listed are theoretical estimates of $R_e(TA)$ based on the approach described above. Both $R_e(TA)_{\text{expt}}$ and $R_e(TA)_{\text{theo}}$ are plotted in Fig. 6(b). The transition from d-wave to s,p-wave screening between Ni and Cu appears

to be present here as well. In this case the magnitude of the d-wave screening is also about 2/3 of the "localized" estimates, while for Cu and Zn the two agree very well. At this level of detail, however, further refinements in the data and/or analysis may modify this conclusion.

Having established above that a "shell effect" in $R_e(TA)$ exists, for an Auger transition with a localized final state, at the 3d-shell closure between Ni and Cu, we can test whether the $(L_3M_4S^M_{45})$ Auger energies are consistent with a localized final state. The relevant equation in this case is

$$R_e(TA) \cong E^F(L_3M_4S^M_{45}) - E^A(L_3) - \epsilon\phi + 2 E^A(M_{45}) + E^O(3d,3d) - 2 E_R(3d) . \quad (37)$$

Proceeding as for the $(L_3M_{23}M_{23})$ case, we have derived values of $R_e(TA)$ from the data in Table XII, and plotted them in Fig. 6(c). The results are certainly consistent with localized 3d hole states and a shell effect between Ni and Cu. We are, however, reluctant to infer that the Auger final states are definitely localized, because we have in a sense assumed this in the structure of Eq. (37).

If the 3d holes were delocalized, the last three terms in Eq. (37) would all be smaller, and $R_e(TA)$ would be smaller than Eq. (37) implies. Thus it could certainly be argued that our analysis tends to exaggerate the localized nature of the hole states by using terms such as $E^O(3d,3d)$ in the estimates of $R_e(TA)$. It seems quite clear that the Cu and Zn Auger transitions involve localized 3d hole states:

the Auger peaks in Cu are narrower than the 3d band and the Auger peak structure in both Cu and Zn follows multiplet splitting predictions quite closely.⁶⁷ For the 3d transition metals, however, further work is needed before the Auger hole states can be taken as localized.

Proceeding to the fifth-row elements, there are as yet too few data available to discuss the systematic variation of R_e (TA) with Z. It is, however, evident that localized hole states are present in the $M_{45}N_{45}N_{45}$ spectrum of silver, as reported recently by Powell.⁸⁵ We have carried out a rough analysis of the available Auger data on this transition in the 4d series Ru, Rh, Pd, and Ag, to derive $R_e [\approx 2/3 R_e (TA)]$ for these elements. The relation

$$R_e \cong E^F (M_{45}N_{45}N_{45}) - E^F (M_5) + E^F (N_{45}) + F^O (4d,4d) - 2 E_R, \quad (38)$$

which follows from Eq. (29) with $R_e \equiv F$ (1,c) was used. Table XIII lists the numerical values of the energy parameters. Several of these energies have been determined experimentally by XPS studies in our laboratory. There is no evidence for an abrupt decrease in R_e from Pd to Ag due to closure of the 4d shell, in contrast to the result for Ni and Cu. There is apparently a large decrease from Ru to Pd and Ag, however. This would be consistent with the atomic ground states, because Pd has a ground-state configuration $4d^{10}$ (whereas Ni is $3d^8 4s^2$); thus R_e (Pd) might be expected to arise mainly from s-wave screening if its d band were nearly full, and hence smaller than R_e (Ru) or R_e (Rh). We are, however, again reluctant to draw a firm conclusion that this is in fact the case until more complete data are available and a more detailed analysis can be made.

For both 3d- and 4d-series Auger spectra we have had to draw only tentative conclusions. Nevertheless there is enough evidence for the effect of shell closure R_g in each case to justify further work. It appears quite possible that with further analysis of R_g values we may be able to determine the extent of localization of d-hole states in transition metals.

c. Extra-atomic relaxation and Auger energies in zinc and sodium salts

To assess the extent to which variations in extra-atomic relaxation energy can affect Auger energies, we have selected the $(KLL;^1D)$ transition in sodium and the $(L_3M_{45}M_{45};^3P,^1G,^1D)$ peak in zinc as examples that are sufficiently well-characterized for this study. These two cases are discussed separately below.

The experimental measurements were done in a Hewlett-Packard HP 5950A ESCA Spectrometer. The sodium metal $(KLL;^1D)$ Auger energy, together with the 1s and 2p binding energies, have been reported earlier.⁸⁶ They are given in Table XIV for convenience. Also listed are $E^F(KLL;^1D)$, $E^F(K)$, and $E^F(L_{23})$ for sodium oxide, obtained from a sodium metal sample after it was slightly oxidized. The XPS spectrum of this sample agreed well with that of Fahlman *et al.*,⁸⁷ who prepared their sample in a similar way. We have also carried out XPS studies on single crystals of NaF and NaI, and Table XIV lists the relevant binding energies and Auger energies. In these cases the reference energy is the top of the valence band in each case. In the NaF work we did not obtain a satisfactory value for $E(1s)$ experimentally, and we assumed that the difference $E(1s)-E(2p) = 1042$ eV,

the value for NaI. (This estimate should be accurate to 1 eV or better, since both the 1s and 2p states are core levels. Empirically, the 1s-2p splitting is nearly constant even from the metal to the salts, as the data in Table XIV show.)

To analyze the sodium data we can use all three methods previously discussed, and they all show quite good agreement. We shall present here a comparison of the atomic Auger energies $E^A(KLL;^1D)$ as calculated from data on one- and two-hole optical states, to test this approach. The two-hole calculation will then be taken as providing an empirical value of the combination of terms $-F(KL;X) + 2 E_R(1)$ in Eq. (30). This quantity will be used to derive extra-atomic relaxation energies in the solids.

For atomic sodium, Eq. (30) becomes

$$E^A(KLL;^1D) = E^A(K) - E^A(L_{23}) - F(2p,2p;^1D) + 2 E_R(2p). \quad (39)$$

We have used the values $E^A(K) = 1079.1$ eV, obtained from optical⁶⁵ and x-ray⁸² data, and also theoretically,⁶⁶ $E^A(L_{23}) = 38.02$ eV,⁶⁵ $E_R = 4.7$ eV,⁸¹ and

$$F(2p,2p;^1D) = F^0(2p,2p) - 2/25 F^2(2p,2p) - 1/4 \zeta + \left\{ [3/25 F^2(2p,2p) + 1/4 \zeta]^2 + 1/2 \zeta^2 \right\}^{1/2}$$

as given by Asaad and Burhop.⁸⁸ Using Mann's values for the Slater integrals⁵⁵ and optical data for the spin-orbit coupling constant ζ ,⁶⁵ we calculated a numerical value $F(2p,2p;^1D) = 32.17$ eV. Thus

$$E^A(KLL;^1D) = 980.3 \text{ eV},$$

as estimated from optical data on one-hole states.

The mean energy of the $1s^2 2s^2 2p^4 (^1D) 3s$ state in Na III lies 101.92 eV above the ground state of NaI.⁶⁵ We can estimate the Auger energy as

$$\begin{aligned} E^A(KLL; ^1D) &= E^A(K) - E^A[1s^2 2s^2 2p^4 (^1D) 3s] \\ &= 977.2 \text{ eV.} \end{aligned}$$

The discrepancy of 5.1 eV between this result and the above one-hole-state estimate is an indication of the accuracy of the latter (note the similar discrepancy of 1.5 eV, in the same direction, for Cu.) The two-hole-state result is preferred because it uses empirical data exclusively. Since it will be necessary to use one-hole energies [Eq. (29)] for analyzing Auger energies in the solids we can combine the above result (977.2 eV) with Eq. (39), $E(K) = 1079.1 \text{ eV}$, and $E(L_{23}) = 38.02 \text{ eV}$ to obtain a reliable empirical estimate of

$$-F(2p, 2p; ^1D) + 2 E_R(2p) = -25.86 \text{ eV}$$

for later use.

The above values of $E^A(KLL; ^1D)$ can be compared with experiment. Sevier⁸⁹ quoted experimental studies of the Na(KLL) Auger spectrum on Na vapor, in which the measured energies were 13-15 eV lower than those reported by Fahlman *et al.*,⁸⁷ for the oxide. This would correspond to $(990 - 13 - 15) = 975-977 \text{ eV}$ for the 1D line, in good agreement with the above value.

The extra-atomic relaxation energies in the solids in Table XIV were obtained from the relation

$$R_c = E^F(KLL; ^1D) - E^F(1s) + 2 E^F(2p) + 25.86 \text{ eV}, \quad (40)$$

which follows from Eq. (29) and the discussion above, with $F(1,c) = R_e$. The largest value of R_e , 9.2 eV, is found in the metal. It agrees very well with the value

$$R_e(2p,3s) \cong [F^0(2p,3s) - 1/2 G^1(2p,3s)]_{Mg} = 9.7 \text{ eV},$$

estimated on the equivalent-cores model.⁸⁶ In the salts, as Wagner and Biloen have pointed out,⁵² screening charges remain on neighboring ions, and R_e should be smaller. This expectation is borne out very nicely in Table XIV. It is pleasing (although perhaps fortuitous) to see that the three salts have R_e values ordered according to their anion electronegativities.

It is not always feasible to calculate R_e in solids from Auger and binding-energy data in the way described above. Unfortunately, neither binding-energy shifts nor Auger shifts alone are very meaningful, because there is no reliable reference energy if these energies are compared from one solid to another. A meaningful energy shift does exist, however; it is the shift in the difference energy between the binding energy of one of the final-state holes and the apparent binding energy in the XPS spectrum of the Auger line, $E_B(jkl) = h\nu - E(jkl)$, where $h\nu$ is the photon energy. Substituting this relation into Eq. (29), with $F(1,c) = R_e$, we have

$$h\nu - E_B(jkl) = E(j) - E(k) - E(l) - F + 2E_R = R_E,$$

$$E(l) - E_B(jkl) = E(j) - E(k) - h\nu - F + 2E_R + R_e.$$

Now $E(j) - E(k)$ is the energy of an x-ray transition connecting two core states. It shifts very little with changes of environment. The combination of terms $-F + 2 E_R$ is an atomic property which should also be constant from one material to another, and of course he doesn't vary. Thus to a very good approximation,

$$\Delta[E(1) - E_B(jk)] = \Delta R_c . \quad (41)$$

That this relationship holds well for Na is shown by comparing the last two columns of Table XIV. It is useful because $E(1)$ and $E_B(jk)$ have a common reference energy; therefore the reference energy need not be known to determine ΔR_c . The relative shifts in $E_B(KLL; 1D)$ and $E(2p)$ for Na, as well as the constancy of $E(1s) - E(2p)$, is illustrated in Fig. 7.

The $L_{3/2}M_{4/2}M_{4/2}$ transition in zinc was studied in the metal, in a single crystal of ZnO, and in several ZnF₂ samples. The Zn Auger spectrum was reported earlier.⁸⁰ The ZnF₂ spectrum is shown in Fig. 8. The ZnF₂ work has been done on single crystals but sample charging shifted the lines by several electron volts, necessitating wide scans in which at least two lines were intercompared, with consequent loss of accuracy. One experiment was also carried out on a single crystal sample at Hewlett-Packard, Inc., in Palo Alto, California, in which charging was neutralized by an electron flood gun. The ZnF₂ energies, which are listed in Table XV, are values obtained by combining the average of the splittings in a total of four experiments with the Zn(3d) binding energy from the flood-gun experiment.

The equation

$$R_e(\text{Zn}) = E^F(L_3^M M_{45}^M M_{45}^M) - E^F(2p_{3/2}) + 2 E^F(3d) + F(3d, 3d; {}^1D) - 2 E_R \quad (42)$$

can be used to obtain R_e for the 1D peak in zinc. It was obtained from Eq. (29) with $F(1,c) = R_e(\text{Zn})$. There are no suitable two-hole optical data available for zinc, to our knowledge. The last two terms in Eq. (42) were therefore taken from Ref. 67, which gave $F(3d, 3d; {}^1D) - 2 E_R = 16.6$ eV. Again the extra-atomic relaxation term R_e is larger in the metal than in the oxide or fluoride, as expected. The apparent binding-energy shift $E(3d) - E_B({}^1D)$ increases by 5.2 eV from ZnF_2 to Zn metal, in reasonable agreement with the 4.0 eV increase in R_e . Thus the Auger shifts in zinc and zinc compounds behave as expected, in agreement with the sodium results.

Returning now to the relation between Auger shifts $\delta E(jkl;X)$ and binding-energy shifts $\delta E(i)$, we can derive from Eqn. (25) the variation of these shifts between two environments as

$$\delta E(jkl;X) = \delta E(j) - \delta E(k) - \delta E(l) + \delta R(kl). \quad (43)$$

We have assumed here that $F(kl;X)$ does not vary with environment.

Equation (43) displays explicitly the important role played by changes in relaxation energy $\delta R(kl)$ relative to binding-energy shifts.

Applying this relation to the $(KLL; {}^1D)$ transition in sodium, and using the data in Table XII, we have for the shifts from metal to oxide:

$$\begin{aligned}\delta E(\text{KLL}, {}^1\text{D}) &= \delta E(1s) - 2 \delta E(2p) + \delta R, \\ - 7.4 \text{ eV} &= - 1.3 \text{ eV} + \delta R, \\ - 6.1 \text{ eV} &= \delta R.\end{aligned}$$

Thus the shift in relaxation energy (- 6.1 eV) is much more important than the net binding-energy shift (- 1.3 eV) in determining the Auger shift of - 7.4 eV in this case. Clearly this is not always true (e.g., the binding-energy shifts are more important in the NaI versus oxide shift), but it would be grossly inaccurate to omit the δR term in Eq. (43).

d. Conclusions

The principal conclusions from this work are listed below:

(i) Auger energies in metals can be predicted from free-atom optical data (in two ways) or from solid-state data, provided that proper account is taken of final-state coupling and extra-atomic relaxation energies. Predicted values agree well among themselves and with experiment.

(ii) Extra-atomic relaxation accounts for energy differences of 10 eV or more between free-atom and metal Auger energies.

(iii) Auger energies in 3d transition metals are consistent with an abrupt drop in extra-atomic relaxation energy between Ni and Cu, which is consistent with expected cessation of d-wave screening of localized 3d hole states.

(iv) Relative shifts of core-level binding energies and Auger energies of 8.7 eV (Na vs. NaF) and 5.2 eV (Zn vs. ZnF₂) were observed. These were attributed mainly to differences in extra-atomic relaxation energies, which were analyzed to be 9.4 and 4.0 eV, respectively.

(v) Thus while shifts in neither core-level binding energy or Auger energy from one solid to another have precise meaning, relative shifts can be interpreted readily.

4. Line asymmetry *

Another manifestation of many-body relaxation effects in the core-level photoemission is the asymmetry of the full-energy peaks. Following the earlier work of Mahan,⁹⁰ Anderson,⁹¹ and others, which suggested that the coupling of the final-state hole to the conduction electrons could be an important effect in spectra involving electronic transitions in simple free-electron metals, there has been considerable discussion of this model,⁹² particularly in reference to the theoretical understanding of experimental x-ray absorption and emission edges in Li, Na, Mg, and Al. Several alternative explanations have also been offered, principally by Dow and co-workers,⁹³ involving Auger and phonon-broadening processes. Experimental data relevant to these questions have not kept pace with the theoretical developments.

Photoelectron spectra of core-electron lines in metals offer the possibility for sensitive tests of the various theoretical models; in particular, it is expected that such electron lines will exhibit an asymmetry, being broader on the high-binding-energy side. Citrin⁹⁴ and Hüfner et al.⁹⁵ have recently reported x-ray photoelectron spectra which exhibit this asymmetry to varying degrees in sodium and in a number of 4d and 5d metals respectively. In the Mahan

* Based on work done in collaboration with L. Ley, F. R. McFeely, J. G. Jenkin, and D. A. Shirley and published in Phys. Rev. B 11, 600 (1975).

model^{90,92} the asymmetry is due to the creation of low-energy conduction-electron-hole pairs by the coupling of the final-state hole to the conduction electrons. This interpretation has been vigorously disputed by Dow et al.^{93,96}

There is clearly a need for quantitative measurements of the asymmetry in XPS core-level spectra. Doniach and Sunjić have suggested⁹⁷ one simple way in which this may be accomplished, namely, by measuring the peak asymmetry index, the ratio of the absolute value of the peak energy minus the half-height energy on the high-binding-energy side to that on the low-binding-energy side of the line. These authors have also furnished a table of the asymmetry index versus the singularity index α , where

$$\alpha = \sum_{l=0}^{\infty} 2(2l+1) \left(\frac{\delta_l}{\pi} \right)^2 \quad (44)$$

δ_l being the phase shift of the l th partial wave for scattering of conducting electrons from the hole potential, in the spirit of the Mahan model.

Several Mg 2s line spectra taken in the present work have excellent statistics and are therefore amenable to accurate analyses of this type. These spectra were taken digitally with 0.04 eV per point. There are no complications due to spin-orbit effects if one chooses a core s level, and spectra were chosen for analysis only if there was clear evidence that the sample was uncontaminated by surface impurities such as oxygen, carbon, or water vapor. In the analysis of these lines we neglected an instrumental broadening of 0.55 eV which was assumed to be symmetrical. Lifetime broadening is taken into account in the

theoretical estimates of asymmetry parameter, alpha. The experimental value for alpha was determined after the subtraction of a smooth inelastic background. Average values for several Mg 2s line spectra are reported in Table XVI, the quoted uncertainties being derived from the deviations of individual results from the mean.

It has been suggested to us^{96,98} that the variation in asymmetry index with valency among the simple metals may be of even greater theoretical interest than the absolute values of such asymmetries. We have therefore re-examined s-core-level XPS spectra from pure samples of⁹⁹ Al and⁹⁹ Li with the results shown in Table XVI. Dow and Sonntag¹⁰⁰ have suggested an empirical prescription ($\alpha_0 \approx 0.068r_s$) for calculating the Mahan exponent α_0 in terms of the electron-gas radius parameter r_s .¹⁰¹ This was done for Al, Mg, and Li by use of the expression for α_1 obtained by Nozières and de Dominicis,⁹² namely

$$\alpha_1 = \frac{2\delta_1}{\pi} - \sum 2(2l + 1) \left(\frac{\delta_l}{\pi} \right)^2 = \frac{2\delta_1}{\pi} - \alpha \quad (45)$$

where $l = 0$ primarily; the Li soft-x-ray absorption edge did not, however, appear to follow this rule precisely.

The present results may be expressed in terms of the measured singularity indices α of Table XVI and α_0 , calculated via r_s ¹⁰¹ and the rule¹⁰⁰ $\alpha_0 \approx 0.068r_s$; see Table XVI. These results may then be compared with the form of the α -versus- α_0 curve calculated from the phase shifts δ_l .⁹⁶ Such a comparison is shown in Fig. 9. No simple relationship is apparent. A quantitative measure of the asymmetry in sodium would be of assistance in seeking to clarify this situation.

Recently, Doniach⁹⁸ has pointed out to us that α may be explained in terms of change in atomic potentials on core-level ionization. Using this concept, he has made the rough estimate $\alpha \sim 1/6$ for these simple metals, in fairly good agreement with the present experimental results. These line asymmetries are the analog of shake-up satellites in gas phase spectra. For the case of polar materials, the linewidths are broadened by phonon broadening^{102,103} which is analogous to vibrational broadening observed in molecules.¹⁰⁴

5. Plasmon-loss spectra^{*}

Figures 10 and 11 show typical core spectra from a metal. Several features may be discerned: (1) the primary peak which is asymmetric, (2) a long tail, and (3) several discrete satellites. Each distinct spectral feature arising from an electron being ejected from free-electron-like metal specimens showed characteristic satellite structure corresponding to energy losses by some electrons through the formation of plasmons of characteristic energies. The Mg plasmons will be discussed here, as an example. Plasmon formation is a well-understood many-body effect. A systematic study of energy-loss peaks in XPS has been previously reported by Pollak et al.⁹⁹

Even the valence band peak in Mg had three identifiable plasmon satellites, as shown in Fig. 11. Also shown is the best-resolved plasmon structure that we were able to obtain in this work, on the 2p line of Mg. The asymmetric shape of the first bulk plasmon

^{*}Based on work done in collaboration with L. Ley, F. R. McFeely, J. G. Jenkin, and D. A. Shirley and published in Phys. Rev. B 11, 600 (1975).

peak is evident. The surface plasmon peak is clearly resolved from the bulk plasmon peak, and a peak that we can assign to one bulk plus one surface plasmon ($P_1 + P_S$ in Fig. 10) is partially resolved. Since this work was carried out on a polycrystalline source with a wide acceptance angle, the energy resolution is not comparable to that available from electron energy-loss studies, but reliable plasmon energies can nevertheless be obtained. Derived plasmon energies are set out in Table XVII. Our weighted average values of

$$\begin{aligned}\hbar\omega_p(\text{surface}) &= 7.3(1) \text{ eV} \\ \hbar\omega_p(\text{bulk}) &= 10.7(1) \text{ eV},\end{aligned}$$

are in excellent agreement with the values of 7.1 and 10.6 eV given by Powell and Swan.¹⁰⁵ Our ratio

$$\frac{\omega_p(\text{bulk})}{\omega_p(\text{surface})} = 1.47,$$

is slightly smaller than their (1.49), but still well above the value $\sqrt{2}$ expected on the simplest theory.

6. Correlation satellites

In the previous sections, we have given several examples of many-electron interactions in photoemission spectra from solids. The consequences of these phenomena on the observed $I(E)$'s were just slight perturbations -- shifting of peak position and extended tailing on core-level peaks, etc. Thus the simple one-electron picture remained a useful framework for the interpretation of photoelectron spectra. We will now consider the role of electron correlations. Electron correlations and many-electron interactions have

received a large amount of attention. References 106-146 give some general references to theoretical discussions on this topic. In this section, we will show some examples where the conventional one-electron picture loses its validity and in fact for the case of the "4p levels" in the elements from about $Z = 48$ to $Z = 69$, it practically breaks down. The origin of correlation satellites in PES has been recently treated theoretically by Martin and Shirley.^{46,147} The particular satellite, in which we are interested, is that due to intra-shell correlation in the final-state and has been observed earlier in a few cases.¹⁴⁸⁻¹⁵³ One of the best examples, both theoretically and experimentally, are the satellites associated with the Mn 3s (⁵S) hole state in MnF₂ (149, 154, and Chapter 4, Sections B and C). In the Mn 3s case the final-state wave function ψ_f cannot be described simply by a single determinant such as

$$|\psi_f\rangle = |[Ne] 3s^1 3p^6 3d^5; (^5S)\rangle.$$

This state mixes very strongly with other configurations such as $[Ne] 3s^2 3p^4 3d^6, (^5S)$ which is related to the $[Ne] 3s^1 3p^6 3d^5 (^5S)$ configuration by a virtual double excitation $3p^2 \rightarrow 3s3d$. Thus the 3d hole state is best described by an admixture of configurations such as

$$|\psi\rangle = a|[Ne] 3s^1 3p^6 3d^5] + b|[Ne] 3s^2 3p^4 3d^6] + \dots$$

or

$$|\psi_1\rangle = C_{11} |3s^1 3p^6 3d^5\rangle + \sum_{j=2}^N C_{ij} |\phi_j\rangle.$$

Since the intensity of PES peaks are proportional to $|C_{ij}|^2$, we would expect to observe peaks corresponding to these roots. These

satellites were predicted by multi-configurational Hartree-Fock (MCHF) calculations performed by Bagus and co-workers¹⁵⁴ and confirmed by experiment.¹⁴⁹ These correlations are principally atomic in nature. The observations we report are from solid specimens. However, the orbitals involved for the most part are very atomic-like. Within the Hartree-Fock one-electron scheme, the simplest way of treating electron correlation and still maintaining a good physical picture is by means of introducing configuration interaction (CI). It should be noted the Hartree-Fock approach already has some correlation -- "pre-correlation"¹³⁵ -- which is included through the use of anti-symmetrized wave-functions which are required by the Pauli Principle. Thus the spin-parallel electrons are surrounded by a "Fermi hole." However, correlation due to the "Coulomb hole" is neglected within the Hartree-Fock approximation.

For our discussion it will be useful to use the terminology of Sinanoglu.^{111,134,141,145} Correlation can be classified into three classes. First one defines the Fermi Sea which is the set of all occupied spin orbitals and all other spin orbitals which are nearly or quasi-degenerate with these. The spin-orbitals which will be employed in these discussions are Hartree-Fock spin-orbitals so in this case the Fermi Sea is the Hartree-Fock (HF) Sea. The three classes of correlation are then classified as: (1) Internal Correlation - This involves virtual transitions of electrons within the HF sea, e.g., for the case of Mn in MnF_2 , the strong mixing of the $3s^1 3p^6 3d^5$ (5S) final-state with the configurations $3s^2 3p^4 3d^6$ via the virtual excitations $3p^2 \rightarrow 3s 3d$ or with the configuration

$3s^1 3p^4 3d^7$ (5S) via a $3p^2 + 3d^2$ excitation are internal correlations.

In the above example, the $3p^2 + 3s 3d$ excitation is only about 10 eV above the Hartree-Fock configuration while the $3p^2 + 3d^2$ excitation is about 100 eV above the HF configuration, thus the first configuration is expected to mix much more strongly with the HF configuration than the second configuration. Note also that by symmetry the $3p^2 + 3s 3d$ excitation cannot yield a 7S final-state. This is responsible for the reduced multiplet splitting between the 7S and 5S final-states in Mn 3s hole-state in MnF_2 , i.e., the

$[Ne] 3s^1 3p^6 3d^5$ (5S) final state is stabilized by correlation but the $[Ne] 3s^1 3p^6 3d^5$ (7S) state is not lowered much by such a CI.

(2) Semi-Internal Correlation - In this case, the virtual excitation includes one electron shifting within the HF sea and another shifting from inside to outside the HF sea. An example of this would be a $3p^2 + 3s 4d$ excitation from the $3s^1 3p^6 3d^5$ configuration. It would be expected that such a correlation would not be as important as the corresponding internal correlation because there would be poorer overlap of such configuration with the HF configuration.

(3) External Correlation - These consist of virtual excitations of pairs of electrons from within the HF sea to outside the HF sea. These should not be as important as internal- or semi-internal correlation. Note also (1) and (2) can only occur for open shell systems (a PES final-state fulfills this condition) and are important because of the near degeneracy of the orbitals involved. This explains the observation that intra-shell correlations are much more

important than inter-shell correlations as demonstrated respectively by the observations of the Mn3s and Mn2s hole states in MnF₂¹⁴⁹ (see Chapter IV, sections B and C) and also 4s and 5s hole states in the rare earths (See Chapter IV, section F).^{155,156}

The result of such correlations, on a PES spectrum, is a satellite which corresponds to a final state resulting from a virtual double excitation from the primary final-state. This satellite "taps" intensity from the primary peak. The correlation also lowers the energy of the primary peak. The lowering of energy by correlation and the loss of intensity of the primary peak to the satellite peak is balanced by the satellite peak intensity and energy according to a sum rule for spectral intensity

$$E_{\text{corr}} = \frac{\sum_{i=1} (I_i/I_{\text{un}}) \Delta_{\text{sat}}}{\sum (I_{\text{corr}}/I_{\text{un}})}, \quad (46)$$

where E_{corr} is the correlation energy of the primary state, I_{corr} is the intensity of the correlated primary state, I_{un} is the intensity of the uncorrelated, "Koopmans' Theorem" primary state, I_i 's are the intensities of the correlation satellites and Δ_{sat} is the energy of the correlation satellite relative to the energy of the uncorrelated "Koopmans' Theorem" primary state energy. Manne and Aberg,¹⁵⁷ Lundqvist,¹⁵⁸ and Martin¹⁴⁷ have derived analogous sum rules. Thus the centroid of the spectral density corresponds to position of the peak without correlation, i.e., Koopmans' Theorem (see Fig. 12). This sum rule has been quantitatively verified for the case of the Mn 3s and 3p levels in MnF₂ (Chapter IV, sections B and C). From

the above classification scheme of correlation we should be able to predict when these correlation satellites would be strong in a PES Spectrum. This should be whenever internal correlation is favorable. Thus other transition metal ions with unfilled 3d shells might be expected to exhibit these satellites in their 3s spectra. These have been observed in the difluorides of Fe, Co, and Ni (Chapter IV, section D). The 3s spectrum for Fe is shown in Fig. 13. Recently Viinikka and Öhrn¹⁵⁹ have studied configuration mixing in the 3s hole state of Fe, Co, and Ni ions. Their calculations yield adequate description of our spectra and confirm the importance of intra-shell correlation. Furthermore, several of the elements prior to the 3d metal series should also exhibit satellites resulting from the virtual double excitation $3p^2 \rightarrow 3s\ 3d$. Such satellites have been observed in the K 3s spectra from KF, KCl and KBr (see, for example, Fig. 14). (There is evidence in KI but the I 4d overlaps the K 3s region.) Also, the Cl 3s level in NaCl and KCl (see Fig. 15) exhibits such features. Wertheim and Rosencwaig¹⁴⁸ observed in this satellite the Cl 3s spectrum of LiCl as well. In the alkali halides the 3s, 3p, and 3d orbitals should maintain much of their atomic character, and this picture of the virtual double excitation works well. It would be interesting to follow this effect in some II-VI compounds where the levels involved are band-like rather than atomic-like. Unfortunately, the compounds which we have studied such as ZnS and CdS, the electron energy loss structure from the very intense cation outermost d-level swamps the expected structure from the sulfur "3s" level. Analogous

correlation effects should be observed in elements of higher rows of the periodic table; that is, the $3p^2 \rightarrow 3s \ 3d$ virtual excitation should be generalized to

$$np^2 \rightarrow ns \ nd . \quad (47)$$

Thus it is not surprising that satellites are observed in the 4s and 5s spectral region for Kr and Xe respectively by Spears.¹⁵² The multiplet splitting in the rare earth 4s level is greatly reduced by intra-shell correlation.¹⁵⁵ We have observed these features in the adjacent alkali and halide ions in our studies of the alkali halides (see Figures 16 and 17). These also appear in spectra from Sr 4s in SrF_2 , SrO, and $SrTiO_3$ and Ba 5s in BaF_2 .¹⁶⁰ Tables XVIII and XIX summarize the observed data for these satellites. Table XIX indicates two trends in the separation of the correlation satellite from the primary peak. First across a row, the separation increases with increasing Z. Secondly, descending a column, the separation decreases with increasing Z. At this point, we do not want to make any comment about trends in intensity, since the relative intensities are very uncertain for several reasons such as possible overlap with discrete loss structure and uncertainty in inelastic scattering contributions. This problem however deserves more detailed attention in the future. The intensities from the gas phase data should be much more reliable.

If we increase l by 1 in (47) we get

$$nd^2 \rightarrow np \ nf . \quad (48)$$

Thus for $n \geq 4$ the double excitations like (48) become possible.

One might thus expect strong configuration mixing in the 4p-hole state.

Satellites may then be expected in the 4p spectra in the region around Xe in the periodic table. Gelius first reported such satellites in Xe and a few of its neighboring elements¹⁶¹ (I through Ba). We have studied the 4p spectral region of the elements in the region $Z = 41$ to $Z = 83$. The trends are shown in Figs. 18-20 (see Appendix A-9 for more detailed spectra). Spectra from compounds of these elements have been reported by Fischer *et al.*¹⁶²

First we describe the evolution of the 4p spectra. We see the 4p spectra for Mo is rather normal and then from Ru to Ag these levels rapidly broaden and by $Z = 48$ Cd, the 4p level is no longer distinct but very broad (~ 20 eV wide). Around Te, a $4p_{3/2}$ peak starts to emerge but there is still a very broad "peak" (~ 40 eV wide). At I, a $4p_{3/2}$ peak becomes well formed but with structure and to higher binding energy there is no evidence of a " $4p_{1/2}$ " peak but in this region there are several sharp discrete features spread over a range of several eV. These features persist in Cs, Ba, La, and Ce. The region Pr ($Z = 59$) through Tm ($Z = 69$) are complicated because multiplet splitting is dominant, but by Yb where the 4f level becomes completely filled, the $4p_{1/2} - 4p_{3/2}$ structure has reformed. The behavior of these spectra can be qualitatively explained as being due to several channels becoming favorable or not compared to the single 4p excitation. As seen from Fig. 21, where various orbital energies are plotted vs. Z , in the region below $Z \geq 50$ (Region I) it takes less energy to ionize the two 4d electrons than one 4p electron and in the region $Z \geq 70$ (Region III) it is less favorable to ionize

two 4d electrons than one 4p electron. In the intermediate region (region II) the two excitations are nearly degenerate and as pointed out by G. Wendin and M. Ohno¹⁶³ there should be a very strong coupling. Thus the 4p hole decays rapidly by a super Coster-Kronig transition, and so the 4p4d4d collective resonance channel accounts for the broad features in region I and II. The sharp discrete features arise from strong configuration interaction via the $4d^2 \rightarrow 4p4f$ virtual excitation. This channel becomes closed at Yb ($Z = 70$) which in its elemental form is divalent and possesses a filled 4f shell. A comparison of Gelius' Xe results with Δ SCF calculations is informative. The relativistic Δ SCF calculations yield core-level binding energies in reasonable agreement with experiment except for the 4s and 4p levels which are about 10 eV lower than predicted. This indicates that these levels are strongly stabilized by internal correlation. Lundqvist and Wendin¹⁶⁴ have given a general discussion of the role of collective effects in these spectra, and preliminary calculations have been carried out by Wendin and Ohno¹⁶³ for Ba and Xe using the Random Phase Approximation with Exchange (RPAE) which confirm the strong collective behavior. Curves similar to Fig. 21 suggest a collective resonance involving a 4d ionization with a double 4f ionization at about Ra ($Z = 88$) (Fig. 22) and a 5p collective resonance (5p ionization with double 5d ionization) around Th ($Z = 90$) (Fig. 23). Bi ($Z = 83$) is the highest Z element we have studied in the course of these investigations and its 4d and 5p spectra (Fig. 24) do not show signs of such a collective resonance. Uranium compounds would be good

cases to look for these possible effects. The 5p spectra might also be expected to exhibit configuration mixing via $5d^2 \rightarrow 5p5f$ excitation channel.*

From the few cases where we have observed these correlations it appears as a general rule of thumb that when there are several possible states, the state of lowest multiplicity is the most affected. In the Mn 3s hole state, it is the 5S state which is affected the most and in the case of the 4p spectra the $4p_{1/2}$ hole-state is the most affected but the high resolution study of Xe 4p spectra by Gelius did show some structure in the $4p_{3/2}$ level. We note also that there are possibilities of observing initial state configuration interaction.¹⁶⁵

We have studied several compounds with Cd, In, Sn, Sb, Te, and I as constituents (see Figs. 25 and 26). The 4p spectra are very similar to that obtained from the pure elements. This is not too surprising since the 4p and 4d orbitals are bona fide core levels and the 4f orbitals are probably very spatially localized and atomic-like as studies of the rare earth 4f levels showed.^{166,167} Future studies which may be useful would include investigation of the elements in the vapor phase and to systematically study compounds and molecules of these elements.

Finally to conclude this section, we would like to make a connection with other experiments. It is obvious that these effects should be observed in experiments which have similar final-states.

$L_{en}(2p-3s)$ x-ray emission spectra should, for example, exhibit

*This may be the explanation for the behavior of the 5p spectra in uranium compounds recently reported by B. W. Veal, D. J. Lam, W. T. Carnall, and H. Hockstra, Phys. Rev. B 12, 5651 (1975).

satellites in the spectra of Cl through Ni similar to the satellites in the 3s PES spectra of these elements. In fact these satellites have been observed for quite some time.¹⁶⁸ However, it was Cooper and La Villa¹⁶⁹ who gave the first clear, correct, and unambiguous identification of these satellites in L emission from Ar and K^+ and Cl^- in KCl. In x-ray emission (XES) work these satellites have been termed "Semi-Auger effect" by those authors¹⁶⁹ and as the "radiative Auger effect" by others.¹⁷⁰ These are exactly the same satellites as the above mentioned correlation satellites. (See Table XVIII) Recently Werne *et al.*¹⁷¹ have obtained high resolution XES results for the ArL emission. ScL emission has also been recently observed¹⁷² and shows features attributable to correlation satellites. Also, previous work on Ti, Cr, Fe, and Ni indicate such satellites¹⁷³ but these cases should be complicated by multiplet splitting. La Villa predicts these satellites in Ca at about 20 eV.¹⁶⁹ They have been observed in XPS of Ca 3s (CaF_2) spectrum at about 16 eV.¹⁷⁴ These satellites have been observed in the Cl emission from chlorocarbon compounds.¹⁷⁵ It would be interesting to systematically study these compounds in detail with high resolution XPS or XES since all the levels involved should be strongly perturbed by molecular orbital formation.

Another experiment which would be expected to exhibit these satellites is the (e, 2e) experiments which are formally equivalent to PES. These experiments do in fact show such a satellite with the Argon 3s level.¹⁷⁶ The intensity appears to be much larger than the

XPS results and this is not fully understood. Strong effect of intra-shell correlation have been observed in AES measurements of the noble gases.¹⁷⁷⁻¹⁷⁹

One other comparison between XPS and XES satellites should be made. Satellites in XPS due to shake-up (charge transfer) are well known.¹⁸⁰⁻¹⁸⁹ These satellites can be especially very intense in the case of the transition metal compounds where the charge transfer is from the ligand p orbital to a metal d orbital. Some examples from our transition metal halide study are given in Figs. 27 and 28 for 2p spectra. These satellites are not observed in the $K\alpha(1s-2p)$ XES spectra¹⁹⁰⁻¹⁹² and can be shown to be forbidden.¹⁹³ Thus comparison of XPS and XES is quite useful in determining the origin of various satellites.

7. Comparison of valence band spectra obtained from PES, AES, and XES: The role of core- and valence-holes.^{*}

Photoemission starts from the N electron ground state of a system and goes to a N-1 electron final state. It is interesting and instructive to compare the XPS representation of the occupied valence electron density of states with those obtained by AES which starts from an initial state already with one hole and proceeds to a final state with two holes and with XES which possesses a hole in both the initial- and final-states. All three techniques have been used to obtain DOS information. We will compare for clean Mg metal the results from XPS VB spectra and photon excited $KL_{23}V$ and KL_1V AES

^{*}Based on work done in collaboration with L. Ley, F. R. McFeely, J. G. Jenkin, and D. A. Shirley and published in Phys. Rev. B 11, 600 (1975).

and the L_{23} XES of Neddermeyer.¹⁹⁴ These spectra are shown in Fig. 29. A scheme for classifying the various initial and final states is illustrated in Fig. 30.

The states are labeled according to the type of hole present, (e.g., $1s$) and the core- and valence-hole "quantum numbers" C and V . The valence-band (local) density-of-states profile will be different for the $C = 1$ states than for $C = 0$ states because the core hole attracts a screening charge. We shall denote the density of states in the $C = 1$ level as $\rho_1(E)$ and in the $C = 0$ levels as $\rho(E)$. In this notation the selection rules are $\Delta(C + V) = 0$ for the x-ray transitions and $\Delta(C + V) = +1$ for photoemission and Auger emission, with the former going upward and the latter downward in energy. The transitions with which we are concerned in Mg are shown in Fig. 30.

Valence-band photoemission to the $3s(01)$ state proceeds within the $C = 0$ manifold: therefore it can in principle measure $\rho(E)$, in the approximation that effects such as cross-section variation across the band and differential final-state relaxation may be ignored. By this argument the experimental spectrum of the Mg valence bands (Fig. 29 top panel) should give a good representation of $\rho(E)$. We note that the experimental spectrum does not have the simple shape that would naively be expected on the free-electron model; viz, a monotonic increase of intensity with energy to E_F and a sharp drop at E_F . Neddermeyer's K β spectrum indicates the p-states concentrated at the top of the valence band and his $L_{2,3}$ spectrum indicates s states dominate at lower part of the band. Detailed comparison must await band-structure calculations of partial density of states weighted by cross-section factors.

The $L_{2,3}$ x-ray emission spectrum of Neddermeyer¹⁹⁴ is reproduced in Fig. 29. The sharp peak at E_F in this spectrum has been variously attributed to a many-body effect -- the Mahan anomaly -- or to one electron-band-structure effects. There is no evidence whatever for such a peak in the photoemission spectrum (the 0.55 eV FWHM instrumental resolution of our spectrometer would broaden such a peak if it were present, but could not obscure it completely). This does not necessarily mean that the peak could not be a band-structure effect, because the "local density-of-states" profile studied in the XPS experiment is that of the $C = 0$ states, with no core hole present. If variations in relaxation energy and cross-section effects across the band can be ignored, XPS would therefore yield $\rho(i)$. Under similar assumptions XES would give $\rho_1(E)$, since $C = 1$ in the initial state (the 2p hole state) in this case.

The XES spectra depends on the dipole coupling matrix between the valence band and the core-state. Due to symmetry selection rules for the dipole matrix element, $L_{2,3}$ spectra sample the density of s and d states. K β spectra would reflect the density of p states.

A better comparison can be made between the $L_{2,3}$ XES spectrum $KL_{2,3}$ V Auger line (Fig. 29). In the $KL_{2,3}$ and the Auger transition, both initial and final states belong to the $C = 1$ manifold. Thus, again neglecting cross-section and relaxation variation across the band, this line should measure $\rho_1(E)$, as does the XES spectrum.

The $KL_{2,3}$ V peak has approximately the same width as the other valence-band peaks (~ 7 eV). Like them, it is relatively steep on the high-kinetic-energy (Fermi edge) side. Its shape differs in

detail from those of the XPS and XES peaks, however. It shows no strong evidence for a peak at the Fermi edge (a shoulder is present), thus suggesting that the XES peak is a collective effect rather than a density-of-states effect. In addition, the $K_{L_{2,3}}$ V Auger peak is more peaked about 2 eV below the Fermi edge than are the XPS or XES peaks. We interpret this as evidence that the 2p hole state tends to attract valence states and concentrate them on the host Mg atom, yielding a peak in the density of states. It would be premature to interpret the valence-band spectra in Fig. 29 further at this time. We can, however, conclude that the x-ray anomaly probably arises from causes other than the density of states, that $\rho_f(E)$ differs from $\rho(E)$, showing the effect of screening of the 2p hole on the valence band, and that cross-section variation is important.

These spectra show that the initial state has large effect. One must take care in interpreting results of these probes especially XES and XPS in terms of initial density of states. This probably accounts for some of the varied success in obtaining densities of states from these techniques.¹⁹⁵⁻²⁰⁸ We will see from Chapter V, XPS DOS appear to give very good pictures of the initial density of states.

D. Conclusions

To summarize the results of this chapter, PLS measures a convolution of (1) final-state effects (modulation by final-state conduction band density of states), (2) initial occupied valence-band density states, (3) transition probability (cross-section), and (4) various many-electron effects. (1) has been shown not to be

important for studies done in the XPS regime.^{11,15} (3) was shown to actually increase the amount of information obtained by PES because it reflects the partial density of states. The effects of (4) were shown, for the most part, to be minor and fairly well (at least qualitatively) understood; however, in certain cases, many-electron effects can completely obviate the one-electron picture. Thus for the most part PES (in XPS regime) gives a good picture of (2), the one-electron density of states.

E. References

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TABLE I. Experimental energies (in eV).

Feature	E_p^F	FWHM	Rel. intensity ^a
2s peak	1196.16(25)	5.5(5)	0.19
2p _{1/2} peak	1045.09(15)	1.95(5)	0.58
2p _{3/2} peak	1021.96(15)	2.00(5)	1
2p satellites	~9 and 14 eV below each 2p peak	2 broad peaks, 8-10-eV total width	0.30(5) relative to each 2p
2p _{1/2} -2p _{3/2} splitting	23.15(5)	...	...
3s peak	139.88(15)	2.62(10)	0.035
3p _{1/2} peak	91.31(15)	2.6(2)	0.039
3p _{3/2} peak	88.70(15)	2.6(2)	0.067
3p splitting	2.60(2)	...	...
3d peak	10.18(10)	1.45(2)	0.042
4s, 4p bands	0 to ≥ 10	≥ 10	0.006

^aThese ratios are accurate to about $\pm 10\%$.

TABLE II. Core-level binding energies in zinc (eV).

Level	$E_B(\text{atomic})^a$	$E_B^V{}^b$	$\Delta E_B{}^c$
2s	1205.3	1199.9	5.4
2p ^d	1036.3	1033.4	2.9
3s	149.4	143.6	5.8
3p ^d	97.9	93.3	4.6
3d ^d	15.3	13.9	1.4
	16.1 ^e		2.2

^aEstimated from results in Refs. 55 and 56 by method given in text.

^bExperimental binding energy referred to vacuum level, using $\phi(\text{Zn})=3.7$ eV.

^c $\Delta E_B = E_B(\text{atomic}) - E_B^V$.

^dMean values without spin-orbit splitting.

^eObtained by using Marn's orbital energy plus the relaxation correction of Ref. 56 for Cu.

TABLE III. Atomic binding energies and rearrangement energies (in eV).

Ground-state configuration	Active orbital	$-\epsilon(\text{HIF})^a$	$-\epsilon(\text{OHFS})^b$	$\Delta E(\text{theo})^b$	$E_B(\text{HIF})^c$	$E_B(\text{OHFS})^b$	$E_B(\text{expt})^d$	$\Delta E(\text{expt})^e$
Na($2p^6 3s$)	$2p$	41.31	41.0	4.4	36.9	36.6	38.05	3.26, 2.95
K($3p^6 4s$)	$3p$	25.97	25.9	...	...	...	24.57	1.40, 1.3
Cu($3d^{10} 4s$)	$3d$	13.22	12.43	5.26	7.96	7.17	10.44	2.78, 1.99
Zn($3d^{10} 4s^2$)	$3d$	21.29	...	(5.26) ^f	(16.03)	...	17.31	3.38
Cd($4d^{10} 5s^2$)	$4d, {}^2D_{3/2}$	(21.06) ^g	...	...	...	...	18.28	(2.78)
Cd($4d^{10} 5s^2$)	$4d, {}^2D_{5/2}$	(20.36) ^g	...	...	...	...	17.58	(2.78)
Na($2p^6 3s$)	$3s$	4.95	5.0	-0.3	5.25	5.3	5.14	0.19, 0.14
K($3p^6 4s$)	$4s$	4.01	4.1	...	...	...	4.34	-0.33, -0.24
Cu($3d^{10} 4s$)	$4s$	6.49	6.86	0.28	6.21	6.58	7.72	-1.23, -0.86
Zn($3d^{10} 4s^2$)	$4s$	7.96	...	...	...	...	9.39	-1.43
Cd($4d^{10} 5s^2$)	$5s$	7.21	...	...	...	...	8.99	-1.78

^aFrom Ref. 55.^bFrom Refs. 56 and 66.^c $E_B(\text{HIF}) = -\epsilon(\text{HIF}) - \Delta E(\text{theo})$.^dFrom Ref. 65. Except for Cd, mean multiplet

energies are given.

^e $\Delta E(\text{expt}) = -\epsilon - E_B(\text{expt})$.^fValue for Cu.^gUsing a spin-orbit splitting of 0.70 eV.

TABLE IV. Comparisons of E_B^V and E_B^{atomic} in gases and metals (in eV).

Level	E_B^V	ϕ^a	E_B^V	E_B^{atomic}	ΔE_B
Cu(3d)	3.0(1) ^b	4.5	7.5	15.44 ^c	2.9
Zn(3d)	10.18(15) ^d	3.7	13.88	17.31 ^c	3.4
Cd(4d _{5/2})	11.46(9) ^e	3.9	15.36	15.28 ^c	2.9
Cd(4d _{3/2})	10.47(9) ^e	3.9	14.37	17.59 ^c	3.2
Pb(4f _{7/2})	136.4(2) ^d	4.03	140.5	144.0(5) ^f	3.5
Bi(4f _{7/2})	157.0(2) ^d	4.3	161.3	164.9(5) ^f	3.6

^aReference 70.

^bReference 67.

^cReference 65.

^dThis work.

^eReference 68.

^fReference 69.

TABLE V. Binding energies from XPS in elemental solids and optimized HFS on atoms (in eV).

Level	E_B^a	ϕ^b	E_B^c	$E_B(\text{theo})^c$	ΔE_R
C 1s ^d	284.44(4)	4	288.4	297	8.6
Al 2s	118.4(2)	3.7	122.1	128	5.9
Al 2p	72.9(2)	3.7	76.6	80.7	4.1
Cu 2p _{1/2}	952.6(2)	4.5	957.1	959.7	2.6
Cu 2p _{3/2}	932.8(2)	4.5	937.3	939.3	2.0
Cu 3s	122.45(10)	4.5	126.95	132.0	5.05
Cu 3p _{1/2}	77.23(10)	4.5	81.7	85.5	3.8
Cu 3p _{3/2}	75.07(10)	4.5	79.6	82.9	3.3

^aFrom work in progress in this laboratory.

^bReference 70.

^cReference 66.

^dGraphite form.

TABLE VI. Additional NPS binding energies and optimized HFS results on atoms (in eV).

Level	$E_B(\text{theo})^a$	$E_B^V{}^b$	ΔE_B
Na 2s	71.9	65	6.9
Na (2p)	36.6	33	3.6
Mg 2s	97.7	93	4.7
Mg (2p)	56.3	56	0.3
K 2s	386	379	7
K 2p _{1/2}	303	299	4
K 2p _{3/2}	309	296	4
Ca 2s	450.4	441	9.4
2p _{1/2}	360.9	353	7.9
2p _{3/2}	356.9	350	6.9
Sc 2s	511	504	7
2p _{1/2}	415	411	4
2p _{3/2}	410	406	4
Ti 2s	574	569	5
2p _{1/2}	473.6	465	8.6
2p _{3/2}	486.6	459	7.6
V 2s	641	632	9
2p _{1/2}	534	524	10
2p _{3/2}	525	517	8
Cr 2s	707.1	699	8.1
2p _{1/2}	593.6	553	5.6
2p _{3/2}	583.6	579	4.6
Mn 2s	785	773	12
2p _{1/2}	666	656	10
2p _{3/2}	653	645	8
Fe 2s	862.5	851	11.5
2p _{1/2}	735.8	729	7.8
2p _{3/2}	721.8	715	6.8
Co 2s	943	930	13
2p _{1/2}	810	799	12
2p _{3/2}	794	753	11
Ni 2s	1027.9	1013	14.9
2p _{1/2}	888.1	877	11.1
2p _{3/2}	869.1	860	9.1

^aFrom Ref. 66.^bFrom Refs. 66 and 70.

TABLE VII. Core-level binding-energy shifts for rare gases in metals (in eV).

Atom	ΔE_2 (Ref. 66) ^a	ΔE_2 (Ref. 67) ^b	ΔE_3 (this work) ^c
Ne	3.4	3.0	
Ar	3.6	3.6	2.8
Kr	3	3.5	
Xe	4	3.2	

^aAverage of several core levels.

^bIn copper.

^cAverage of $2p_{1/2}$, $2p_{3/2}$ and $3p$ shifts.

TABLE VIII. Experimental reduction in binding energies, and theoretical estimates based on atomic integrals for exciton states.

Element	Core level	Exciton state	$\Delta E_B(\text{theo})^a$	$\Delta E_B(\text{expt})$
C(graphite)	1s	2p	12.5	8.6 ^b
Na (in Cu)	(c)	3s	4.0	3.0 ^b
Na	2s, 2p ^c	3s	5.0	5.3 ^b
Ni	2s, 2p	3p	4.9	2.5 ^b
Al	2s, 2p	3p	6.0	5.1 ^b
Ar (in Al)	(c)	4s	3.1	2.8 ^b
K	2s, 2p	4s	3.9	5.5 ^d
Ca	2s, 2p	3d	10.7	8.4 ^d
Sc	2s, 2p	3d	12.0	6.5 ^d
Ti	2s, 2p	3d	13.2	6.6 ^d
V	2s, 2p	3d	13.2	9 ^d
Cr	2s, 2p	3d	15.2	6.6 ^d
Mn	2s, 2p	3d	13.3	10.5 ^d
Fe	2s, 2p	3d	17.3	9.4 ^d
Co	2s, 2p	3d	13.3	12.3 ^d
Ni	2s, 2p	3d	13.4	12.5 ^d
Cu	b, c	4s, 4p	5.0	3.6 ^b
Cu	3d	4s, 4p	4.8	2.9 ^b
Zn	b, c	4p	5.0	5.2 ^b
Zn	3d	4p	4.8	3.4 ^b
Kr (in Cu)	(c)	5s	2.9	2.5 ^d
Cd	4d	5p	4.2	3.0 ^d
Xe (in Cu)	(c)	5s	2.5	2.2 ^d
Pb	4f _{1/2}	6p	5.2	3.5 ^d
Bi	4f _{1/2}	6p	5.6	2.5 ^d

^aCalculated from Mann's integrals (Ref. 55) using model discussed in text.

^bFrom work reported herein or in progress in this laboratory.

^cAverage of several core levels.

^dReference 73.

^eIn several cases the average shift for 2s and 2p electrons, from Table VI, was used for brevity. Data are from Ref. 66.

^fReference 68, and Table IV.

^gReference 69, and Table IV.

TABLE IX. Energies in the atomic copper ($L_3M_4M_4$; 1D) Auger transition.

Quantity in Eq. (10)	Identity of this quantity	Numerical value (eV)	Reference
$E^A(j)$	$E(L_3)$	940.1	a, b
$E^A(k)$	$E(M_4)$	10.44	b
$E^A(l)$	$E(M_4)$	10.44	b
$\mathcal{F}(k, l; X)$	$\mathcal{F}(M_4M_4; ^1D)$	25.9	b
$E_P(l)$	$E_P(3d)$	5.3	c

^aThe $\alpha_{12} L_3 M_4$ x-ray energy was taken from Ref. 82.
The optical $3d$ energy was taken from Ref. 65.

^bReference 65.

^cThis is termed the "reorganization energy" in Ref. 81.

TABLE X. Summary of results for the ($L_2M_{41}M_{41}; {}^1D$) energy in copper.

Method	Est. quantity	Value (eV)	R_e (expt) (eV)	R_e (theo) (eV)
E_B (solids)	$E^P({}^1D) - \mathcal{F}(M_{41}, c)$	911.5	$\mathcal{F}(M_{41}, c) = 6.5$	11.0
E_B (atoms)	$E^A({}^1D)$	903.9	$R_e(TA) = 9.6$	15.5
E_B (atoms, two-hole states)	$E^A({}^1D)$	902.4	$R_e(TA) = 11.1$	15.5

TABLE XI. Values of parameters used in Eq. (16) to estimate $R_s(TA)_{\text{opt}}$ for the ground state of transition metal atoms.

Element	$E^A(L_p)^a$	$E^A(G_p)^a$	$F^0(3p, 3p)^b$	σ^0^c	E_N^d	$E^F(L_{3d}M_{3d}Ni_2)^e$	$R_s(TA)_{\text{opt}}^f$	$R_s(TA)_{\text{opt}}^g$
K	300	24	17.1	2.2	(1.9)	248.9	8	11
Ca	357	31	19.3	(2.3)	(2.4)	289.6	12	17
Sc	410	39	20.9	3.5	(2.9)			19
Ti	467	45	22.5	4.3	3.4			21
V	525	51	24.0	4.3	(4.9)			23
Cr	584	83	25.2	4.5	(4.4)			26
Mn	653	63	27.0	4.1	(4.9)			28
Fe	722	70	28.4	4.5	5.3	596.7	23	32
Co	794	76	29.8	5.0	(5.8)	651.0	24	43
Ni	869	84	31.3	5.15	6.3	716.5	29	48
Cu	939	84	32.5	4.65	7.2	773.7	16	16
Zn	1028	95	34.1	3.7	(7.2)	832	16	14

^aFrom Refs. 81 and 66.^bFrom Ref. 55.^cFrom Ref. 83, except K and Zn, from W. Gordy and W. J. O. Thomas, J. Chem. Phys. **24**, 439 (1956); and Ca estimated.^dFrom Ref. 81. Values in parentheses are interpolated.^eRef. 84.^fFrom Eq. (37).^gEstimated as described in Ref. 67. Screening orbitals were assumed to be 4s, *p* (K), 4*p*, 3*d* (Ca), 4s, *p* (Cu), 4*p* (Zn), and 3*d* otherwise.

TABLE XII. Values of parameters used in Eq. (37) to estimate $R_p(TA)_{\text{opt}}$ for the $(L_2M_{23}M_{43})$ transition (in eV).

Element	$E^A(L_2) - E^A(3d)^a$	$E^A(3d)^b$	$E^A(3d, 3d)^c$	ϕ^d	E_R^e	$E^F(L_2M_{23}M_{43})$	$R_p(TA)_{\text{opt}}$	$R_p(TA)_{\text{exp}}$
Ti	452.2	8.3	17.0	4.3	2.0	452 ^f	17	26
V	511.3	(9.5)	18.7	4.3	(2.5)	510 ^f	17	28
Mn	637.4	10.8	21.9	4.1	3.6	637 ^g	21	33
Fe	705.0	(11.6)	23.4	4.5	(3.9)	701.2 ^h	19	37
Co	776.2	12.7	24.8	5.0	4.1	722.8 ^h	22	39
Ni	851.5	(13.5)	26.3	5.15	(4.5)	848.0 ^h	22	39
Cu	929.7	10.4	26.0	4.65	5.3	918.0 ⁱ	10	15.5
Zn	1011.7	17.3	29.1	3.7	(5.3)	991.8 ⁱ	12.4	17

^aFrom $L\alpha_{12}$ x-ray energies, Ref. 82.^bFrom Refs. 81 and 66. Numbers in parentheses are based on interpolated reorganization energies. The Cu and Zn values are based on optical data (Ref. 65).^cFrom Ref. 55.^dAs in Table XI.^eFrom Ref. 81.^fT. W. Haas, J. T. Grant, and G. J. Dooley, Phys. Rev. B **1**, 1449 (1970).^gP. W. Palmberg, in *Electron Spectroscopy*, edited by D. A. Shirley (North-Holland, Amsterdam, 1972), p. 835.^hFrom Ref. 84.ⁱReference 67.

TABLE VIII. Parameters used in Eq. (78) to estimate R_p for the MN_4N_1 transition in eV.

Element, Z	$E^F(M)^a$	$E(N_4)^a$	$E^a(4d, 4\bar{d})^b$	E_K^c	$E^F(MN_4N_1)$	R_p
Ru, 44	541(1)	1.0(1)	15.3	7.7	286 ^d	10.1
Rh, 45	507.5(10)	2.0(2)	16.3	8.2	306 ^d	10.6
Pd, 46	335.4(10)	1.5(2)	16.3	9.0	328.6 ^d	3.5
Ag, 47	368.5(3)	5.5(2)	18.1	10.6	351.7 ^d	1.7

^aThis work. These energies were obtained by us in survey experiments, and do not represent the best accuracy obtainable.

^bFrom Ref. 55.

^cThe reorganization energies from corresponding 3d elements were used, from Ref. 81

^dT. W. Haas, J. T. Grant, and G. J. Dooley, Phys. Rev. B 1, 1449 (1970).

TABLE XIV. Energy parameters for the Na(*KLL*; ¹*D*) Auger transition (in eV).

Sample	$E(1s)^a$	$E(2p)^a$	$E(KLL; ^1D)^a$	R_p^b	$\Delta[E(2p) - E_D(KLL)]^c$
Metal	1071.7	30.4	994.2	9.2	(8.7)
NaI	1070.3	28.3	991.9	4.1	4.3
Oxide ^d	1075.2	32.8	986.8	3.1	3.7
NaF	(1066.8)*	24.8	991.9	(-0.2)	(0)

^aReference energies: top of valence bands (NaI and NaF); sodium Fermi level (metal and oxide).

^bFrom Eq. (40).

^cSee Eq. (41). NaF was used as the reference.

^dThin oxide layer on metal.

*Estimated using $E(1s) - E(2p) = 1042.0$ eV.

TABLE XV — Energy parameters for the $\text{Zn}(L_3M_1M_{25}; {}^1D)$ Auger transition (in eV).

Sample	$E^F(\omega_{p,12})$	$E^F(3d)$	$E^F(L_3M_1M_{25}; {}^1D)$	R_2 ^a	$\Delta[E(3d) - E_D({}^1D)]$
Metal	1021.96 ^b	10.18 ^b	991.8 ^b	6.8	5.2
ZnO	1022.2	10.44	987.4	2.7	1.0
ZnF ₂	1021.5	10.9	985.9	2.8	(0)

^aFrom Eq. (42).^bFrom Ref. 67

TABLE XVI. Asymmetry of XPS core-level lines.

Line	Asymmetry index	α	r_s (Ref. 101)	α_s (Ref. 100)
Mg 2s	1.27 $\pm$ 0.04	0.132 $\pm$ 0.012	2.65	0.190
Al 2s	1.35 $\pm$ 0.02	0.161 $\pm$ 0.008	2.07	0.141
Li 1s	1.42 $\pm$ 0.10	0.18 $\pm$ 0.03	3.25	0.221

Table XVII. Plasmon energies in magnesium (in eV).

Primary prob.	Kinetic energy of primary	P_1	P_2	P_3
$2p$	1437	7.3(1)	10.7(1)	21.5(2)
$2s$	1398	7.4(3)	10.7(1)	21.6(2)
$1s$	183	7.2(3)	10.9(4)	21.8(4)
$KLL(1D)$	1133	...	10.8(1)	21.3(2)
$KLL(1P)$	1140	...	10.6(1)	21.9(5)
Valence limit	1482	...	~10.8	~21.4
Weighted average		7.3(1)	10.7(1)	21.4(1)

Table XVIII. Intrashell correlation satellites

<u>Compound</u>	<u>Method</u>	<u>ΔE_{sat} (eV)</u>	<u>Relative Intensity (%)</u>
<u>Cl 3s</u>			
NaCl ^a	XPS	5.8(3)	26(5)
NaCl ^b	XPS	5.7(3)	--
KCl ^c	XPS	5.6	~ 30
KCl ^d	XES	6	35(5)
LiCl ^e	XPS	6	--
<u>Br 4s</u>			
NaBr ^a	XPS	4.0(5)	50(5)
KBr ^a	XPS	4.1(4)	36(13)
<u>I 5s</u>			
NaI ^a	XPS	3.6(3)	74(10)
KI ^a	XPS	h	h
<u>K 3s</u>			
KF ^a	XPS	14	~ 40
KCl ^a	XPS	14	64(7)
KCl ^e	XPS	14	~ 40
KCl ^f	XPS	13.6	40(8)
KCl ^d	XES	14	21(4)
KCl ^b	XPS	14	--
KBr ^a	XPS	13.7(3)	55(7)
KBr ^e	XPS	14	~ 40
KBr ^f	XPS	13.7	55(15)
KI ^a	XPS	i	i
<u>Rb 4s</u>			
RbCl ^f	XPS	10.1	64(10)
RbCl ^e	XPS	~ 11.5	~ 100(30)

Table XVIII. Intrashell correlation satellites (continued)

Compound	Method	ΔE_{sat} (eV)	Relative Intensity (%)
<u>Cs 5s</u>			
CsCl ^f	XPS	9.3	120(20)
CsI ^k	XPS	~ 10	--
<u>Ar 3s</u>			
Ar ^f	XPS	9.4, 11.9	19(2), 6(3)
Ar ^d	XES	11	35(3)
Ar ^k	(e,2e)	10.7	~ 70
<u>Kr 4s</u>			
Kr ^f	XPS	6.5	31(3)
<u>Xe 5s</u>			
Xe ^f	XPS	4.2, 5.6	11.3, ~ 60
Xe ^k	XPS	4.6, 5.6, 8.0	25(4), 52(4), 20(3)
<u>Ca 3s</u>			
CaF ₂ ^j	XPS	16(1)	--
<u>Sr 4s</u>			
SrF ₂ ^j	XPS	14.1(10)	--
SrO ^a	XPS	13.3(5)	~ 60
SrF ₂ O ₃ ^a	XPS	13.2(4)	--
<u>Ba 5s</u>			
BaF ₂ ^j	XPS	9.9(10)	--
Ba(NO ₃) ₂ ^k	XPS	~ 10	--

Table XVIII. Intrashell correlation satellites (continued)

^aThis work.

^bRef. 153.

^cK. Siegbahn, J. Electron Spectr. 5, 3 (1974).

^dRef. 168. (2p - 3s emission spectrum.)

^eRef. 148.

^fRef. 152.

^gRef. 175.

^hK 3p overlaps.

ⁱI 4d overlaps the correlation state.

^jG. Apai, unpublished data.

^kRef. 161.

Table XIX. Correlation satellite separation from main peak (eV).^a

<u>3s</u>			
Cl	Ar	K	Ca
6	11(25)	14	16
<u>4s</u>			
Br	Kr	Rb	Sr
4	6.5(30)	11	13.5
<u>5s</u>			
I	Xe	Cs	Ba
3.6	6.0(58)	9.3	9.9

^aNumbers in parentheses for the rare gases represent the relative intensity of the correlation satellite to the primary peak.

FIGURE CAPTIONS

- Fig. 1. XPS spectrum of the $n = 2$ peaks of zinc. Alternate points are omitted for clarity except in the 2p peaks. Satellite structure is indicated by arrows at 9 and ~ 14 eV below each 2p peak.
- Fig. 2. XPS spectrum of the 3s, 3p peaks of zinc. Except in peaks themselves, only every fifth point is shown.
- Fig. 3. XPS valence-band spectrum of zinc, on a semilogarithmic scale.
- Fig. 4. Experimental excess binding energies in solids versus theoretical extra-atomic relaxation energies based on model described in text. Line through points has a slope of 0.66.
- Fig. 5. Experimental excess binding energies (points) and theoretical estimates based on atomic-orbital approximation to exciton states, using model described in text (lines connecting calculated points). Top panel: results for 3d series metals. Note break at filled d shell, from Cu to Zn. Bottom panel: rare gases embedded in metals.
- Fig. 6. (a) Difference between core-level binding energies for 3d-transition elements as atoms and metals, after Ref. 80, showing break between Ni and Cu due to reduction in extra-atomic relaxation energy on 3d-shell closure.
- (b) Total extra-atomic relaxation energy for the $L_{3^2}M_{23}M_{23}$ peak in these elements, with a localized final state.

Fig. 6. (continued)

(c) Same for the $L_{3M_{45}M_{45}}$ transition, showing that the final state may be localized. In (a), (b), and (c) points represent experimental results while lines connect predictions of theory described in text.

Fig. 7. Sodium 1s, 2p, and 1D Auger lines as observed in an XPS spectrum, plus free-atom energies. The 2p peaks are made to coincide. For the measured energies see Table XIV.

The 1s peaks nearly coincide, showing that the energy difference $E(1s) - E(2p)$ is nearly constant, while large shifts arising from differences in extra-atomic relaxation are observed in the 1D Auger lines. The free atom values are denoted by the arrows and bold lines. The lower binding energy component of the doublet in the Na 2p region in the NaF spectra is the F 2s peak.

Fig. 8. The $L_{2,3M_{45}M_{45}}$ Auger spectrum of ZnF_2 .

Fig. 9. Values of the singularity index α as a function of the Mahan exponent α_0 from the present experimental results ($\bullet$) and from the calculations of Dow and Franceschetti (Ref. 96), shown —. See the text for details.

Fig. 10. The 1s, 2s, and 2p X-ray photoemission spectra of atomically clean Mg metal, showing plasmon structure. Binding energies are given relative to E_F .

Fig. 11. Plasmon structure on the valence-band peak (top) and the 2p peak (bottom). Note scale changes.

- Fig. 12. Schematic comparison of Koopmans' Theorem spectrum with a correlated spectrum. This representation illustrates the partitioning of energy and intensity through the sum rule (Eqn. 46).
- Fig. 13. The Fe 3s (FeF_2) spectrum. The features to higher binding energies than the Fe3s level are correlation satellites.
- Fig. 14. a) K 3s (KCl) spectrum exhibiting correlation satellite.
b) K 3s (KBr) spectrum exhibiting correlation satellite.
- Fig. 15. Cl 3s (NaCl) spectrum exhibiting correlation satellite.
- Fig. 16. Br 4s (NaBr) spectrum exhibiting correlation satellite.
- Fig. 17. I 5s (NaI) exhibiting correlation satellite.
- Fig. 18. The 4s 4p region of the elements Mo ($Z=42$) to Te ($Z=52$) demonstrating the evolution of the 4p4d4d collective resonance.
- Fig. 19. XPS spectra of the 4s 4p region of La ($Z=57$), Ce ($Z=58$), Yb ($Z=70$), Lu ($Z=71$), and Ta ($Z=73$). La and Ce exhibit sharp discrete features due to correlation states. The $4d^2 \rightarrow 4p4f$ channel is closed at Yb and Lu where the 4f shell is filled. Both the $4p_{1/2}$ and $4p_{3/2}$ levels are observed; however, these lines do display a satellite.
- Fig. 20. XPS spectra of the $4p_{1/2}$ $4p_{3/2}$ region from Ta ($Z=73$), W ($Z=74$), Re ($Z=75$), Ir ($Z=77$), Pb ($Z=82$), and Bi ($Z=83$).

- Fig. 21. Orbital energies from Ref. 57, illustrating final-state effects in the 4p shell. The energy for I ($Z=53$) is adjusted to fit data of Gelius. In region I the collective resonance coincides with 4p states because $\epsilon(4p) + \epsilon(4f) \sim 2\epsilon(4d)$. In region II, the same condition is met but the $d^2 \rightarrow pf$ excitation yields a bound state, hence discrete shakeup lines. This structure is obscured for $Z > 58$ by multiplet splitting. The 4f channel is closed for $Z > 70$ and the simple $4p_{1/2}$ $4p_{3/2}$ structure is restored by $Z = 73$.
- Fig. 22. Orbital energies from Ref. 57 illustrating possible final state effects in the 4d shell.
- Fig. 23. Orbital energies from Ref. 57 illustrating possible final state effects in the 5p shell.
- Fig. 24. a) 4d spectrum of Bi metal.
b) 5p spectrum of Bi metal.
- Fig. 25. I 4p spectra from NaI.
- Fig. 26. I 4p spectra from KI.
- Fig. 27. Co 2p (CoF_2) spectrum.
- Fig. 28. Ni 2p (NiF_2) spectrum.
- Fig. 29. Comparison of XPS VBDOS and photon-excited KL_{23}V and $\text{KL}_{1\text{V}}$ Auger and L_{23} XES (Neddermeyer) for Mg metal.
- Fig. 30. Schematic comparison of shapes of KL_{23}V Auger peaks with XPS spectrum and L_{23} emission spectra. The various states involved are classified using C and V "quantum numbers" as explained in the text.

XBL732-2349

Fig. 1

XBL732-2350

Fig. 2

XBL 732-2353

Fig. 3

XBL732-2352

Fig. 4

XBL732-2351

Fig. 5

XBL736 - 3136

Fig. 6

Fig. 7

Fig. 8

XBL736-3135

Fig. 9

XBL 744-2889

XBL7311-4439

Fig. 10

Fig. 11

Fig. 12

XBL 755-3050

Fig. 13

Fig. 14a

XBL 763-769

Fig. 14b

XBL 763-770

Fig. 15

XBL 763-768

XBL 763-759

Fig. 16

XBL 763-756

Fig. 17

XBL753-2534

Fig. 18

XBL 753-2533

Fig. 19

XBL 755-1381

Fig. 20

Fig. 21

XBL 753-2531

XBL 763-2460

Fig. 22

XBL 763-2456

Fig. 23

Fig. 24a

XBL7511-8678

Fig. 24b

XBL 761-2153

Fig. 25

XBL7510-4159

XBL7510-4174

Fig. 26

Fig. 27

XBL 757-3401

Fig. 28

XBL 757-3402

184, 191 - 2279

Fig. 29

Fig. 30

III. EXPERIMENTAL ASPECTS OF PES AND AES: APPARATUS AND TECHNIQUES

A. Introduction

This chapter will cover various aspects of the experimental techniques and instrumentation used in these investigations of the electronic structure of solids and surfaces. The basic components of a PES system, which are indicated in Fig. 1 of Chapter 1, are 1) the excitation source plus possible monochromator, 2) the electron energy analyzer and other components of the electron optics, and 3) the detection system and its associated electronics. Furthermore, other experimental requirements concern magnetic shielding, sample manipulation and, of utmost importance for solid-state and surface studies, a good vacuum environment. These experimental aspects will be discussed below. These requirements are very similar for AES experiments. Usually, the excitation source in AES is an electron impact source rather than a photon source. In the Auger studies reported here, however, AlK α x-rays were used as the excitation source. All of these various functions must be integrated for a successful experiment, with each component optimized for the mutually exclusive qualities of resolution and sensitivity.

The primary limits to attainable linewidth include the following: 1) the inherent, or natural, width of the level from which the electron is being ejected. (This is a fundamental quantity which has theoretical significance. It is mostly due to lifetime and vibrational

effects (in molecules and solids). To obtain information about the natural linewidth requires instrumental resolution much less than this; 2) the inherent width of the incident radiation which is usually < 20 meV for UV sources and 0.7 to 2.0 eV for the common X ray sources without monochromatization (about 0.2 to 0.5 eV with monochromatization); and 3) the resolving power of the electron analyzer (this is often the limiting factor for the resolution attainable in UPS). The sensitivity depends on a number of factors such as the differential partial photoionization cross-section of the level being studied (an intrinsic factor), the intensity of the incident radiation, geometrical factors (solid angle, etc.), transmission through any grids, and collection efficiency. For general information about many experimental aspects of PES see Ref. 1 to 4.

The basic instrument used in the studies that are reported in this thesis is the HP #5950A electron spectrometer system, which has been previously described.^{5,6} This system has been modified in a number of ways for our investigations of solids and surfaces. First the system was modified for ultra-high vacuum capabilities (UHV)* (including a sample introduction system, sample treatment chamber, and versatile sample manipulation capabilities⁷), a chamber for a double-pass cylindrical-mirror analyzer (CMA) with a UV source and grazing incidence electron impact source was added, and a completely

* By UHV we mean Pressures P such that $P < 1 \times 10^{-9}$ torr. Note, 1 torr = 133.322 Pa, where Pa (Pascal) is the approved SI unit. We will use the more common unit of torr throughout.

digital data collection system based on a dedicated mini-computer was constructed. An overall photograph of the system is shown in Fig. 1. Figs. 2-4 show close-ups of various sections of the system. In the following sections, we will discuss in turn the excitation sources, the electron energy analyzers, the counting system, the vacuum system, and the sample preparation techniques employed in these studies.

B. Photon Sources

Conventional laboratory sources for PES are either X-ray tubes (characteristic lines) or rare gas resonance lamps. Some common photon sources and their energies are listed in Table I.

X-ray sources for PES investigations usually employ the $K\alpha$ lines (1s-2p) transition of the light elements. These lines have energies in the soft-x-ray region. Because they have relatively narrow linewidths and are relatively easy to handle, Mg $K\alpha$ and Al $K\alpha$ are used almost exclusively in XPS studies. The linewidths of the $K\alpha$ lines increase rapidly with Z for two reasons -- first, the $K\alpha$ line actually consists of two spin-orbit split components whose spin-orbit splitting increases with Z; and secondly, the intrinsic linewidth of each component increases with Z due to lifetime effects. Thus higher Z elements have $K\alpha$ linewidths in excess of 1 eV and are not suitable for high resolution studies. There are three ways to obtain a narrower source width than the natural width of Al $K\alpha$ or Mg $K\alpha$: 1) $K\alpha$ radiation from a lower Z element is one possible alternative. Na, the next lowest Z element, is difficult to handle because it

oxidizes very readily. This can be circumvented either by using an Na alloy (or compound),⁸ or by in situ deposition of Na onto the anode.^{9,10} Ne would be a still better source, but it presents difficulty in obtaining reasonable intensity since it must be used as a gas or imbedded in a matrix. The next lowest Z solid element is C; while it would have a very narrow 1s level, its 2p electrons are valence electrons and not core-like. These levels are about 10 eV wide because of solid-state effects.¹¹ 2) Other characteristic lines such as YM_{ℓ} may be employed.^{12,9} 3) The third way of attaining improved X-ray linewidth is by monochromatization. For the work reported here, the $AlK\alpha$ source of the HP #5950A was used. This source is monochromatized by means of a dispersion compensation scheme.^{5,6,13} This scheme utilizes three spherically bent quartz crystals (10T0 plane). The wavelength dispersion of the X-ray line across the sample, is coupled to the dispersion of the electron optics to yield monochromatization. Other schemes of monochromatization have been proposed,^{3,4,14} and the Uppsala group have successfully developed an instrument employing the fine focusing scheme.¹⁵⁻¹⁷

Monochromatized sources have three important advantages over non-monochromatized characteristic x-ray sources: 1) The resolution is improved. $AlK\alpha$ has a natural linewidth of about 0.9 eV. This linewidth is reduced by monochromatization to 0.2 to 0.5 eV.^{5,16-20} 2) Background due to Bremsstrahlung radiation is eliminated.

3) X-ray satellites* are eliminated. Until the implementation of monochromatization, factors 2) and 3) made it especially difficult to study the valence electronic levels of solids.²⁰ Monochromatization, however, greatly reduces the X-ray intensity. In order to gain back this intensity, the HP #5950A system has incorporated a multi-channel electron detector (see Sec. D).^{5,6} Another approach would be to use a rotating anode to increase the power which can be dissipated at the anode.⁴

It is really desirable to have several photon sources of various energies available on a PES system, to permit use of the cross-section variations discussed in Chapter II, and because of the dependence of electron escape depth on energy. Therefore, a UV source is being developed for the HP#5950A system. Several lamps based on either dc or microwave discharge have been described in the literature.²¹⁻³⁰ An early version of the lamp under development at Berkeley is shown in Fig. 5, and close-ups of the lamp attached to the system are shown in Figs. 2 and 3.³¹ Fig. 6 shows a schematic of the lamp. The two basic design considerations are that the lamp must be UHV compatible, and that it yield useful output of HeII radiation. Table II lists the major components in an He discharge. The actual relative intensities of the various components are very sensitive to the particular lamp design and its operating conditions, but generally the radiation consists mainly of HeI α resonance radiation

*K $\alpha_{1,2}$ has several satellites such as the K $\alpha_{3,4}$ line, which are separated from the K $\alpha_{1,2}$ by about 10 eV and have about 10% of its intensity in the cases of Al and MgK α .

with several percent HeII α . Conditions of higher voltages and lower pressures generally increase the percentage of HeII.²¹

The design of the lamp under development is similar to that of Poole et al.²¹ The major difference is the use of a window to act as both a filter to increase the HeII:HeI ratio and as a partial vacuum window. Carbon films of 10 $\mu\text{g}/\text{cm}^2$ ⁽³²⁾ were successfully employed to filter out most of the HeI radiation.³³ The lamp is differentially pumped, so the vacuum in spectrometer chamber is usually $< 5 \times 10^{-9}$ torr. Operating conditions are presently 80-100 mA and 600 V. Preliminary valence spectra of Ag, Cu, and GaSe have been obtained with this lamp. The spin-orbit splitting of the Ga 3d, in GaSe which is less than 0.4 eV, has been partially resolved. Currently, work is in progress to optimize the lamp characteristics and to increase its intensity and stability.

The system also has a grazing incidence electron gun for use as an excitation source with the CMA. This makes possible electron-excited AES measurements. Normally, in AES, an intense electron beam is used as an excitation source. This has several deleterious aspects in the case of solid-state studies; several of the more important effects being: sample heating, radiation damage, and a high background of scattered electrons. The last, in most cases, necessitates data being displayed in a derivative format, rather than as $I(E)$ directly. For these reasons, we have used an ArK α source to minimize beam induced effects and to allow data to be collected digitally and displayed directly as $I(E)$ instead of

in a derivative format. However, since the kinetic energy and line width of Auger electrons are independent of excitation source, the dispersion compensation of the IEP electron optic system is not of use in the Auger studies; in fact, it would tend to make all Auger lines 1 eV wide since the optic system is set for the dispersion of the crystal monochromator, which disperses the X-rays 1 mm across the sample resulting in a 1 eV variation in energy across the sample. This is demonstrated by Table III for the case of Mg metal evaporated onto a strip narrower than 1 mm. The FWHM of the $\text{MgKLL}(^1\text{D})$ line is decreased by about 30% when a narrow strip is used. The intensity was decreased by almost a factor of 3. Note that the Mg 2p line is only slightly narrower (~ 10%). This improved resolution for the photoelectron line may be due to the narrow strip being a de facto slit or to the three monochromator crystals not being perfectly aligned. An adjustor which allows for the adjustment of the position of the monochromator crystal mount is shown in Fig. 7. The adjustment is made by turning a mini-rotary motion feedthrough (see Fig. 4). This allows the adjustment to be made without breaking the vacuum. The adjustment is made by measuring the intensity and resolution of the $\text{Au } 4f_{7/2}$ line as a function of the position of the crystal mount. This procedure can only adjust the three crystals collectively. The alignment of the three crystals with respect to each other must be performed outside the vacuum.³⁴ The PES/AES system also has a 3 KeV electron gun (Physical Electronics Model PHI-04-015). This is used with the double stage CMA (see Fig. 3) and is mounted at a

at a grazing-incidence angle. Thus the differences between photon impact and electron impact AES can be investigated with this system.

As mentioned in Chapter I, there are few good laboratory photon sources in the region between HeII (40.8 eV) and NaK α (1032 eV), except for the M $_{\text{C}}$ ^{9,12} X-ray lines, which so far have not been applied to solid-state studies. Increasing use is being made of synchrotron radiation, which is emitted by electrons and positrons in circular accelerators and storage rings.³⁵⁻⁴⁶ At relativistic energies, the radiation is emitted into a very small angular cone tangential to the path of the particle. As the particle energy is increased, the spectral distribution extends higher in energy. For example, the spectral distribution at two electron energies from the electron-positron storage ring SPEAR at the Stanford Linear Accelerator Center is given in Fig. 8. Table IV summarizes some of the unique features of synchrotron radiation. Thus, with proper monochromatization,⁴⁷ one has a tuneable source from the UV region into the X-ray region. Valuable information has already been learned about the photoemission process from experiments utilizing synchrotron radiation.⁴⁸ Synchrotron radiation is also proving to be a very valuable source for many other experiments besides photoemission.³⁹⁻⁴⁴

C. Electron Analyzer and Optics

The quantity which one desires to measure precisely in most PES measurements is the electron kinetic energy, which, through the energy conservation relationship (Chapter I, Eqn. 1), gives the binding energy. Therefore, the central part of a PES system is the electron energy analyzer. Some requirements for an analyzer are:

1) high resolution ($\Delta E/E \sim 10^{-4}$); 2) high sensitivity (because x-ray sources are not intense and are a couple of orders of magnitude less intense than UV sources); 3) convenient access to source, sample, and detector; and 4) compatibility with UHV operation. Various types of electron energy analyzers have been extensively described.^{1,2,4,49-89} The analyzers are either electrostatic or magnetic and either dispersive or non-dispersive. For high intensity pulsed sources (e.g., from high power plasmas or electron-positron storage rings) time of flight analysis has been suggested.⁸⁷⁻⁸⁹ Several commercial PES systems are available and have greatly aided the development of PES. Several comparisons of these various systems have been published.⁹⁰⁻⁹⁴ The main instrument in these studies was the hemispherical electrostatic analyzer (15.5 cm central radius) of the HP #5905A system.^{5,6} This type of analyzer was first described by Purcell.⁵⁶ As part of its electron optics, the HP #5950 also employs a four element electrostatic lens system which serves to focus and magnify the sample image and decelerate the electrons' kinetic energy to 115 eV. The lens is an integral part of the dispersion compensation scheme, which has been described by Siegbahn et al.^{5,8,9} and was developed by the Hewlett-Packard Company (Palo Alto, California).^{5,6} The monochromatization is accomplished by matching the dispersion of the X-rays with that of the electron optics. This results in a 10 eV range of electron energies being focused in the focal plane at the detector. This is advantageous for multi-channel electron detection. A schematic is given in Fig. 9. Unfortunately, the dispersion compensated optics requires that the specimen be flat and sets a

narrow limit on the specimen height. Otherwise the resolution will be degraded and the peak position shifted. For work with other excitation sources (UV discharge lamp and grazing incidence electron gun), a double stage cylindrical mirror analyzer^{69,72} (Physical Electronic Industries Model PHI-255 and 255G) with spherical grids for retardation has been incorporated into our PES system. A schematic is shown in Fig. 10. Figures 11-13 show the CMA and its Mu-metal shielding. Figures 1-3 show the CMA as part of the PES system. This analyzer is operated in a retarding (constant resolution) mode. The resolution is determined by the pass energy and is optimized to give the best resolution with reasonable intensity.⁷² With a CMA, the sample position is very critical.^{72,73} Also, the CMA is not well suited for measurements requiring angular resolution unless an aperture is provided.⁸⁵

D. Spectrometer Control and Data Acquisition

A schematic of our modified HP #5950A spectrometer control and data handling system is shown in Fig. 9. By means of the dispersion compensation scheme, the electrons are focused at the exit plane onto an array of parallel lines 10 eV across, each line corresponding to a particular energy. The electron detection system consists of a large area position sensitive electron detector array which consists of a tandem micro-channel plate assembly, a phosphor screen, and a television camera. This system is equivalent to an array of 250 x 60 high-gain electron multipliers. Thus a 10 eV energy range is detected simultaneously. This detection scheme is necessitated to

compensate for the approximately two orders of magnitude reduction in X-ray flux caused by the monochromatization. Spectra are obtained by stepping the retarding voltage. The electrons are retarded (decelerated) to 115 eV, with the analyzer set to accept electrons with kinetic energy between 110 and 120 eV. After the electrons are amplified by the electron multiplier, they are accelerated onto a phosphor screen and create light pulses. These light pulses are imaged and stored on the photosensitive target layer of a vidicon television tube (see Fig. 14 and 15) until converted into electrical pulses and erased by a television raster scan by the vidicon electron beam. Each spot is counted and assigned a particular energy. The lines of the TV raster are arranged such that each line corresponds to a different electron energy. Figures 16 and 17 show the Au 4f lines displayed on a TV monitor picture of the image at the phosphor plate. The vertical direction corresponds to energy (increasing from bottom to top). Two horizontal lines corresponding to the gold $4f_{5/2}$ and $4f_{7/2}$ lines can clearly be seen. The TV signal is processed by an interface. A low pass filter removes the high frequency noise and a high pass filter smooths the variation in the dark level throughout the T.V. picture. When the pulse height exceeds the discrimination level, which is adjusted to be above the dark noise, an output pulse is generated. An electronic circuit has been devised and implemented to assist in determining the proper discrimination level. This circuit adds a black dot to the middle of each scintillation displayed on the TV monitor (see Fig. 17) when the pulse height is

higher than the discriminator level. The discrimination level is easily adjusted by a 10 turn pot on the front panel. This detection scheme using a TV camera has the advantage that the signal is easily conducted through the vacuum enclosure and the image can be stored long enough to be read out. One problem with this system is that it can be easily saturated. The Au 4f lines can saturate the detector at 1/4 of the available X-ray intensity. Also, the vidicon has a very limited lifetime (~ 2000 hours). We have recently started to use a silicon tube instead of the vidicon. So far it has not proven feasible to collect amplified electron pulses directly at the detector output. This, however, should be possible with a MOS field effect transistor array or a CCD array.^{4,95,96}

We always had observed a systematic periodic noise superimposed on our spectra which required counting times of about 10 times that required by normal counting statistics. Several steps were undertaken to try to eliminate this source of noise. The first attempt to clean up the noise involved shielding and filtering the X-ray generator, separation of the primary power for the spectrometer voltages and detection system from that for the X-rays and ion pumps, etc., and improved grounding precautions. At this stage, the non-random noise actually appeared to get worse because much of the random noise, which had served to mask the systematic noise, was eliminated. At this stage, it was decided to build a completely digitally based control and detection system. A schematic of the system is shown in Fig. 9b. Previously the retarding voltage was swept continuously and

the MCA, which was being used to store the data, was addressed by an analogue signal. There existed a mismatch between the number of horizontal vidicon lines and the number of MCA channels which might be a source of the "beat" in the spectrum. The digital addressing system did improve the resolution, but it did not eliminate the non-statistical noise. The third step in the attempt to eliminate the unwanted "noise" was to eliminate the counting of a scintillation several times. The dots on the phosphor have a finite size which extends over several horizontal TV lines and thus each scintillation gets counted several times. (We determined that each well focused scintillation would be counted on the average of about five TV lines.) A single channel video data counting system was built (see Fig. 9).⁹⁷ The system counts each scintillation on the first detectable video line and an anti-coincidence circuit blanks out the pulse if it is detected at the corresponding point of the next TV line. Currently the computer control program computes the energy assigned to each data channel to compensate for the average shift of 2-1/2 lines. Eventually the system may be modified so that the data count will be put in the memory location corresponding to the centroid of each scintillation. This single channel video data system succeeded in eliminating the coherent noise, which was introduced by the scintillations being counted in several TV lines.

For cases of small samples or when better resolution is required, a variable electronic window (this window is a variable gate which effectively reduces size of the sample in the direction in which the

X-rays are not dispersed in wavelength) was built.⁹⁷ This can be seen in Fig. 16. The two vertical lines indicate the window, and everything not between these lines is blanked out and not counted. Its width can be continuously varied from completely open to completely closed by means of a 10 turn pot. Narrowing of the window does actually improve resolution ~ 10% because of various non-linearities. The position of the window may also be shifted by means of another 10 turn pot. This allows various portions of the sample to be examined.

The center of the PES system is a dedicated mini-computer (HP #2114A with 12 K of memory). The system program DIGAD controls the, now, completely digital spectrometer control and data system. The HP #5950A system program DIGAD has four functions.

1) Input Function - This allows the experimental parameters to be preset, via the keyboard of a teletype. 2) Data Acquisition and Control Function - This function coordinates the data collection. The detected pulses are stored in the computer memory; the storage address codes are generated by the computer, which counts the TV synch pulses and produces a unique address for each line of the TV frame. The program automatically steps the retarding voltage. The energy between adjacent TV lines is approximately 0.040 V. The voltage step is made equivalent to this difference or a multiple of a power of two. For each TV frame, data is taken from 192 of the 215 to 225 data lines that contain video information. The data acquisition and control uses the following algorithm. The number of

steps for a scan ΔW eV wide is determined by

$$\text{No. of steps} = \frac{\Delta W}{10} \times 256 + 192$$

and the time for one scan is

$$\text{Time(sec)} = \frac{\text{No. of steps}}{30} \times 2.$$

Thus a 10 eV wide scan requires 448 steps and 14.9 sec to complete one scan. After each step, the storage address is shifted by one. The voltage is stepped in both directions and data is continuously accumulated. Stepping allows scans of more than 10 eV wide to be accumulated and removes the effect of the detector signature (variation in gain across the channel plate) and the lack of uniformity in the TV camera. In this mode, V_4 is monitored (see Fig. 9a) by a 0.001% digital voltmeter (DVM) (Dana Model 5900) via a 1000:1 attenuation string, which has been calibrated by the National Bureau of Standards.* This voltage is monitored at a specified frequency (usually every tenth scan). This allows accurate binding energies to be obtained and the stability of the system to be monitored during runs which require long accumulation times (such as some valence band spectra). The stability of V_4 has been about ± 20 mV over 12-hour accumulation times. During accumulation, the spectrum is continuously displayed by the MCA display system (see Fig. 9a). 3) Output Function - This allows output of data via either the teletype unit, parallel printer, magnetic tape unit,

* This has been recalibrated after a year of operation and found to be within 0.001% of its original value.

and/or x-y recorder. 4) Data Massage Function - Some preliminary on-line data analysis and massaging is possible. At any time, the data collection may be "paused" by means of a control button, which will stop data collection when the scan is completed. Data collection may be recommenced by means of another control button. While in "pause" or when data collection has been terminated, a constant background may be added or subtracted to the accumulated spectrum. The spectrum may be multiplied by a constant, or it may be smoothed with either a 9 or 17 point quadratic, cubic routine⁹⁸ or differentiated with a 9 or 17 point quadratic routine.⁹⁸ Also there is a routine to determine the peak position and FWHM.

DIGAD has several input parameters which allow the experimenter to select, via the teletype, the number of runs NR (i.e., the number of spectral regions scanned), where NR = 1,2,3, or 4, and the parameters for each of these runs. The window width WW is the width of the energy range in eV to be scanned ($WW = 10 \times 2^N$ where $N = 0,1,2,\dots,7$). WW must be selected such that: $10 \text{ eV} \leq WW \leq 1280 \text{ eV}$. The number of memory channels NC required for a spectral region is determined by $\frac{WW}{10} \times 256$. One may reduce the required NC by putting data from MD lines (MD being a memory divisor) into the same memory location. It is advantageous for the ratio WW/NC to be as small as possible when high resolution is desired. Usually for valence band studies $\frac{WW}{NC}$ is chosen to be $\frac{40}{1024}$; for a quick scan over an impurity region, $\frac{20}{256}$; and for an overall scan, $\frac{1280}{1024}$. Also, NC is restricted by the available computer memory such that

NR
 $\sum_{1}^{NC} \leq 2000$ channels. The binding energy (offset energy) BE is also selected by the experimenter for each run ($BE \leq 999.9$ eV). When $NR > 1$, a frequency factor NS must be selected for each spectral region. This determines the number of times that each spectral region is scanned before progressing to the next spectral region. After all NR spectral regions have been scanned their respective number of NS scans, the cycle is repeated. This continues until halted by the experimenter. Thus, for example, one might want to accumulate data for a valence band overnight and periodically check the level of contamination; one might set up 4 scans: $NR = 1$, the valence band, with $NS = 30$; $NR = 2$ a core level, with $NS = 5$; $NR = 3$, the oxygen 1s region, with $NS = 5$; and $NR = 4$, the carbon 1s region, with $NS = 5$. A sample teletype input is given in Appendix A-7. Appendix A-8 gives a table of the various teletype commands.

The double pass CMA is operated from the same data system. Its system program AUGER is only slightly different than DIGAD.⁹⁹ The CMA system is much simpler; its detector is a single channel electron multiplier¹⁰⁰ (Bendix spiraltron electron multiplier Model SEM-4219), and direct pulse counting in the saturated pulse mode is employed. A schematic of the system is given in Fig. 10. A photograph of the electronics for the PES/AES system is shown in Fig. 18. Fig. 19 shows a spectrum from Si 2p to demonstrate the system performance.

E. Vacuum System and Sample Preparation Techniques

The apparatus for a photoemission experiment must contain the necessary photon sources for excitation, an electron analyzer, and an electron detector. It must also provide a suitable vacuum environment for the measurements. For a gas phase measurement, the vacuum requirements are modest, the pressure must be at least 10^{-4} torr to insure that the photoelectrons possess a sufficient mean free path to reach the detector without any collisions with the residual gas. However, for the study of solids and especially surfaces, there is a further, more stringent, requirement which is that the apparatus must be constructed to insure the ability to produce, characterize, and preserve atomically clean surfaces. This necessitates a much stricter vacuum requirement (i.e., the residual vacuum must be UHV) to insure sufficient accumulation time before the sample becomes contaminated (at $P = 10^{-6}$ torr, it will take one second for monolayer coverage to form -- assuming sticking coefficient of unity). This prerequisite of UHV arises from the sampling depth of PES which, as can be seen from Fig. 20, is energy dependent and of the order of 5 to 20 Å (2 to 8 atomic layers).¹⁰¹⁻¹¹⁷ The universal curve indicates that YM_{ζ} would be especially good for surface studies. This extreme surface sensitivity demands not only a UHV system but also in situ sample preparation.¹¹⁸⁻¹⁵⁴

The surface sensitivity of PES has been apparent for awhile. The first stage of these experiments were carried out in the poor vacuum ($\sim 10^{-5}$ torr) of the diffusion pumped Berkeley Iron Free

Spectrometer. This spectrometer has been previously described by Fadley.¹⁵⁵ It was quickly obvious that such a system was not well suited for solid-state studies. Even in the much cleaner ion pumped HP #5950A system ($P \sim 10^{-8}$ torr), it was very difficult to obtain results from most chemically active solids. It was quickly decided to upgrade the vacuum to UHV standards and to provide for in situ sample treatment. The initial stage of the modification of the HP #5950A system into a UHV system is described by Pollak.⁷ The vacuum system has been slightly modified, in that a stage has been added for a double pass CWA, with ports for a UV discharge lamp (see Section III-B), and a grazing incidence electron gun. (See Figs. 1-3.) This allows sequential UPS, XPS, photon-excited AES, and electron-excited AES, all to be performed on the same specimen under UHV conditions. The sample transport system is that described by Pollak.⁷ A new sample preparation chamber and introduction chamber were designed and fabricated (see Figs. 2 and 3). The transport system has been fairly trouble free. It has undergone many bakeout cycles. The only problem has been periodic (but not very frequent) loss of the vacuum integrity of the bellows in the rotary motion feedthroughs, which rotate and drive the sample into the various treatment and measuring stations.

The sample turn-around procedure includes loading the sample, which is mounted on a sample platen, onto the sample inlet part of the system, with the rest of the system isolated by bakeable straight-through valves. Fig. 21 is a schematic block diagram of vacuum system. The sample inlet system is usually not let up to air for

sample changeovers, but backfilled with dry nitrogen. The port is then sealed with a blank flange and a copper gasket, and then the inlet system is roughed out with a cryosorption pump. The inlet system is then baked out (~ 500 - 550°C) for about six hours into an ion pump external to the inlet system. After the chamber has cooled, the sample rod is moved into position for one of the various sample treatments described below. Next the sample is analyzed *in situ* for common contaminants. If the sample is "clean," the desired experiment is performed with periodic *in situ* analysis to confirm that the specimen has not become contaminated. If the sample is not sufficiently clean, or if it becomes contaminated during the course of a measurement, a new specimen is prepared.

Occasionally, the whole system must be baked out if it has been up to air for maintenance (to change or clean the anode, etc.); if there has been a vacuum failure; or if, after doing a number of experiments, the residual vacuum has become degraded. The entire vacuum system is then enclosed in an insulated oven and baked out at $\sim 200^{\circ}\text{C}$ into an external ion pump while its own ion pumps are off. The temperature is monitored at several points, including the analyzer sphere and base plate with thermocouples, and controlled by preset thermal switches. It usually takes about 24 hours to reach the bake temperature and the system is maintained in this condition until the pressure bakes out. During this time the ion pumps are periodically "flushed" to help clean them; and all the filaments in the system are turned on [the X-ray filament ($\sim 10\text{mA}$), ion gauges, TSP filaments, etc.]

to outgas them. After this stage, the system is isolated from the external pump and put on its own ion pumps and left in this stage for approximately one day. Then the system is allowed to cool, with the TSP periodically being flashed. It takes the analyzer spheres several days to reach ambient temperature because they are well insulated. This procedure usually gets the system into the 10^{-11} torr range (measured with a nude Bayard-Alpert ion gauge).

The need to prepare representative well characterized specimens makes sample preparation one of the most important experimental aspects of PES studies of solids and surfaces. Samples, of necessity, must be for the most part prepared in situ. Table V lists the methods used to generate clean specimens in these investigations.

Cleaving or fracturing is a very good method of preparing fresh surfaces from single crystals of most semiconductors and insulators. Before the UHV modification was completed, the standard HP #5950A inlet system was used. We enclosed it with a large glove bag surrounding the sample introduction port. This glove bag was filled with dry nitrogen boiled off from a liquid nitrogen dewar. The glove bag was flushed several times before samples were cleaved with either a chisel-like tool and hammer or with a razor blade (See Fig. 22). The sample is then quickly mounted on a sample platen, placed onto the sample rod, and inserted into the spectrometer vacuum, as quickly as possible without the sample ever seeing the air. This technique worked well and is the technique used to study the III-V, II-VI, and alkali halide compounds discussed in Chapter V. In situ chemical analysis by means of scans

of oxygen and carbon 1s regions showed oxygen contamination usually less than a monolayer and little, if any, carbon contamination. This allowed us to obtain representative bulk density of states for the many semiconductors and insulators reported here.

The UHV system provided us with the capability of preparing samples by cleavage in situ. A sample, mounted for in situ cleavage, is shown in Fig. 23. The sample is next inserted onto the sample rod. The introduction chamber is continuously backfilled with dry N_2 . The sample introduction chamber is then evacuated first by the rough pumping system and then by the external ion pumping system. The chamber is then baked out for 5 or 6 hours into the external ion pump. The ion pump of the introduction chamber is then turned on. After awhile, the system is isolated from the external pumping system and eventually allowed to cool to room temperature. Once the system has cooled down, the sample is cleaved by means of the device which is shown in Fig. 24. This consists of a linear motion feedthrough with "linear travel" (Varian Model 954-5049) and a lathe tool bit attached to it. The thrust bearings, bearing housing, coupling shaft, drive sleeve, and counter assembly have been removed. This device is attached to a 2-3/4" port on the sample introduction chamber. The sample to be cleaved is aligned with the cleaver by looking through a view port on the sample introduction chamber and adjustment of the sample transport and rotary motion system. When the bakeout is finished and the specimen is ready to be cleaved, the plunger of the linear motion feedthrough is pulled back and released. This

operation cleaves the sample. This usually provides for a sample which is oxygen and carbon free as determined by the in situ analysis.* This procedure has been used to prepare specimens of the 3d metal halides, chalcopyrite compounds, and $\text{Pb}_{1-x}\text{Sn}_x\text{Fe}$ alloys. Both this method and the one above produce excellent mirror-like surfaces (often accompanied by some faceting) of the natural cleavage planes. In light of the results of McFeely et al.,^{15b} the crystal face of a sample can have a very important effect on a spectrum and this must be carefully considered.

In the study of layered compounds, a fresh surface was cleaved in a dry nitrogen atmosphere by applying adhesive tape to the surface of the crystal and gently pulling away the tape. This produced a surface with no detectable oxygen or carbon.

Most metal samples are easily prepared as thin films by means of in situ evaporation. A platen with a flat substrate is placed on the sample rod (see Figs. 25 and 26). A filament, which has a high-purity charge spot welded to it or wrapped around (sometimes a boat configuration is used), is mounted on an electrical feedthrough (see Fig. 27) and then mounted on either a sample introduction chamber (Fig. 25) or sample preparation chamber port. After the system has been baked out, and the filament and charge thoroughly outgassed, the platen is made to face the evaporator which is resistively heated until sufficient material is evaporated onto the

* Occasionally carbon contamination has been detected which appears to be from the material used to hold the stainless steel spacers, which secure the crystal, in place. Either Epo-Tek epoxy or GE Adhesive varnish is usually used for this purpose.

substrate (this can usually be determined visually). Careful outgassing of the filament or boat is extremely important. The filament or boat material is usually either W, Ta, or Mo. The appropriate material is determined by looking at the phase diagrams of these materials with the sample metal. Charges which alloy with the filament material, usually cause the filament to become brittle and break before a sufficient amount of sample can be evaporated onto the substrate. Flash evaporation is useful for samples which require particularly high temperatures for evaporation. Evaporation either by electron bombardment or by laser heating is also possible but was not used in these investigations. The resistive heating method has limitations due to the limited amount of input power and possible contamination from support materials, which should always be checked by in situ analysis. Some evaporations have been done with a high power oven designed by E. C. Miner (See Fig. 27). This yields a well defined sample (see Fig. 28). Evaporations by either method often took several attempts before a suitable sample was obtained in the case of the very reactive metals but generally a successful evaporation produced a surface with no detectable oxygen or carbon. Most samples, even very reactive samples (except Cr, Ce, and La), once successfully prepared, remained clean.

Sputtering from a crystal onto a substrate is another useful technique to prepare thin films of samples. Cathodic sputtering processes are reviewed by Chopra.¹³⁰ Glow discharge was used to prepare several metal samples. In this procedure a metal crystal is

glued with a silver coating (Engelhard Industries Flexible Silver Coating 16) onto an electrode (see Fig. 29). Argon gas is let into the system ($\sim 200\mu$) and a glow discharge is set up. This usually results in an amorphous sample unless the substrate is heated or the sample is annealed. Even for metals, amorphous samples may give different results than crystalline samples. For studying binary semi-conductors, it is necessary to RF sputter (instead of dc sputter) to compensate for the immediate build-up of surface charge of positive ions on the front side of the crystal which would prevent further sputtering. The substrate temperature has an effect on the topology of the sample. We used RF sputtering in some studies of amorphous binary semiconductors (see Appendix A-5). We sputtered until a stoichiometric ratio of the two components, as determined from comparison with single crystal data, was achieved. Reactive sputtering is another useful preparation technique but was not employed in any of these investigations.

We used ion bombardment for preparing many specimens of metal crystals. In this technique a focused beam of ions^{*} (usually Argon at $P \sim 5 \times 10^{-6}$ torr) is accelerated onto the specimen surface, and the surface layer is sputtered off. Usually the specimen has been previously prepared by standard metallographic techniques -- spark cut and mechanically polished and/or electro-polished -- and then inserted into the vacuum. The surface of such a sample is,

* This was accomplished with a sputter ion gun (PHI 04-161).

of course, heavily contaminated through interactions with the ambient. As with the sputtering techniques above, ion bombardment creates an amorphous surface. Also, Argon tends to get imbedded into the surface and must be removed by annealing. Pure Argon is essential so that the treatment itself does not contaminate the sample. In this system the Argon is passed through a FSP before reaching the sample preparation chamber. The sputtering is done in a static mode, i.e., a fixed amount of Argon is let into the system. One also needs a well-focused and well-positioned ion beam, otherwise the specimen may become contaminated from the sample holder or from material from the walls of the preparation chamber. Ion bombardment under controlled conditions allows the possibility of in situ elemental and chemical depth profiling.¹⁵⁷

Other useful in situ techniques include heating samples in conjunction with some chemical treatment such as using a H₂ atmosphere to reduce oxides (Fadley),¹⁵⁸ or a reactive environment where the reaction products can be volatilized at a higher temperature, leaving a clean surface (e.g., burning off carbon contamination with oxygen). In heating the sample to high temperatures, possible surface segregation of impurities must be watched out for. An electron bombardment gun (PHI 04-121) is situated in the preparation chamber (see Figs. 2 and 3) for heat treatments. Various gases may be introduced from the gas inlet manifold in controlled amounts into the preparation chamber via a UHV bakeable leak valve.

The above preparation methods are difficult to apply to alloys with confidence. Alloys are usually difficult to cleave or fracture. Ion bombardment will alter the concentration because of the different sputtering yields for the various components. It is difficult to evaporate a controlled composition. Heat treatment may alter the composition within the sampling depth by diffusion and by differences in surface tension as well as by segregation of contaminants at the surface. We have therefore built a device for in situ mechanical cleaning of samples (Fig. 31). This device is capable of both linear and rotary motion. Various cutting tools (see Fig. 32) may be attached to the vacuum end. The specimen is machined to be either press-fitted into the platen or placed in a specially made platen which holds the alloy specimen in place with two set screws. After a bake-out, the tool is positioned on the sample surface with the linear motion adjustment, and the surface is mechanically cleaned by the rotary motion. This technique has been successful in cleaning several alloys such as NiAl, α -Brass, many rare earth intermetallics, and a few Hersler alloys. Interdiffusion and co-sputtering are two other techniques for producing alloy specimens.

For a wide variety of reasons, we chose not to use powdered samples in these studies. Some techniques used for powdered samples have been discussed by G. E. Theriault et al.¹⁵⁹ For studying films of compounds, the techniques of molecular beam epitaxy should prove very useful for preparing high quality specimens.¹⁵⁴ Many other techniques may also be used to prepare specimens (e.g., the Langmuir-Blodgett method or electrodeposition).

The above techniques which are common practice in UHV work are discussed in the context of the XPS and AES experiments reported in this thesis. They are applicable to many other techniques which require UHV-in situ sample treatment. It is clear that desirable characteristics for a PES system for solid-state and surfaces studies include: 1) UHV; 2) Modular design (to allow convenient incorporation of several photon sources and other experimental probes: AES, LEED, SIMS, work function probe, etc.); 3) Flexibility of sample manipulation; 4) Bakeability -- at least to 200°C; 5) An isolatable treatment chamber; and 6) Availability of many sample preparation techniques.

F. Sample Charging

The measurement of absolute binding energies of semiconductors and insulators has two important difficulties associated with it -- the first is one of a theoretical nature -- that is, what is the appropriate reference energy; and secondly, there is the experimental problem of charging, i.e., the shift of the spectrum of such a material caused by charge build-up as a result of the photoemission process (see Ref. 160). In the work discussed in this thesis, both problems were by-passed: absolute binding energies of levels of the semiconductors and insulators investigated were not necessary because the top of the valence band was a suitable reference for comparison with theoretical band-structure calculations (see Chapter V, section B); and in the derivation of the ionicity scale $[F_i^{XPS}(AB)]$ (see Chapter V, section C), splittings between levels were used.

Also, in the studies of multiplet splitting and in the differential extra-atomic relaxation studies only relative energies were needed. However, charging does present a problem even if absolute binding energies are not required. While shifting of the entire spectrum did not matter for these experiments, charging usually tended to broaden the spectra because of inhomogeneous charging, and this affected the resolution attainable. Two measures were taken to minimize inhomogeneous broadening. Whenever possible, smooth faces of the natural cleavage planes of single crystals were used. Secondly, the surfaces of these specimens were bathed with low energy electrons from an electron flood gun (HP #18622A).^{161,162} The flood gun improved the linewidth in the case of the 3d metal fluorides by better than 25%.^{163 *} In the case of MnF_2 , this allowed new structure to be observed in the Mn 2p levels for the first time, permitting an unambiguous test of a recent calculation (see Chapter IV, section C).

*The flood gun settings were determined empirically for each case by optimizing the electron emission and energy for best resolution as determined by FWHM of a convenient core level.

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Table I. Common photon sources

<u>Source</u>	<u>Energy (eV)</u>	<u>FMM (eV)</u>
H (Lyman α)	10.20	
HeI	21.218	< 0.01
HeII	40.81	.02
NeI	16.67, 16.85	
NeII	26.81, 26.91	
ArI	11.62, 11.83	
ArII	13.30, 13.48	
YM _{ζ}	132.3	0.47
ZrM _{ζ}	151.4	0.77
NbM _{ζ}	171.4	1.21
MoM _{ζ}	192.3	1.53
RhM _{ζ}	260.4	4.0
NeK $\alpha_{1,2}$	848.6	0.28
NaK $\alpha_{1,2}$	1041.0	
MgK $\alpha_{1,2}$	1253.60	0.78
AlK $\alpha_{1,2}$	1486.6	0.85
CrK α_1	5414.72	2.1
CrK α_2	5405.51	
CuK α_1	8047.83	
CuK α_2	8027.78	

Table II. Major components of Helium discharge.

<u>Component</u>	<u>Energy (eV)</u>
HeI _{α}	21.218
HeI _{β}	23.087
HeI _{γ}	23.742
HeII _{α}	40.814
HeII _{β}	48.370
HeII _{γ}	51.015

Table III. FWHM of MgKLL(1D) Auger and Mg 2p lines of Mg metal from a normal size sample (5mmx5mm - active area 5mmx13mm) and a narrow strip (5mm x 0.3mm).

	FWHM (eV)	
	<u>MgKLL(1D)</u>	<u>Mg 2p</u>
Normal	1.55	0.8
Narrow	1.12	0.7

Table IV. Properties of synchrotron radiation.

- Continuous spectral distribution over a wide energy range.
- Highly polarized.
- Highly colimated.
- Pulsed time structure of beam.
- Radiation is in ultra-high vacuum.
- High intensity over much of the spectral distribution.

Table V. Sample preparation methods.

<u>Method</u>	<u>Samples</u>	<u>Comments</u>
Cleavage/Fracture	Crystals of group IV and V, III-V and II-VI compounds; alkali halides; 3d metal halides; chalcopyrites; layered compounds	usually O and C free when done in situ, when done in inert atmosphere usually small contamination (< monolayer C and O).
Evaporation	Li, Na, Mg, Al; 3d metals; rare earth metals	resistive heating can usually prepare specimen without any detectable O or C if the filament is carefully outgassed prior to evaporation.
Sputtering: Glow Discharge	Transition metals, rare earth metals;	amorphous specimen for alloys or compounds
RF Sputtering	binary semiconductors;	alters composition.
Ion Bombardment	metals	
Heat and/or Chemical Treatment	Metals	
Mechanical	Alloys; intermetallic compounds	

FIGURE CAPTIONS

Fig. 1. Overall view of the UHV-PHS/AES system.

- 1) Cryosorption (rough) pump;
- 2) External 500 l/s Ion pump;
- 3) Rotary motion feedthrough with turns counter-linear motion drive;
- 4) Rotary motion feedthrough with turns counter-rotary motion drive;
- 5) Roughing line;
- 6) Gas inlet manifold;
- 7) Analyzer housing (HP #5950A);
- 8) Analyzer housing - CMA (PHI-255).

Fig. 2. Close-up view of introduction and preparation chambers.

- 1) UV source;
- 2) CMA housing;
- 3) Sample Preparation Chamber;
- 4) Sample Introduction Chamber
- 5) Inlet line for UV source
- 6) Evaporator
- 7) Analyzer housing
- 8) Dry N_2 backfill line;
- 9) Leak Valve;
- 10) Ion gauge;
- 11) Monochromator Adjustor;
- 12) Differential Pumping Line for UV Source.

Fig. 3. Close-up view of sample introduction and preparation chambers.

- 1) Preparation Chamber;
- 2) Introduction Chamber;
- 3) Electron Bombardment Gun (specimen heating);
- 4) Bakeable Straight-through Valves;
- 5) Thermal Switches (Bakeout Control);
- 6) Heat strip;
- 7) Grazing Incidence Electron Gun;
- 8) Ion Bombardment Gun;
- 9) Water cooled jacket for Titanium Sublimation Pump (TSP);
- 10) Bellows;
- 11) 60 l/s Ion Pump;
- 12) UV Photon Source (see Figs. 5 and 6);
- 13) UV Source inlet line;
- 14) OMA Housing;
- 15) 220 l/s Ion Pump.

Fig. 4. View of backend of UHV-PES/AES system.

- 1) Bakeout oven insulation (when system is being baked-out, there is a matching top, such that the system is entirely enclosed);
- 2) Variable Temperature Probe - This probe allows the specimen to be measured in a temperature region from $\sim 80^{\circ}$ to $\sim 1000^{\circ}\text{C}$. This system was not used in these studies and will be described elsewhere;

- 3) Crystal Monochromator Adjustor;
- 4) Pre-amp and discriminator for CMA;
- 5) Feedthroughs for X-ray Chamber;
- 6) Vac Sorbs;
- 7) TV Camera;
- 8) Viewport - X-ray Monochromator Chamber;
- 9) Analyzer Chamber - HP #5950A;
- 10) Grounding Cable;
- 11) Electrical feedthrough strip for analyzer (HP #5950A).

Fig. 5. Ultraviolet photon source.

Fig. 6. Schematic of ultraviolet photon source.

Fig. 7. Monochromator adjuster.

Fig. 8. Spectral distribution of synchrotron radiation from the storage ring, SPEAR, at Stanford (after H. Winick, Proc. IX Intl. Conf. on High Energy Accelerators, AEC CONF - 740522, SLAC (1974) p. 685.

Fig. 9. a. Schematic of the HP #5950A system.

b. Schematic of the Single Channel Video Data System.

Fig. 10. Schematic of the CMA System.

Fig. 11. CMA with Mu metal shields.

Fig. 12. CMA with outer Mu metal shield removed.

Fig. 13. CMA with both Mu metal shields removed.

Fig. 14. TV camera in place. Notice special camera mount which allows for convenient adjustment of camera position, azimuthal angle, and polar angle.

- Fig. 15. Close-up of TV camera and adjustable mount.
- Fig. 16. TV monitor. The $Au\ 4f_{5/2}$ and $4f_{7/2}$ lines are visible as dense strips of scintillations in the horizontal direction. The two dark vertical lines are the variable electronic window described in the text.
- Fig. 17. Close-up of TV monitor. Note the black dots within the scintillations which are within the electronic window.
- Fig. 18. Photograph of the electronics of the UIN-PES/AES system.
- Fig. 19. Silicon 2p spectrum obtained with this system.
- Fig. 20. "Universal Curve" - The curve is drawn as a wide band to indicate that it is only approximately "universal." Energies of several photon sources are denoted. YM_{ξ} is shown to be near the minimum in the curve and thus a good photon source for high surface sensitivity.
- Fig. 21. Block diagram of vacuum system. The system is depicted without the variable temperature probe (Fig. 4) but with a chamber for a residual gas analyzer (Quad 250). For convenience the differential pumping system for the UV source is not shown.
- Fig. 22. Two tools used in cleaving crystals in a glove bag (not shown) -- filled with dry N_2 . (See text.)
- Fig. 23. A specimen (single crystal of SiC) mounted for in situ cleavage.
- Fig. 24. In situ Crystal Cleaver.

- Fig. 25. Sample Introduction Chamber with a sample platen mounted on the sample rod. The platen has a blank substrate. Note feedthrough to be used for evaporator.
- Fig. 26. Close-up of mounted specimen platen.
- Fig. 27. Two evaporators - At left, a specially designed oven; and at the right, a feedthrough with a W ribbon with a gold foil wrapped around the ribbon.
- Fig. 28. Substrate with an Sc film (circular spot) evaporated onto it from the oven.
- Fig. 29. Sputtering electrode with a Sb crystal attached to its end.
- Fig. 30. Sputtering electrode completely assembled and ready to be attached to a sample preparation port.
- Fig. 31. Mechanical Cleaning Device.
- Fig. 32. Close-up view of the Mechanical Cleaning Device, various attachments used for cleaning (diamond tool, W brush, WC cutting tools), and NiAl alloy specimen press fitted into sample platen.

XBB 757-5765A

Fig. 1

XBB 757-5762A

Fig. 2

XBB 757-5764A

Fig. 3

XBB 757-5761A

Fig. 4

XBB 756-4253

Fig. 5

UV DISCHARGE LAMP

Fig. 6

ABE 757 3595

XBB 757-5769

Fig. 7

NBL 758-1901

Fig. 8

Fig. 9a

*Front panel control (10 turn Pot.)

✱ Rear panel connector

Single channel video data system

8B1 7632451

Fig. 9b

Fig. 10

XBB 754-2827

Fig. 11

XBB 754-2825

Fig. 12

XBB 754-2828

Fig. 13

XBB 757-5763

Fig. 14

XBB 757-5759

Fig. 15

XBB 757-5768

Fig. 16

XBB 757-5767

Fig. 17

XBB 757-5760

Fig. 18

XBL7510-4177

Fig. 19

XBL 755-3056

Fig. 20

XBL 763 2462

Fig. 21

XBB 756-4250

Fig. 22

XBB 7511-8417

Fig. 23

XBB 756-4248

Fig. 24

XBB 757-5771

Fig. 25

XBB 757-5770

Fig. 26

XBB 756-4247

Fig. 27

XBB 7511-8416

Fig. 28

XBB 756-4252

Fig. 29

XBB 756-4251

Fig. 30

XBB 757-5647

Fig. 31

XBB 757-5646

Fig. 32

IV. MULTIPLY SPLITTING OF TRANSITION METAL AND RARE EARTH METAL CORE-LEVELS

A. Introduction

In this chapter, we will consider multiplet splitting of metal atom core-levels in metals, compounds, and alloys. Multiplet splitting studies give useful information on initial-state spin S_1 and also exhibit effects of intra-shell electron-electron correlations which are now understood quantitatively in the case of s-level splittings. By multiplet splitting, we mean we will be examining the cases where the initial ground state of the system possesses unpaired electrons in an outer level and upon photoemission from a core-level, structure is observed due to the several possible ionic final states which arise from the various possible couplings of angular momentum. We will not be considering satellites due to other sources:

- 1) Chemical Shift Phenomenon - This occurs when an atom is in several different chemical environments and may be due to: surface contamination or mixed valency;
- 2) Crystal-Field Splittings - The first reported splittings of core levels from solids was for the $5p_{3/2}$ levels of some compounds of heavy atoms¹ and several gold compounds² by Novakov and Hollander and proposed to be due to internal electric field gradients.^{1,2} Gupta and Sen³⁻⁷ have discussed this question in theoretical terms. The only theoretical calculation on the Au $5p_{3/2}$ levels, which is

by Apai et al.,⁸ give an order of magnitude lower splitting than measured. Recent high resolution studies on AuCN⁹ also cast doubts on the origin of these splittings. Recently indirect inference for the crystal field splitting of core levels has been drawn from line broadening in Sn 5d levels in tin compounds.¹⁰ This is somewhat dubious because linewidths in solids have several causes:

- a) Charging, b) phonon-broadening¹¹, and
- c) core-level asymmetry.^{2,3}

Thus, this question remains very open. Crystal field splitting in outer d-levels is, however, firmly established.¹⁴ (See Chapter VII.)

- 3) Configuration Interaction (Final-State) - These satellites were discussed in Chapter II, section C-6. They will be discussed here in that they are important in explaining the magnitude of multiplet splitting due to different correlation in high-spin and low-spin multiplets (intra-shell case).
- 4) Configuration Interaction (Initial-State).¹⁵⁻¹⁸
- 5) Shake-Up and Shake-Off¹⁹⁻²² - These are in a sense formally the same as (3).
- 6) Characteristic Energy Losses (CEL) - These include inter- and intra-band transitions and bulk- and surface-plasmons (extrinsic).^{23,24}

- 7) Intrinsic Plasmons (bulk and surface) - As yet there is no firm experimental evidence for their existence, though several groups have searched for intrinsic plasmons.
- 8) Final-State Effects.²⁵⁻²⁶
- 9) Autoionization and Auger Processes.

Fadley,^{27,28} Shirley,²⁹ and Freeman et al.³⁰ have reviewed multiplet splitting in PES. Below we will give just a few brief general considerations and then discuss results of some experimental measurements. In the photoelectric process, a photon of energy $h\nu$ ejects an electron from the system with initial energy E_i , yielding a final-state energy E_f plus an electron of kinetic energy K . Energy conservation yields:

$$h\nu = E_f - E_i + K. \quad (1)$$

Thus for a given $h\nu$, there is a one-to-one correspondence between the kinetic energy spectrum and the energy difference $E_f - E_i$. Since the initial state E_i of the sample is always the same, the kinetic energy spectrum will, in fact, reflect the final-state energies E_f . No work function appears in Eq. 1 because the binding energy ($E_f - E_i$) is referred to the Fermi level E_F . Most XPS spectra exhibit a single peak for each atomic core level because the "passive" orbitals form 1S states and no coupling to the hole state is possible. When the "passive"-orbital configuration has non-zero L or S, coupling to more than one final state is possible and in this case multiple peaks are to be expected in the XPS spectra.

We can conveniently classify XPS multiplet-splitting cases in ℓ, s coupling according to the sets of value $[\ell, L]$ taken by the orbital angular momentum ℓ of the photoelectron (before photoemission) and the total angular momentum L of the "passive" electrons. In this scheme S is allowed to vary and $s = 1/2$. The sets are:

$$\ell = 0, L = 0 \quad (2a)$$

$$\ell \neq 0, L = 0 \quad (2b)$$

$$\ell = 0, L \neq 0 \quad (2c)$$

$$\ell \neq 0, L \neq 0 \quad (2d)$$

In the following two sections, we will be discussing in detail measurements on Mn levels in MnF_2 and clearly only cases (2a) and (2b) (Parent $d^5 6S$) apply. Two examples of each will be discussed.

Photoemission from the accessible $\ell = 0$ levels (2s and 3s) presents the simplest cases for analysis. The more complicated $\ell \neq 0$ cases 2p ($\ell=1$) and 3p ($\ell=1$) will be examined in section C.

First we will consider the simplest possible example of multiplet splitting -- the lithium atom -- the ground state of Li is $(1s^2 2s)^2S$. If a 1s core-electron is ejected, there results two possible ionic final states $Li^+(1s^1 2s^1)^3S$ or $Li^+(1s^1 2s^1)^1S$. These two final states have different energies due to the exchange interaction with the 3S state being lower in energy. Thus photoelectron spectra of the 1s level from atomic lithium would yield two peaks with the relative intensity given by the multiplicity ratio:

$$\frac{I(L, S+1/2)}{I(L, S-1/2)} = \frac{2S+2}{2S} \quad (3)$$

or in the Li case, 3:1 and the energy separation is given by Van Vleck's Theorem:³¹

$$\Delta E_{ns}^{VV} = \frac{(2S_i+1)}{(2L+1)} G^L(ns, n'l) \quad , \quad (4)$$

where S_i is initial-state spin and $G^L(ns, n'l)$ is the appropriate atomic exchange integral. For lithium, using the exchange integral from Mann,³² we obtain for the 1s level-splitting:

$$\Delta E_{1s}^{VV} (Li) = \frac{2}{1} G^0 (1s, 2s) \quad (5a)$$

$$\Delta E_{1s}^{VV} (Li) = 0.78 \text{ eV} \quad . \quad (5b)$$

There have been no measurements on Li atoms, however, we have measured Li1s level from Li metal, where the 2s electron is part of the valence band. Since Li metal is a Pauli paramagnet, $S_i = 0$ and so no splitting is observed as expected (see Fig. 1).³⁴

The first observation of multiplet splitting in PES core-level spectra was by Hedman, et al.³³ in the 1s level of the paramagnetic gases, O_2 and NO and in solids by Fadley, et al.^{35,36} in the metal 3s levels of several transition metal compounds. Since then there have been a number of studies of this effect in compounds of the 3d transition series and lanthanide series.³⁷⁻⁴⁶ Multiplet splitting of core-level peaks in PES are of interest both as a probe of the fundamental interactions between electrons in atoms, molecules, and solids and as a diagnostic tool for acquiring information about the initial-state unpaired spin S_i in chemical systems.

This chapter will be divided into several parts. Detailed studies of MnF_2 will be discussed to illustrate our current state of understanding of the multiplet splitting phenomenon. These results represent the most detailed measurements of multiplet splitting in XPS. First we will discuss the 2s and 3s levels. These levels are simplest to start with because in the simple one-electron picture we would expect only two peaks [e.g., Mn^{+2} in MnF_2 goes from initial-state $\text{Mn}^{+2}(3s^2 3p^6 3d^5)^6S$ to the final states of $\text{Mn}^{+3}(3s^1 3p^6 3d^5); ^5S$ or 7S]. Early studies of Fadley, *et al.*^{35,36} on MnF_2 found two anomalies

- 1) The observed multiplet ratios were in general too high, and
- 2) the measured splitting in the outermost s levels were roughly one-half of that predicted using Van Vleck's Theorem³¹ even with G calculated using state-of-the-art wavefunctions.

These anomalies will be explained in the next section with observation of new structure due to electron correlation in the $\text{Mn}3s$ level in MnF_2 . Levels with $l \neq 0$ will give rise to more complicated structure than a simple two peak structure. Section C deals with the $\text{Mn}2p$ and $3p$ levels in MnF_2 in detail. Section 4 briefly summarizes the core-level data for several transition metal compounds. The results from the 3s levels of the 3d metals in the 3d series Sc through Zn are discussed in section D. In section E the core-levels of the rare earth metals from La through Lu are discussed. Section F deals with the use of multiplet splitting as a diagnostic tool and examples of the application of multiplet splitting to some intermetallic alloy systems are given.

MnF_2 was chosen to be the case for intensive study of multiplet splitting for three reasons: 1) Of the manganous compounds, MnF_2 is among the most stable against decomposition in the spectrometer vacuum. As Fadley and Shirley³⁶ indicated earlier, the equilibrium constant for the reaction of MnF_2 with O_2 to form MnO_2 and F_2 is 10^{-50} , while the corresponding constant for MnCl_2 is 10^{+5} . Thus, the next most stable halide is very labile. 2) MnF_2 is highly ionic. Thus, for comparison with calculations, Mn in MnF_2 may be considered to be a dipositive ion to a good first approximation. 3) Mn^{+2} has the maximum possible number of unpaired d-electrons, 5 and the exchange integrals $G^2(3s,3d)$ and $G^2(3p,3d)$ for Mn are fairly large. Thus, the observed splittings should be nearly maximum and easily observed.

Several experimental factors should be noted: 1) the use of monochromatized X-rays, 2) ultra-high vacuum conditions, and 3) minimization of charging, which were all important for the MnF_2 studies. Monochromatization of the X-rays besides improving the resolution from ~ 1.0 eV to ~ 0.5 eV, more importantly for these investigations filtered out: 1) the $\text{AlK}\alpha_{3,4}$ satellites -- making the analysis of the spectra easier, especially for the complicated 2p and 3p spectra and 2) the Bremsstrahlung radiation -- significantly increasing the signal to background which was especially helpful in facilitating the observation of the ^5S correlation satellites in the Mn3s spectrum. Ultra-high vacuum conditions and good sample preparation techniques were important in ruling out spurious surface

contamination effects. Charging is always a nuisance in the study of non-conducting solids. Since we are not interested in absolute binding energy shifts but in relative separations, this was no problem as long as the peaks of interest were obtained in the same spectrum. However, inhomogeneous charging tends to broaden peaks in spectra quite a bit. Inhomogeneous broadening was minimized in two ways, 1) using single crystal samples and 2) using an electron flood gun to neutralize the sample surface. This last aspect was quite important in facilitating the analysis of the Mn2p spectrum from MnF_2 .

B. New Multiplet Structure in Photoemission from MnF_2 ^{*}

Early (XPS) studies^{35,36} of multiplet splitting in transition-metal ions established the effect but left some basic questions unanswered. In particular, for the 3s doublet in the XPS spectra of Mn^{2+} and Fe^{3+} compounds, neither the intensity ratio (2:1) rather than the multiplet ratio 7:5) nor the magnitude of the splitting was completely understood. This situation was unsatisfactory: multiplet splitting of hole states should be understood both as a problem in atomic physics and because of its application as a diagnostic tool to solid state and chemical problems. In fact, recent studies in which multiplet splitting has been correlated with the initial-state spin^{37,38} S or used to derive information about covalency^{39,40} have emphasized the urgency of acquiring a truly quantitative understanding of the essential phenomenon.

^{*} Based on work done in collaboration with R. A. Pollak, L. Ley, and D. A. Shirley and published in Phys. Rev. B 7, 4009 (1973).

Sasaki and Bagus⁴⁷ have recently carried out a configuration interaction calculation of Mn^{2+} that appears to explain the 2s and 3s hole-state multiplet structure observed earlier. Their results provide definite predictions about additional features of these states. In this section, we report detailed, quantitative confirmation of those predictions in the XPS spectrum of MnF_2 .

Spectra were obtained from single-crystal specimens in a Hewlett-Packard #5950A ESCA spectrometer. The crystals were cleaved in an inert atmosphere and introduced directly into the spectrometer vacuum at 8×10^{-9} torr. The 1s lines of carbon and oxygen (the two most common surface contaminants) were monitored in situ before and after the Mn 2s and 3s spectra were recorded. Very little carbon and no oxygen were detected. The peak intensity ratios relative to the Mn 3p (7P) peak were

$$Mn\ 3p\ (^7P):O\ 1s > 20:1$$

$$Mn\ 3p\ (^7P):C\ 1s \approx 9.3:1 .$$

The simplest description of the 2s and 3s XPS spectra from Mn^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$; 6S) is obtained by coupling each s hole state to the valence shell. Two final states may be reached by one-electron photoemission from either the 2s or the 3s shell. These final states have 7S and 5S symmetry in each case. In the 7S states the remaining 2s or 3s electron is coupled parallel to the d-shell spin $S = \frac{5}{2}$, while in the 5S states the two spins are anti-parallel. For either the 2s or the 3s case the photoemission spectral line intensities should be the multiplet ratio $^7S:^5S = 7:5$ in this

approximation, while the two components should be split by $(\frac{6}{5})G^2(sd)$ according to Van Vleck's Theorem.³¹ Here, $G^2(sd)$ is the appropriate sd Slater-exchange integral. At this level of interpretation it would seemingly be straightforward to use the observed splitting diagnostically to deduce covalent character.

More careful consideration leads to several modifications of the above model. These have been covered in detail recently by Freeman, Bagus, and Mallow,³⁰ who have made calculations on MnF_6 clusters, and this discussion leans heavily on their paper. First it should be pointed out that estimates of the 5S - 7S splitting based on ground-state unrestricted Hartree-Fock (UHF) calculations may give fortuitously good agreement with this experiment because two effects of opposite sign have been omitted. A more realistic hole-state calculation increases the splitting, both because it properly couples final-state spins and because it allows the orbital to relax properly in the hole state.³⁰ Electron correlation, however, tends to reduce the splitting because the 5S state's energy is lowered more than that of the 7S state. This is true because the s and $3d$ electrons of like spin (in the 7S state) are already relatively well correlated due to the use of antisymmetrized wave functions in HF or UHF theory to satisfy the Pauli principle. Correlation of the motion of the antiparallel s and $3d$ pairs in the 5S states thus improves these states' energies more. Pressing this line of reasoning further, one might intuitively expect better agreement between the Hartree-Fock splittings and experiment when the one-electron hole states and the magnetic shell have different

principal quantum numbers. This follows because an increase in radial separation of the s and d or s and f pairs would diminish the importance of correlation between antiparallel electrons on the multiplet splitting. Thus in rare earths the Hartree-Fock estimates of splitting should be more accurate for the 5s than the 4s shell (as observed)^{38,44} while the 2s splitting would be predicted more accurately than the 3s splitting in the 3d ions (see below). Freeman et al.³⁰ have reached the same conclusion using configuration interaction arguments.

Going beyond Hartree-Fock estimates, Sasaki and Bagus⁴⁷ made configuration-interaction calculations on the $\text{Mn}^{3+} [3s^1 3p^6 (3d^5, 6s)]$ states. They found, for example, that 5S states formed from the configuration $3s^2 3p^4 3d^6$ were very important. By considering a total of seven ways in which 5S states and two ways in which 7S states can be formed by internal correlation,⁴⁸ they were able to make three predictions that could be experimentally tested. First, the 7S - 5S splitting was reduced to 4.7 eV (or to 7.8 eV if semi-internal correlations were also considered), in reasonable agreement with the experimental value of 6.62 eV (see Table I). Second, the intensity ratio of these two peaks is correctly predicted as 2.2:1, thereby clearing up a vexing anomaly.

The third prediction, which is tested for the first time here, is that 5S satellite peaks should appear in the spectrum. These satellites may be understood by writing the seven (or more if semi-internal correlations are considered) eigenstates of 5S symmetry as

$$|\psi_i\rangle = C_{i1} |3s^1 3p^6 3d^5\rangle + \sum_{j=2}^7 C_{ij} |\phi_j\rangle,$$

where $i = 1, 2, \dots, 7$, and $|\phi_j\rangle$ represents the j th admixed configuration.

Since the intensity of a 3s-photoemission line from the $(3s^2 3p^6 3d^5; {}^6S)$ ground state is proportional, for one-electron transition, to $|C_{i1}|^2$ (neglecting small deviations from unity of the overlap between the initial- and final-state passive electron), it follows that the intensity lost from the main 5S line, viz., $1 - |C_{i1}|^2$, must appear at eigenenergies E_i of the states $|\psi_i\rangle$.

In this way Sasaki and Bagus predicted peaks at ~ 25 and ~ 43 eV relative to the 7S peak position, with the first, more intense peak arising from two neighboring eigenstates. Our spectra (Fig. 2) confirm this prediction very nicely. We identify these satellites with the observed peaks at 20.7 and 37.8 eV below the 7S peak.

Furthermore, the ratio of the intensity of the septet peak to the sum of the intensities of the quintet peaks, 1.3 ± 0.2 , compares well with the value 1.4 expected from multiplicity considerations. A detailed comparison is made in Table I. An earlier, tentative assignment of the peak at 20 eV to inelastic losses³⁵ is not supported by the present more detailed study of line structure and satellites on MnF_2 single crystals.

This provides an example of the correlation sum rule which was discussed in Chapter II, section C-6. This is illustrated in Fig. 3. The weighted average of the 5S peaks yields $E({}^5S) = 14.2$ eV relative to 7S in excellent agreement with 14.3 eV calculated by

Freeman et al.³⁰ using one-electron multiplet-hole theory.

Thus the correlation satellites steal intensity from the main 5S peak -- via roots arising from off diagonal matrix elements connecting the $3s^2 3p^4 3d^6$ configuration to the one-electron (Hartree-Fock) configuration of the $3s(^5S)$ hole state.

The 2s line (Fig. 4) shows doublet structure, as expected. Both the splitting and the relative intensity are in very good agreement with the predictions of multiplet-hole-theory (Table 1): thus the 2s-hole-state 7S - 5S splitting is not strongly reduced by correlation and the 7S : 5S ratio is very nearly the multiplicity ratio.

The hole structure for $Mn^{3+}(2s^* \text{ or } 3s^*)$ final states is now quantitatively understood; theory and experiment show good agreement in splitting, relative intensity, and satellite structure. The complexity of the 3s spectrum precludes the quantitative validity of simplistic correlations of 3s splitting with total spin or covalent character (at least without further analysis), although qualitative trends of this nature have already been observed. On the other hand, the existence of observable 3s satellite structure should prove useful in studying interactions with ligands if this structure is sensitive to ligand properties.

C. Multiplet Splitting of the Manganese $2p$ and $3p$
Levels in MnF_2 Single Crystals

1. Introduction

Multiplet splitting of core-level peaks in X-ray photoemission (XPS) spectra is of interest both as a probe of the interactions between electrons in atoms, molecules, and solids, and as a diagnostic tool for acquiring information about unpaired spin in chemical systems. Since the first reports of multiplet splitting in paramagnetic gases by Hedman, *et al.*³³ and in solids by Fadley and co-workers,^{35,36} there have been a number of studies of this effect in the metals and compounds of the first transition series and the lanthanide series.^{34,37-46} These studies have been confined primarily to the core s levels because of the simplicity of their spectra.

Multiplet splitting is expected to be observed in an XPS spectrum if the specimen possesses unpaired electrons in its outer valence shells. The splitting arises when, upon ejection of a core electron, the resulting partially filled core shell can couple with the open valence shell to form several multiplets of different energy.²⁷⁻³⁰ The simplest spectrum is expected for a core s level. This should result in two peaks with an energy separation given by Van Vleck's theorem,³¹ (Equ. 4). The relative intensities expected from this simple picture is given by the multiplicity ratio $(S + 1)/S$. This level of interpretation neglects electron correlation

*Based on work done in collaboration with L. Ley, F. R. McFeely, and D. A. Shirley and published in Phys. Rev. B 11, 1721 (1975).

and is only approximately correct. Recently a more careful consideration^{30,47,49} of the multiplet splitting of core s levels in transition metal ions has shown that intra-shell electron correlation can drastically alter the spectra of ns levels when $n = n'$ (see previous section). The understanding of multiplet splitting of ns peaks now appears to be on firm quantitative ground.^{46,50} Only recently have the 2p levels in transition metal compounds been given a comprehensive theoretical treatment.⁵¹ The few reports of experimental evidence for splittings in these levels have been largely indirect.^{36,52,53} The XPS spectra of 3p levels of the transition metal compounds exhibit very complex spectra for which the Hartree-Fock one-electron model gives a poor description.^{30,35,47,49,54} As a step toward understanding the multiplet structure in XPS spectra of non-s levels, we have studied the multiplet splitting of the Mn 2p and 3p levels obtained in high resolution XPS measurements of MnF_2 single crystals. The experimental procedure is outlined in section C-2. The results are presented and discussed in section C-3 and 4. Conclusions are given in section C-5.

2. Experimental

High-resolution XPS measurements were performed with a Hewlett Packard #5950A electron spectrometer employing monochromatized Al K α X-rays. The resolution of this instrument has been determined to be 0.55 eV.⁵⁵ The specimens were MnF_2 single crystals, cleaved in the spectrometer vacuum of $< 5 \times 10^{-9}$ torr. No oxygen or carbon could be detected in scans of the O 1s and C 1s regions. No lines of other contaminants were observed in a 0 to 1280 eV overall scan.

It is well known that under typical XPS measuring conditions, insulating and semiconducting samples become charged and the resulting peaks are shifted and broadened. Since in this study we are interested in peak splittings, and not absolute peak positions, the shifting of peaks does not hinder us but the peak broadening can be very deleterious. In fact, in the earlier XPS experiments on MnF_2 ,^{36,46} charging effects broadened the Mn 2p spectra to such an extent that no direct evidence of multiplet splitting could be obtained. To minimize charging, the specimen crystals were flooded with low energy electrons.^{56,57} This resulted in greatly improved resolution and allowed accurate determination of Mn 2p line shape. The flood-gun settings were determined by empirically optimizing the electron emission and energy for best resolution as determined by the full-width at half-maximum (FWHM) of the F 1s line. The best settings for this experiment were determined to be 0.5 ma emission and 0.5 eV electron energy.

3. The Mn 2p structure

Figure 5 shows the raw Mn 2p spectrum of MnF_2 . To facilitate analysis of multiplet structure, we have subtracted the inelastic background and characteristic energy loss structure by means of a suitable response function.⁵⁸ The resulting corrected spectrum is shown in Fig. 6.

The most striking feature of Fig. 6 is that the Mn $2p_{3/2}$ peak is asymmetric toward higher binding energy and the Mn $2p_{1/2}$ peak is asymmetric to lower binding energy. This agrees qualitatively with

early X-ray emission data on the 3d metals and their compounds, in which the $K\alpha_1$ ($2p_{1/2} - 1s$) emission line has α close to but less than 1.0.⁵⁹⁻⁶² Here α is defined as the ratio of the half-width at half-maximum on the high binding-energy side, W_H , to the half-width at half-maximum on the low binding energy side, W_L . The spectrum of Fig. 6 yields $\alpha(2p_{1/2}) = 0.8$ and $\alpha(2p_{3/2}) = 1.6$ in good agreement with the X-ray emission work. Recent high resolution X-ray emission work of Pessa is in good agreement with our results.⁶³ It was proposed by the X-ray workers that the asymmetry of the $K\alpha$ lines arose from multiplet splitting. In the first XPS work on MnF_2 , Fadley and Shirley³⁶ postulated the existence of multiplet effects in their Mn 2p spectra from indirect arguments based on line widths. Later, Frost, et al.⁵² studied the 2p levels of cobalt ion complexes. These workers observed that the separation of the peak maxima between the Co $2p_{1/2}$ and Co $2p_{3/2}$ levels was systematically larger by 1 eV in the high spin ($S = 3/2$) complexes than in the low spin ($S = 0$) complexes. This was interpreted as indirect evidence of multiplet splitting, in which the degeneracy of J is broken by the exchange interaction with the states of higher J shifting to lower binding energy for the $2p_{3/2}$ and to higher binding energy for the $2p_{1/2}$, thus yielding an apparent increase in the spin-orbit splitting. For MnF_2 , we found the splitting of the $2p_{3/2} - 2p_{1/2}$ peak maxima to be 13.0(1) eV and the mean peak separation to be 12.1(1) eV, versus 11.18(25) for both in Mn metal.⁶⁴ It has already been shown that there is less uncompensated spin in the metal than in MnF_2 ,³⁴

so the interpretation of increased splitting being due to multiplet effects is in the same direction as in Co. Similar results have been obtained for the oxides of Ni and Co in comparison to the metals; however, diamagnetic ZnF_2 has the same splitting (within experimental error) as Zn metal. These data, which provide further support for the multiplet interpretation, are summarized in Table II. So far the only report of direct observation of splitting has been for the Co $2p_{3/2}$ level in Co ($S = 1/2$) complexes by Briggs and Gibson; however, these authors did not observe any splitting in the Co $2p_{1/2}$ level.⁵³

Besides the asymmetry of the peaks and the enhanced $2p_{1/2} - 2p_{3/2}$ splitting, two other features of Fig. 6 should be noted. First, a rather substantial area remains between the two main peaks after background correction. If our correction procedure is right, this area must represent structure. A similar correction procedure for ZnF_2 gave no intensity in this region, reinforcing the interpretation that the additional intensity in the MnF_2 spectrum is intrinsic. Secondly, the tops of the $2p_{1/2}$ and $2p_{3/2}$ peaks show signs of possible structure.

Recently Gupta and Sen⁵¹ (GS) have calculated the expected 2p XPS spectrum for MnF_2 by working out the levels of the p^5d^5 system, employing Hartree-Fock results on the Mn^{+2} ground states. The calculations were done on three levels of sophistication. At level one, they considered only the effect of electrostatic interaction. At the second level, the spin-orbit interaction was introduced.

Crystal field effects were included at the last level. For the 2p levels, we will compare our results with GS level-two results (their Fig. 1), since the spin-orbit interaction is comparable to the electrostatic interaction and crystal field effects did not significantly alter their results. The solid bars in Fig. 6 show the positions and intensities of the twelve eigenstates found by GS. Their energy scale was reduced by 4% to match the experimental spectrum. Adjustments of this magnitude are not surprising, because GS did not do a relaxed hole-state calculation. Figure 6 shows the GS calculation to be compatible with our XPS spectrum in considerable detail. The two peaks are asymmetric in direction that agree with the GS results. In fact, when the latter were broadened with Lorentzian functions of appropriate intensities the resulting simulated spectrum showed asymmetries of $\alpha(3/2) \sim 1.7$ and $\alpha(1/2) \sim 0.5$ in fair agreement with the experimental values of 1.6 and 0.8, respectively, mentioned above. The $2p_{3/2}:2p_{1/2}$ peak intensity ratio is greater than 2:1 because the six lowest-intensity lines correspond to states formed mostly from the $p_{1/2}$ level. The residual structure in the experimental spectrum just to the right of the $p_{1/2}$ peak is attributable to these states. The failure of these states to appear as sharper structure (as their intensities would require) probably indicates that these states are in fact distributed further by electron correlation effects not considered in the GS calculation. Both main peaks also show small residual tails on their left (high binding energy) sides. This tailing is chronic in our XPS spectra. We are uncertain of its origin,

but we do not attribute it to the kind of multiplet splitting under discussion. On the basis of the comparison shown in Fig. 6, we conclude that the GS calculation explains the essential features of the $2p_{1/2} - 2p_{3/2}$ XPS spectrum of MnF_2 .

Figure 7 shows the $K\alpha_1$ X-ray emission spectrum of MnF_2 , after Nefedov.⁶¹ This spectrum is to be compared to the $2p_{3/2}$ part of Fig. 6. The spectra are qualitatively very similar with the X-ray spectrum appearing to show more resolved structure. Both spectra have a FWHM of 3.7 eV. The components in Nefedov's spectrum are about 1.0 eV apart. A least-squares fit of our XPS $2p_{3/2}$ spectrum with four Gaussian functions restrained to have the relative intensities given by the GS results are separated by a similar amount. The agreement with the GS calculation is not quite so good. The results of the two experiments and the GS calculation are summarized in Table III. The agreement is fair for the $2p_{3/2}$ peak and not quite so good for the $2p_{1/2}$ peak. Also given in Table III are the recent results of Pessa.⁶³

It seems useful at this point to comment on the extent to which the anomalous $2p_{1/2} - 2p_{3/2}$ results for MnF_2 should be generally observable in transition metals and their salts. In doing so we must first acknowledge the pioneering work of Nefedov on the manifestation of this effect in X-ray spectra⁶¹ and the recent discussion by Frost, et al., on its influence in XPS spectra.⁵² Our comments are largely based on theirs.

The $2p_{1/2}$ and $2p_{3/2}$ peaks are separated by $3/2 \xi_{2p}$, where ξ_{2p} is the spin-orbit coupling constant, given as the expectation value of the operator

$$(\xi)_p = - \frac{e}{2m} \frac{1}{c^2} \frac{\partial v}{\partial r} \quad (6)$$

where $v(r)$ is the electrostatic potential. Now in the interior of an atom $\frac{\partial v}{\partial r}$ is affected very little by changes in the valence shell, and the observed anomalies in $\Delta E(2p)$ are much too large to be attributed to any real variation in ξ_{2p} . That such anomalies do exist was demonstrated by Nefedov⁶¹ in his Fig. 1. We have made a similar plot (Fig. 8) using new X-ray data and XPS data from this Laboratory. The object of this plot is to display any anomaly that may exist in $\Delta E(2p)$. To this end, the x-ray difference $E_B(p_{1/2}) - E_B(p_{3/2}) = E(2p)$ was plotted against Z for $13 \leq Z \leq 42$. Data for each element in elemental form were used. Because ΔE varies rapidly with Z , the reduced quantity

$$E_r(2p) = \frac{\Delta E(2p)_Z}{\Delta E(2p)_{Al}} \left[\frac{(Z-2)}{Z} \right]^4, \quad (7)$$

was actually plotted. This form was suggested by the fact that in a Coulomb field $V(r) = Ze/r$ the operator ξ takes the form

$$\xi = \frac{Ze^2}{2m} \frac{1}{c^2} r^{-3}, \quad (8)$$

and (r^{-3}) is proportional to Z^3 . We used $(Z-2)^4$ rather than Z^4 to account for shielding of the $2p$ electrons by the $1s$ shell. Data and references are given in Table IV. Also listed are

$E_r(\text{HFS}) = E(2p)/E(2p)_{\text{HFS}}$, where $E(2p)_{\text{HFS}}$ are the free-atom

Hartree-Fock-Slater orbital energy differences calculated by Lu, et al.⁶⁵ Finally, points representing the compounds in Table II are included in Fig. 8.

The anomalous behavior of $\Delta E(2p)$ for the transition series metals is very obvious from Fig. 8. The anomaly is even larger for compounds. Nefedov explained this effect in terms of exchange coupling between the unpaired 3d spin S and the $2p_{3/2}$ and $2p_{1/2}$ holes, with the highest-spin state in each case being pushed to the extremes of the multiplet pattern. That this is the essence of the GS calculation is apparent from Fig. 2, in which the intensities of the eigenstates are nearly proportional to their multiplicities. The extreme eigenstates are thus the $J = 3$ state with the total angular momentum of the $2p_{1/2}^{-1}$ state coupled parallel to the $3d^5$ spin of $5/2$ and the $J = 4$ state with $S = 5/2$ and $J(2p_{3/2}^{-1}) = 3/2$ parallel. The additional configurations considered by GS have the effect of introducing additional eigenstates between the two main peaks. These will have interacted and pushed the outermost states further apart. It would appear that this is a rather general phenomenon for cases in which there is unpaired spin in the 3d shell. Transition metals cannot be discussed in terms of simple configurations such as $3d^5, ^6S$; but they are known to possess localized 3d spins, at least in the series Cr-Ni, and the enhancement of $\Delta E(2p)$ apparent in Fig. 8 is qualitatively understandable.

A cursory search for a similar anomaly in $\Delta E(3p)$ from X-ray data on the 4d transition metals failed to show any effect. From a practical point of view, the 2p transition metal photoemission lines are often the most intense features in the spectra of transition metal compounds; thus they would be the first choice to use in diagnostic work. However, with the presently available resolution in XPS the structure is at best barely resolvable, and the value of these lines as a "spin fingerprint" is limited. There are, however, two features from our above analysis which allow these lines to be used as a "spin probe." These are the line asymmetry and the $2p_{1/2} - 2p_{3/2}$ peak maximum separation, which should scale with spin. The 2p lines also have some disadvantages. First the peaks are usually superimposed on a high and often rapidly varying background. Second, this area of the spectrum is often complicated by Auger lines. The 3s and 3p spectra, while of much lower intensity, are usually on a low and flat background. These spectra, however, have the problem of being complicated by electron correlation effects which are largely absent in spectra of $N = 2$ lines. These correlation effects are discussed below.

4. The Mn 3p structure

Figure 9 shows the high resolution XPS spectrum of the Mn 3p region of MnF_2 . The features of this spectrum are summarized in Table IV. The spectrum is qualitatively the same as the earlier work of Fadley, et al.^{35,36} but the features are better resolved. The satellite structure is also less ambiguous, because the present

study employed monochromatized X-rays, and the spectrum is free of $\text{AlK}\alpha_{3,4}$ satellites from the Mn 3s peaks and Bremsstrahlung background. Improved vacuum conditions (5×10^{-9} vs. 10^{-6} torr) plus in situ cleavage of the specimen crystal add further confidence that the structure in this region is intrinsic to MnF_2 .

We note also that $K_{\beta\beta'}$ (3p-1s) X-ray emission spectra⁶⁶⁻⁶⁹ have shown considerable structure. This has been given the same interpretation as the XPS results.

Fadley, et al.,³⁵ demonstrated the inadequacy of the Koopman's Theorem approach in explaining the 3p multiplet structure. Multiplet-hole theory (MHT) gave some improvement but the agreement was still somewhat less than satisfactory. Their theoretical results have been duplicated and confirmed by Gupta and Sen.⁵¹ It was suggested by Fadley, et al.,³⁵ that part of the discrepancy between the experimental results and theory might be due to spin-orbit and crystal-field effects. These two effects were studied by GS and found to have a negligible effect.

The next step would appear to be the inclusion of electron-correlation effects. Correlation should be more important for the 3p-3d interaction than for the 2p-3d interaction analogous to the situation that obtains in the 3s and 2s levels.⁴⁶ Electron correlation effects are crucial in understanding the Mn 3s spectrum in MnF_2 .^{46,47} Inclusion of correlation effects leads to more 3s peaks than the Hartree-Fock one-electron model and affects the distribution of intensity among the peaks. These predictions have been confirmed

by experiments.⁴⁶ Intra-shell correlations are thus usually important in XPS multiplet spectra, while inter-shell correlations are not. Thus correlation must be considered in the Mn 3p spectrum even though the 2p spectrum could be explained without taking correlation into account.

Correlation can be introduced into a Hartree-Fock multiplet-hole calculation by including configuration interaction.⁴⁷ This approach, which worked very well in explaining the anomalies in the Mn 3s spectrum, does not appear to work for 3p spectra.⁵⁴ Bagus and Wahlgren⁵⁴ have performed a Hartree-Fock calculation with configuration interaction to predict the Ni 3p spectrum in a NiO_6^{10-} molecular cluster. This calculation gave satisfactory agreement with XPS results of Ref. 70, although a detailed comparison with experiment was not possible because of the rather complicated nature of the spectra. The new peaks in the cluster calculation were attributed to the symmetry of the cluster being lower than in the free ion, enabling the nickel d electrons to rearrange themselves in more ways than possible in the free ion. These results suggest that perhaps the XPS results of MnF_2 can be explained in similar terms. The simpler spectrum of MnF_2 makes it a good test for a correlated MFT calculation.

While a detailed comparison with theory is not yet possible, the good resolution in the 3p spectrum in Fig. 9 allows us to perform a sum-rule test that has not been feasible before. The weighted average of the energy of the satellites, $\bar{E}(^5P)$ can be used to define an average $^5P - ^7P$ energy separation $\Delta\bar{E}$, given by

$$\Delta E = \bar{E} (^5P) - E (^7P) . \quad (9)$$

From this data in Fig. 9, we obtained $\Delta E = 14.5$ eV in MnF_2 . This should be comparable to Koopman's Theorem results which predict only two 3p peaks. Values of 13.5 and 13.7 eV have been obtained with the Koopman's Theorem description.^{35,36} Also the intensity ratio of the area of the 7P peak to the sum of the area of 5P peaks was 1.1 or fairly close to the multiplicity ratio of 1.4. This good agreement provides further support to the multiplet-hole theory of the 3p spectrum even though we do not as yet have a theory that can predict the positions, or even the number, of final-state 5P peaks.

5. Summary

High-resolution XPS spectra were obtained for the Mn 2p levels in MnF_2 . Structure attributable to multiplet splitting was observed. The evidence for multiplet splitting is fourfold: 1) The asymmetry of the $2p_{3/2}$ peak is greater than unity and the asymmetry of the $2p_{1/2}$ peak is less than unity; 2) the separation of the peak maxima of the $2p_{1/2}$ from $2p_{3/2}$ lines is significantly larger in MnF_2 than in pure Mn metal; 3) after the subtraction of inelastic background and characteristic energy loss structure, there remained significant intensity in the region between the main $2p_{1/2}$ and $2p_{3/2}$ peaks; and 4) the XPS spectrum was shown to be in qualitative agreement with the calculation of Gupta and Sen. The XPS spectrum also agreed with earlier $K\alpha$ X-ray emission studies.

More generally, a review of X-ray $K\alpha_{12}$ spectra and XPS data showed an anomalously large $2p_{1/2} - 2p_{3/2}$ splitting in the transition elements Sc through Ni, as noted earlier in the X-ray literature. Since the $2p_{1/2}^{-1}$ and $2p_{3/2}^{-1}$ states are expected to couple to an unpaired spin S in the 3d shell in such a way as to place the maximum J states ($S = 1/2$ and $S = 3/2$, respectively) at extreme energies, it is likely that the anomalous values of $\Delta E(2p)$ arise through multiplet coupling of 2p and 3d electrons.

The Mn 3p spectrum of MnF_2 was measured with improved resolution. Effects of electron correlation and crystal symmetry were concluded to be extremely important. It was suggested that a calculation on a MnF_6^{4-} cluster would be a good test of the correlated MFT theory. There is still a need for high resolution XPS work on transition metal compounds, to test and encourage theoretical work in this area. These results indicate that a qualitative understanding of the 2p and 3p spectra of transition metal ions is possible within the framework of existing theoretical models.

Besides attempting to understand these spectra as a problem in atomic physics, we can try to use these spectra as a probe of unpaired spin density in transition metal compounds. While the presently available XPS resolution does not yet allow the intense 2p lines in transition metals to be used as a definitive spin "fingerprint," these lines can still be used to probe spin density in two ways. The asymmetry of the $2p_{1/2}$ and $2p_{3/2}$ line should scale with spin, as should the separation of the $2p_{1/2}$ and $2p_{3/2}$ maxima. The 3p spectra were also shown to have possible diagnostic value by converting the

"CI spectrum" into a "Koopman's Theorem Spectrum." It would be very valuable if this approach could be systematically applied to a series of transition metal salts, because the separation of the high- and low-spin centroids in the Koopman's Theorem Spectrum should be a good measure of the total 3d spin.

D. Multiplet Splitting: Transition Metal Compounds (Halides and Oxides)

1. Introduction

In this section we discuss core-level spectra for several transition metal compounds, namely MnF_2 , FeF_2 , CoF_2 , NiF_2 , ZnF_2 and CoO , NiO , and ZnO . The spectra of these compounds will be discussed primarily in terms of the detailed analysis of MnF_2 in the previous two sections.

These experiments were performed on single crystals except in the case of NiF_2 which was prepared by heating anhydrous NiCl_2 in a stream of fluorine at 450°C . Subsequently, it was sublimed in a stream of HF at 1200°C . All the fluorides were cleaved in situ ($P \sim 5 \times 10^{-10}$ torr) and no oxygen or carbon could be detected (except NiF_2 which showed signs of small carbon contamination.)

The oxides were cleaved in an inert atmosphere (flowing N_2 boil off from an L. N. dewar) and immediately inserted into spectrometer ($P < 5 \times 10^{-9}$ torr) without exposure to ambient atmosphere. These samples showed slight carbon and oxygen surface contamination.

2. 3s and 2s spectra

The spectra of the 3s region from several transition metal compounds are given in Figs. 2, 10-15 and the observed splittings are given in Table VI along with recent calculations which included configuration-interaction (CI). As discussed for the case of the Mn^{+3} hole state, intra-shell correlations have a very large effect on the magnitude of the multiplet splitting and the distribution of the spectral intensity. As discussed in section 8, the one-electron Hartree Fock approaches predict core-level splittings much too large when the core-level has the same principle quantum number as the unpaired electrons. This can be seen from Table VII, where values from various one-electron approaches are listed for the transition metal ions. This is due to the uneven treatment of correlation in the Hartree-Fock scheme. The parallel electrons are well correlated because of the requirements of the Pauli Principle which introduces a "Fermi hole."⁷¹ However, there is no provision for a "Coulomb hole." Also given in Table VII are the parameters employed in Eqn. 4 to predict the 3s splittings in these transition metal compounds. Fig. 16 shows the variation of $G^2(3s,3d)$ across the 3d metal series. Fig. 17 shows the variation of S_1 across the transition metal ion series, as well as Van Vleck's Theorem predictions for this series. This figure illustrates why previous attempts to correlate ΔE_{3s} directly with S_1 have failed.⁴¹ The exchange integral "skews" the symmetrical S_1 vs. number of 3d electrons curve. Fig. 17 also allows us to empirically account for correlation. An empirical scaling factor for correlation can be

obtained by dividing the calculated splitting for Mn (either $\Delta E_{3s}^{VV} [Mn^{+2}]$ or $\Delta E_{3s}^{MFF} [Mn^{+3}]$ by the experimentally observed $\Delta E_{3s}^{XPS} [MnF_2]$). This reduction factor is nearly exactly constant across the 3d series and has been attributed to pairwise additivity of the electron-electron or hole-hole correlation energies (~ 2.7 eV/spin).⁷² Table VIII shows in fact that the empirical values are in better agreement with experiment than even the CI calculations, though the CI results are much improved over the straight one-electron calculations. The deviation of CI predictions from observations may be due to the fact that it is just a mathematical method of attempting to treat electron correlations -- really a many-bodied problem. To be tractable, one includes in a CI calculation the physically intuitive and reasonable configurations. The advantage of the CI approach to electron correlation is that it maintains a conceptually physical, albeit imperfect, picture.

The 2s spectra of transition metals in the transition metal compounds are hard to measure accurately since they are very broad (lifetime effects) and have low signal to background. Also for several of these elements using the common soft-X-ray sources, the LMM Augers fall in this region and may overlap the core level spectra. MnF_2 is the best case (see Fig. 4) and is our only reliable value. Our measurements agree quite well with the results of Wertheim, et al.⁷³ (see Table VII).

3. 3p and 2p spectra

The 3p spectra for several transition metal compounds are shown in Figs. 9, 10, and 13-15. As was the case with MnF_2 , these spectra are very complicated. For the same reasons (intra-shell correlations), the Hartree-Fock one-electron model fails to predict the 3p spectra of these compounds. The CI approach for the treatment of correlation, which worked very well in the case of the 3s electrons (see the discussions in previous sections), does not predict correctly either the number of peaks or relative intensities of the peaks for the 3p case.^{35,54} A promising theoretical approach is a CI calculation on clusters (metal ion and its nearest neighbors treated explicitly). Bagus and Wahlgren performed such a calculation on a NiO_6^{10-} cluster.⁵⁴ These authors noted that the quartet-doublet splittings were considerably smaller for the clusters than for the free ion which was an indication of the importance of covalency. This calculation (see Fig. 18) gives reasonable agreement with experiment. One interesting result found by Bagus and Wahlgren was that some of the doublet states have lower energy than quartet states. As pointed out by Bagus and Wahlgren, the physical mechanism responsible for the spectral distribution in their calculation is the rearrangements of Ni d-electrons among e_g and t_{2g} shells. While the agreement with experiment is pleasing (see Fig. 18), it is somewhat ambiguous because the spectra have several broad peaks, and various shake-up and multi-electron mechanisms⁷⁴ are thought to be important. Thus calculations on clusters representing MnF_2 and FeF_2 would be important in

separating out these effects, since these compounds exhibit little shake-up structure. Similar multiplet effects have been observed in K β X-ray emission spectra.^{64,66-69,75,76} It has recently been suggested^{64,77,78} that comparison of XES (K β) with the XPS 3p be used to separate the so-called "shake-up satellites" from the multiplet structure (see Chapter II, section C-6). In the case of MnF₂, where there is little "shake-up" intensity, recent high-resolution K β study (XES) of Pessa⁶⁴ which parallels our XPS study of Mn 3p levels in MnF₂, yielded a spectrum similar to the XPS spectrum. Likewise, K β studies of Asada, *et al.*⁷⁷ on Ni compounds (NiO and NiCl₂) yielded spectra similar to the XPS 3p spectra, but minus the shake-up satellites. These authors also studied the effect of 10 kV on the spectral distribution.

The 2p spectra for the compounds under consideration are shown in Figs. 5, 19-23. Gupta and Sen have carried out a series of calculations similar to the Mn⁺² and Fe⁺³ calculation of Ref. 51 for a large number of transition metal ions spanning the whole 3d series.⁷⁹ It is unfortunately not presently possible to carry out detailed analysis similar to the MnF₂ case (section C) due to resolution and the linewidths. It appears that these lines are multiply split. Earlier X-ray emission studies of K α lines also showed asymmetries presumably due to multiplet splitting.^{59,61,64,68,69,75,77}

FeF₂ and MnF₂ show weak satellites to the high binding energy side of both the 2p_{1/2} and 2p_{3/2} peaks. These satellites are much more intense in the Co and Ni compounds (Figs. 20-23). The possible origin of these satellites which were first observed in some Ni and Co

compounds by Novakov^{19,80,81} have been discussed in detail by Kim.^{74,82,83} These satellites have also been observed in earlier members of the 3d metal series.⁸⁴⁻⁸⁶ K α emission spectra exhibit no shake-up satellites.^{64,77} Table III compares our MnF₂ results with the high resolution XES measurements of Pessa.

One of the interesting and unanswered questions is that the intensity [especially obvious in CoO and NiO (Fig. 23)] of the satellites relative to the main peak are different in the 2p_{1/2} and 2p_{3/2} cases. Kotani and Toyozawa^{25,26} have recently proposed a mechanism for these satellites in which in the final state, d level is lowered below the Fermi level. So far they have carried out just qualitative model calculations.

E. Multiplet Splitting of 3s Core Levels of the 3d Transition Metals Sc Through Zn*

1. Introduction

The phenomenon of multiplet splitting of core-level binding energies is well known in the XPS spectra of transition metal halides and oxides (see previous section). It arises because the hole produced by photoemission can couple either parallel or antiparallel to the majority 3d spin of the ion, producing final states of different energy. The simplest description of the splitting is obtained by neglecting electron-electron correlation and using Van Vleck's Theorem³¹ which yields for the 3s splitting

$$\Delta E(3s) = \frac{(2S_i + 1)}{5} G^2(3s, 3d) \quad (9)$$

* Work done in collaboration with F. R. McFeely, L. Ley, and D. A. Shirley. The results for α -Mn have been published in Solid State Commun. 15, 1051 (1974).

where S_i is the initial-state spin. In fact, electronic correlation effects are in general not negligible. This tends to reduce the splitting from the above value and produce satellite peaks.

Despite these not easily calculable many-body effects, multiplet splitting has some advantages in comparison with other methods. Magnetic susceptibility can be measured quite accurately and can yield valuable information on the existence or nonexistence of localized moments. Its disadvantage lies in the more complicated systems, in which one cannot be sure a priori that all the ions are magnetically equivalent. In these cases, the observed average atom moment could reflect either a well-defined moment present on every atom or a wide distribution of moments with this average value. Neutron diffraction is another powerful technique, particularly for the study of antiferromagnetically ordered states, in which extra magnetic periodicity gives rise to well-defined diffraction features. By analysis of the structure and form factors associated with the magnetic scattering, it is possible to study both the magnitude and relative orientation of the spins. Above the transition temperature, one can measure only diffuse magnetic scattering. From the magnitude of this background an average moment can be calculated. The difficulty arises from the fact that neutron scattering is a relatively slow process, with a typical interaction time of $\sim 10^{-12}$ sec. Thus if the fluctuation time of the moments is much faster than 10^{-12} sec., the analysis could yield a spurious zero result. X-ray photoemission, however, is a fast process occurring on a timescale of $\sim 10^{-16}$ sec.,

and is certainly faster than any spin fluctuation time. In addition XPS, being a spectroscopic technique, can distinguish between single-valued moment systems and distributions of moments by the number and widths of the photoemission lines.

In the 3d transition series, one can distinguish three distinct classes of magnetic behavior, "normal" Pauli-type paramagnetism in which the susceptibility is only weakly temperature dependent, anti-ferromagnetism, and ferromagnetism. Scandium, titanium, and vanadium comprise the first class, manganese and chromium the second, and iron, cobalt and nickel the third. We shall consider each of these classes in turn. The measurements were made on films prepared in situ under UHV conditions either by vacuum deposition or by sputter deposition and in some cases by both. The only detectable contaminant was oxygen and it was always never more than a small fraction of a monolayer.

2. Scandium, titanium and vanadium

In a sense, Sc, Ti, and V exhibit the solid-state effects on the 3s spectra most strongly. A free atom or dipositive ion of any of these elements would be expected to show detectable multiplet splitting; however in the solid this splitting disappears. As can be seen in Fig. 24, the 3s spectra appear as single, rather broad lines. They are somewhat asymmetric, but this feature is generally found in photoemission spectra of core levels in metals. It arises from the self-consistent screening of the final (core hole) state by the valence electrons.

The absence of multiplet splitting in these metals is consistent with the picture of itinerant 3d electrons well described by one-electron band theory. In this picture a paramagnetic metal is described as having spin-up and spin-down bands equally populated, with no resultant spin density at any site. This lack of unpaired spin density is reflected in the absence of multiplet splitting in these metals. This picture is further borne out by the magnetic susceptibility measurements on these metals,⁸⁸ which show no strong temperature dependence.

3. Chromium and manganese

Chromium and manganese are both antiferromagnetic, but their magnetic structures differ in one important way. Below $T_N(310^\circ\text{K})$ the magnetic periodicity of Cr is incommensurate with the lattice periodicity,⁸⁹ with the result that the local spin densities at crystallographically equivalent sites are unequal. As a result, the antiferromagnetism in Cr has been described as a collective phenomenon of the itinerant valence electrons, resulting from the peculiar "nesting" properties of the Fermi surface.⁹⁰ In the case of Mn no such "periodicity mismatch" was observed.⁹¹

While the Mn results are straightforward and amenable to a Van Vleck's theorem type of analysis, the chromium results suffer from an unfortunate experimental ambiguity. Because the Neel temperature of 310°K is so close to room temperature, we cannot be sure whether the surface of our sample, under intense X-ray bombardment, was above or below T_N . Below T_N neutron diffraction^{92,93} has shown that the sinusoidal modulation of the atomic moments has a

periodicity 27 times that of the unit cell at T_N , and that the maximum in the magnetic moment distribution corresponds to $\sim .59 \mu_B$. Above the Neel temperature, incoherent neutron scattering detected no component of any random moment fluctuating with a frequency less than ~ 0.1 eV/h. However, spin-density-wave theory would predict spin fluctuations at a frequency characteristic of the d-bandwidth ~ 4 eV/h, too fast to be detected by neutron scattering.

The photoemission spectrum of the Cr 3s region as shown in Fig. 25 reveals a broad structure of two peaks separated by 2.8 eV. If one takes the simplistic Van Vleck's theorem approach and derives $(2S_1 + 1)$ from the 3s splitting in CrF_3 , it appears that the splitting in Cr metal corresponds to a moment of $\sim 1.7 \mu_B/\text{atom}$. As our measurement was probably performed on Cr above T_N , due to intense X-ray bombardment of the sample, this result bears an interesting similarity to that in Mn. In both cases the simple analysis suggests that the moments in the paramagnetic phase are considerably larger than they are in the antiferromagnetic phase. The widths of the individual components of the Cr spectrum are considerably larger than in Mn, perhaps reflecting a distribution of moments in Cr. At this time it is, however, impossible to state anything quantitative. It would be useful to measure both the splitting and linewidth as a function of temperature starting well below T_N and continuing well past it.

Alpha manganese is unusual among metals of the 3d transition series. it has a complex b.c.c. lattice with 29 atoms per unit cell. Its magnetic structure is also unusual. Shull and Wilkinson found⁹⁴

that α -Mn is antiferromagnetic below ~ 100 K, and they reported an average magnetic moment of $0.5 \mu_B$ in the paramagnetic phase up to 500 K, using neutron diffraction. Recent NMR⁹⁵ and neutron diffraction⁹⁶ studies have indicated at least four different magnetic moments below T_N with a weighted average of $0.63 \mu_B$, but d.c. susceptibility measurements⁹⁷ on the paramagnetic phase have been analyzed to yield an average moment of $2.37(7) \mu_B/\text{atom}$, in contrast to the neutron diffraction value. To elucidate the nature and magnitude of the atomic moment in the paramagnetic phase we have carried out X-ray photoemission experiments. Multiplet splitting of the 3s and 2s lines reveal the presence, on the 10^{-15} sec. time scale, of a localized 3d spin, corresponding to a localized magnetic moment of $\sim 2.5 \mu_B$.

The 3s and 2s spectra (Fig. 26) both show doublet structures due to multiplet coupling of the final 3s (2s) hole state with the incomplete valence shell of Mn. The 3s peaks were fitted to Lorentzian lineshapes by a non-linear least squares procedure. The analysis of spectra obtained from two different samples yielded values of $4.12(10)$ eV and $4.05(10)$ eV for the separation of the two peaks. The intensity ratio of the peaks was approximately 1.3 in each case. Due to the high degree of inelastic scattering associated with the 2s photoemission lines, we were not able to fit these spectral features to analytic peak shapes; however, the two components of this feature appear to be separated by ~ 3.5 eV.

Since the discovery of antiferromagnetism in α -Mn by Shull and Wilkinson, the exact nature of the magnetic moments, both in the ordered and paramagnetic states, has been a subject of considerable controversy. The problem is complicated by the fact that the α -Mn structure has four crystallographically inequivalent sites, with 1, 4, 12, and 12 atoms respectively. These sites may of course carry different moments. On the basis of neutron diffraction data, several models for their magnitude in the antiferromagnetic state have been proposed.^{98,96} However, the NMR work of Yamagata and Asayama⁹⁵ indicates that atoms even on crystallographically equivalent sites may carry different moments. This result, along with the suggestion by Sato and Arrot⁹⁹ that the wavevector characterizing the magnetic ordering might deviate from $[1,0,0]$, would necessitate a spin-density wave treatment of the antiferromagnetic state. However, the single-crystal neutron diffraction work of Yamada, et al.,⁹⁶ revealed no such deviation, and these workers suggested a localized-moment model, with a weighted average moment of $0.63 \mu_B$.

In the paramagnetic state, the first determination of the average moment was made by Shull and Wilkinson on the basis of the paramagnetic diffuse neutron scattering intensity. They deduced an average moment of $\sim 0.5 \mu_B$ and suggested that this was due to a mixture of atoms with 0 and $1 \mu_B$. Recently, however, Nagasawa and Uchinami⁹⁷ measured the magnetic susceptibility of α -Mn in the paramagnetic state below 300K and determined a value of $2.37(7) \mu_B$ for the average magnetic moment. These two observations are not necessarily

contradictory. Neutron scattering would detect moments with correlation times of $\sim 10^{-12}$ sec. or longer. The d.c. susceptibility -- a macroscopic quantity -- is independent of correlation time.

Multiplet splitting in the core-level spectra of manganese salts is well known.^{27,35,36,40,41,46,73} The simplest interpretation of the 3s multiplet splitting ΔE would neglect electron correlation and employ Van Vleck's Theorem,³¹ for exchange splitting of a $3s^1 3d^n$ final state in which the d electrons couple to spin S. Given the essential constancy of the exchange integral $G^2(3s\ 3d)$ -- an atomic parameter -- equation (4) can be used to deduce S from $\Delta E(3s)$, if G^2 is known. In fact the situation is substantially complicated by electron correlation, and the relation

$$\Delta E(3s) \cong (\text{const.}) (2S + 1) , \quad (10)$$

is expected to be only approximately correct even in salt. In a metal such as Mn, further complications are introduced by the partially itinerant nature of the 3d electrons and by the presence of the s-p conduction bands. Electrons in these bands can screen the 3s-3d and 3d-3d interactions, reducing both the correlation effects responsible for additional satellite peaks and thus the intensity ratio of the two observed peaks in Mn relative to Mn^{2+} , as observed.

It is difficult to assess the importance of these complications. We note that the 3s-4s exchange integral $G^0(3s\ 4s)$ is small relative to $G^2(3s\ 3d)$. Also, the sp band is probably itinerant and largely unpolarized. Thus we shall neglect the effect of sp bands on $\Delta E(3s)$. Since the 3s orbital lies well within the atom (as evidenced by the

value of $r_{3s} = 0.464$). The dominant contributions to the exchange integrals should come from within the atomic core and thus be relatively insensitive to changes in bonding. To the extent that this is true, $\Delta E(3s)$ should be proportional to $(2S + 1)$. On this basis we have plotted $\Delta E(3s)$ of MnF_2 , MnF_3 , and MnO_2 against the nominal value of $(2S + 1)$ in Fig. 27, and plotted a line through these three points, obtaining $\Delta E(3s) = 1.0(2S + 1) + 0.6$. The non-zero intercept necessitated by this fit must be regarded as an empirical parameter, and reflects the insufficiency of the Van Vleck's Theorem treatment. From this equation the $\Delta E(3s) = 4.08$ of α -Mn corresponds to a $2S + 1$ value of 3.50, hence to a "spin only" magnetic moment of $\sim 2.5 \mu_B$. This is in excellent agreement with the susceptibility value of $2.3 \mu_B$. The multiplet splitting spectrum provides a spectroscopic measurement of this localized moment, albeit with low resolution: we can infer from the spectrum that most or all of the sites in α -Mn have a moment near the nominal value of $2.5 \mu_B$. Also on Fig. 27, we plotted some values for Fe and obtain $\mu = 2.2 \mu_B$ for Fe metal in excellent agreement with the well known value for Fe^{100} and thus giving us further confidence in using the "calibration curve" for obtaining S_i or μ .

Both the excellent agreement of this derived moment with the susceptibility data and the agreement between $\Delta E(2s)/\Delta E(3s)$ in Mn and MnF_2 (~ 0.9 in each case) support our interpretation. We believe, however, that this agreement may be in part fortuitous, and we do not wish to emphasize its quantitative aspects. These observations

appear to establish the following attributes of paramagnetic α -Mn:

1) Localized spins exist on the Mn atoms on the time scale of 10^{-15} sec.,¹⁰¹ 2) they have an average spin $S \sim 1.25$, and presumably a moment $\mu \sim 2.5 \mu_B$, and 3) most or all of the Mn sites have values of S not too far from this average value. Any viable theoretical model for α -Mn should be consistent with these three features.

4. Iron, Cobalt, and Nickel

Iron, cobalt, and nickel are all ferromagnetic at room temperature, exhibiting a macroscopic magnetic moment. The 3s spectra thus is expected to show multiplet splitting. In Fig. 28, considerable structure is indeed apparent in the 3s photoemission spectrum. There is, however, a striking difference between the appearance of these spectra and those of Cr and Mn. In Cr and Mn, the spectrum was clearly composed of two fairly well defined peaks of comparable linewidth, while if the ferromagnetic spectra were regarded as being composed of two lines, the low-spin component would have 2-3 times the width of the high-spin component. This effect is unlikely to arise from a distribution of moments, as in that case the high spin peak would be equally broadened. It could be suggested that this effect results from excess lifetime broadening of the low-spin hole state. This could be rationalized on the basis that there is an excess of "spin up" electrons in the ferromagnetic state, which can fill the 3s hole without flipping spins. There are, however, two factors which argue against this: 1) The lines are not clearly Lorentzian in shape, and lifetime broadening is always Lorentzian; and

2) Fadley and Shirley³⁶ studied the 3s spectrum of iron below and above the Curie point, and while their spectra were of lower resolution they would have detected any dramatic decrease in broadening for $T > T_C$, and none was observed. We are thus led to conclude that the width of this structure arises from correlation effects.

Correlation effects are well known to cause dramatic effects in XPS core-level multiplet splitting experiments. In addition to reducing splittings by a factor of two from Hartree-Fock estimates, configuration interaction in the final state can produce low-spin satellite peaks of appreciable intensity, as in the case of MnF_2 .⁴⁶ It is not unreasonable to assume that in a metal, where there exists a continuum of one-electron orbitals of strongly mixed angular momentum, strong interconfiguration mixing could produce a quasicon- tinuum of final states. That strong interconfiguration mixing should be present in a ferromagnetic metal is furthermore quite plausible, as single determinantal theories are quite unsatisfactory for the description of ferromagnetic states (e.g., they cannot explain spin-waves, while theories involving linear combinations of determinants can).¹⁰²

Figure 29 shows Cu and Zn 3s spectra. These metals have filled 3d shells and low values of $N(E)$ at E_F . Their 3s XPS lines show no indication of multiplet splitting. The 2s, 2p, 3p, and LMM Auger Spectra of Sc through Zn are given in Appendix A-9.

F. Multiplet Splittings of Core Levels in the Rare Earth Metals*

1. 4s and 5s levels *

We have measured the 4s and 5s splittings of most of the rare earth metals. The samples were all prepared by in situ vapor deposition under UHV conditions. Representative spectra are shown in Figs. 30-32.

Our measured 4s and 5s splitting of the metals are given in Table IX and compared with earlier work on several trifluorides. The good agreement of the metal results with those of the trivalent ions is not surprising, since it has been shown earlier that the XPS spectra of the 4f region of the metals compare well with optical data of the trivalent ions and with XPS results on the trifluorides.

The simplest estimate of the splitting ΔE_{ns} is obtained by invoking Van Vleck's theorem³¹ which yields

$$\Delta E_{ns}^{WV} = \frac{(2S + 1)}{7} G^3 (ns, 4f) , \quad (11)$$

where S is the initial-state spin. These results are given in Table IX and plotted in Fig. 33 along with the experimental results. The use of Mann's atomic Slater integrals,³² G^3 is justified because the 4f states are essentially core-like. Eqn. (11) reproduces ΔE_{5s} quite well; however, it systematically predicts a value that is 80% too high for ΔE_{4s} . This result is analogous to that in the 3d metal series, where it has been theoretically shown and experimentally verified that intra-shell correlations are extremely important, while

*Based on work done in collaboration with F. R. McFeely, L. Ley, and D. A. Shirley and published in Phys. Letters 49A, 301 (1974).

inter-shell correlations are much smaller because electrons in different principal shells are already spatially correlated. The reason for the overestimated of ΔE_{4s} by Van Vleck's theorem is quite simple. In the high-spin final state, the 4s and 4f electrons are spatially separated by the antisymmetry requirements of the Pauli Principle. Thus inclusion of correlation will lower the energy of the low spin final state more than of the high spin final state, reducing the splitting. To obtain accurate theoretical values for ΔE_{4s} , it would be necessary to do a configuration interaction calculation on the final state as was done for the transition metal ions.^{47,49}

Figure 33 graphically demonstrates that Eu and Yb metals are not trivalent like the other metals but are divalent due to stability of half-filled or completely filled shells. Figure 33 also suggests that Y-Ce at room temperature is trivalent.

2. X-ray photoemission spectra of the 4d levels in rare earth metals^{*}

Rare earth metals and rare earth compounds, with their large number of unpaired 4f electrons, should present particularly interesting cases for study of multiplet structure. Earlier XPS studies have in fact revealed multiplet structure in rare earths. Early work on gaseous Eu showed an anomalous 4d photoelectron spectrum.³⁶ Cohen, et al,³⁸ observed and assigned multiplet structure in rare-earth trifluorides. Recently, Signorelli and Hayes⁴²

*Based on work done in collaboration with N. Edelstein, F. R. McFeely, L. Ley, and D. A. Shirley and published in Chem. Phys. Letters 29, 491 (1974).

reported complex structure in the 4d spectra of compounds of La, Ce, Pr, Eu, and Yb, which they attributed to "monopole excitation" (correlation peaks) and electrostatic coupling (multiplet structure). To further elucidate the origins of the rare earth 4d photoemission spectra, we have studied the 4d regions in all the rare earth metals, except Pm. The metals have certain advantages over compounds; in particular, ligand field effects should be negligible. In this letter, we report the 4d spectra of selected rare earth metals near the middle and ends of the 4f series. These cases were chosen on the basis of their relative simplicity.

Figure 34 shows the 4d spectra of La and Lu, which have a completely empty and a completely filled 4f shell, respectively. These spectra exhibit only well-defined spin-orbit split doublets with separations of 2.85(10) and 10.0(2) eV, respectively, in reasonable agreement with theoretical values of 3.2 and 10.2 eV.⁶⁵ Recently, it has been suggested that there were highly localized and occupied 4f levels near the Fermi level in La metal.¹⁰³ Our results, which do not exhibit any multiplet structure, do not support this hypothesis. Also shown in Fig. 34 is the 4d spectrum of Yb, which is a divalent metal with a $4f^{14}$ ion-core configuration. Here again the 4d spectrum consists simply of $4d_{5/2}$ - $4d_{7/2}$ spin-orbit doublet split by 8.90(15) eV, in excellent agreement with the value 8.8 eV given by Hagstrom et al.,¹⁰⁴ but between the atomic value 8.4(1) eV and the theoretical value of 9.5 eV.⁶⁵ The binding energies of the $4d_{5/2}$ lines in La, Yb, and Lu are 103.7(1) eV,

181.4(1) eV, and 196.1(1) eV, respectively, relative to the Fermi energy. The simple spin-orbit doublet character of the 4d doublet in Yb is interpreted as further confirmation of the $4f^{14}$ configuration in this metal. The region to higher binding energy of Yb and Lu should be noted, as should the significantly larger width of the $4d_{3/2}$ component in each doublet. These features are not completely understood presently but are most likely associated with many-electron effects, i.e., electron correlation.

Figures 35-41 show the XPS spectra in the 4d region of Ce, through Tm. These spectra exhibit complex structure due to the $4d^9 4f^n$ interaction. The complicated structure in the Ce metal spectra confirms the trivalent nature of this unique metal at room temperature. This structure should be a useful fingerprint to study the possible valency change that Ce undergoes. We shall discuss only the $4d^9 4f^7$ cases, Eu and Gd, as only these have not as yet been analyzed in detail and are the simplest cases other than trivial, completely empty or filled 4f shell cases. The discussion below applies particularly to Eu. The Gd spectrum has not been as well resolved as yet. For these two metals the initial open-shell configuration and level is $4f^7; {}^8S$. Thus emission of an n ℓ electron can lead only to the two terms $n\ell^{4\ell+1} 4f^7; {}^9L$ and $n\ell^{4\ell+1} 4f^7; {}^7L$, where $|L| = |\ell|$. For the $\ell = 2$ case of interest here, each term consists of five levels with J ranging from $|S-2|$ to $|S+2|$. The configuration $f^7({}^8S)d^1$ was treated by Judd.¹⁰⁵ By reversing the sign of the d-shell spin-orbit coupling constant ζ , we can use his discussion essentially verbatim

for $f^7(8s)d^9$, noting that the d-f exchange terms require no modification because the 4f shell is exactly half full. Figure 42 is a plot of the level ordering within the $9D$ and $7D$ multiplets using the reduced variables η and ξ defined by Judd¹⁰⁵ (cf his Fig. 5).

The parameter η scales as energy for any particular value of ξ , which is itself an index of the degree of j-j coupling in the 4f shell:

$\xi = 0$ for pure L-S and -1 for j-j coupling. The five-peak fine structure on our $9D$ peak in the Eu spectrum (Fig. 36) shows excellent agreement with this interpretation, while the $7D$ fine structure is unresolved. Judd attributed a similar effect in the GdI spectrum to a contraction of the $7D$ multiplet through interaction with an excited term $7D$ multiplet through interaction with an excited term $7D$ or f^7d , derived from the level $6P$ of the core.

We can qualitatively explain the difference in appearance and structure of the $7D$ and $9D$ terms but cannot account quantitatively for the contraction of the $7D$ term on the basis of our simple model. However, we can set a lower limit on ζ of -0.47 (Fig. 42). The main uncertainty is in the value of G for which we can set a lower limit $G > 4.4$ eV. Energies calculated on Judd's model are compared with experimental values in Table X. The derived value of the effective 4d spin-orbit coupling constant within the $9D$ manifold is $\zeta_d = 1.4(2)$ eV. This is somewhat smaller than estimates based on theory ($\zeta_d = 2.2$ eV) or obtained by interpolation using the La, Yb, and Lu experimental values [$\zeta_d = 1.8(3)$ eV]. Again, this contraction within the $9D$ manifold is probably attributable to interaction with excited states.

A noteworthy feature of the Eu spectrum is the apparent reduction in multiplet separation between the 7D and 9D terms. According to simple theory,¹⁰⁵ this separation would be given by

$$G = \frac{24}{35} G^1(4d,4f) + \frac{32}{105} G^3(4d,4f) + \frac{528}{1524.6} G^5(4d,4f) ,$$

or 18.91 eV, using Mann's³² exchange integrals. The lower limit we give for G is 4.4 eV, corresponding to a reduction factor of 0.23. A large reduction factor is expected for multiplet splitting cases involving two subshells with the same principal quantum number, because of the large intrashell correlation energy. A factor of 0.6 has previously been observed for 4s 4f multiplets in rare earth salts³⁸ and metals.⁴⁴ Closure of the multiplet energy gap arises primarily through configuration interaction of the low-spin term (7D in this case) with excited states of the same symmetry. This should lead to two other observable spectral features: the ${}^7D/{}^9D$ intensity ratio should be less than the multiplet value of 7/9, and "correlation peaks" should be present at higher binding energies, as observed⁴⁶ in Mn^{2+} and other transition metals ions. Large background intensities in our spectra, arising from elastic scattering, preclude a really quantitative interpretation, but both of the above features appear to be present. Figure 38 shows a wider energy scan of the 4d region in Gd metal, showing peaks that can be tentatively assigned as correlation satellites of the 7D multiplet.

It is ironic that the main 9D and 7D multiplet peaks resemble a $4d_{5/2} - 4d_{3/2}$ doublet so closely at lower resolution that they were so interpreted in two earlier studies, on atomic Eu^{36} and on EuO^{42}

Photoabsorption measurements in rare earths have also been analyzed in terms of multiplet effects,¹⁰⁶ but because of different selection rules these spectra are not directly comparable to ours. X-ray emission lines involving the 4d level should also reflect the various coupling of 4d and 4f electrons. Salem and Scott¹⁰⁷ recently interpreted the $L_{\beta 2,15}$ and $L_{\gamma 1}$ emission lines as having multiplet structure. While they deconvoluted their spectra into only two discrete lines, they suggested it was possible that the d-levels were more complicated. It is obvious from our results that the situation is more complicated. It seems probable that even more structure will be resolvable when higher-resolution photoemission and X-ray experiments become possible.

3. XPS spectra from other core levels in the rare earth metals

We have already discussed the 4p spectra in the region of the rare earths in Chapter II with respect to collective resonances and configuration interaction.¹⁰⁸ The 4f levels will be discussed in Chapter VI with the valence bands of the rare earths. The 5 p's exhibit complicated spectra as might be expected (see Chapter VI, Figs. 15-18, 20, 21). The 3d spectra exhibit structure similar to those reported by others for compounds.^{42,109-112} These are seen in Figs. 43-51. In this case the spin-orbit interaction is large

compared to multiplet splitting. There appear to be satellites which are reminiscent of the 2p satellites in the 3d metal compounds. Several mechanisms have been proposed.^{25,26,42,109-112} Two features should be noted. These satellites' intensity vary with ligand in compounds and alloys. Once the origin of these satellites become better understood they may be quite useful in studying the electronic property of rare earth metals in different environments. Secondly, La, Ce, and Sm appear to have these satellites at lower binding energy. Since these structures do not arise from multiplet splitting, we will not discuss them further. Using the Al_K radiation and our electron analyzer, the 3d levels were the deepest core-levels of rare earths which we were able to study.

G. Multiplet Splitting: Diagnostic Tool

Detailed studies of MnF₂ have given us a more fundamental understanding of multiplet splitting and in the case of penultimate s-core level splitting a quantitative understanding which can give us some confidence in using multiplet splitting to probe S_i. We have already seen several examples of multiplet splitting in previous sections, which indicate the value of multiplet splitting for diagnostic purposes. Fig. 52 shows three transition metals, one from each class: Sc (Pauli paramagnetic), Mn (antiferromagnetic) and Fe (ferromagnetic). Each has a characteristic line shape as discussed in section E. Through the use of Van Vleck's Theorem, we can obtain information on the strength of the exchange interaction ($G^2[ns,n\ell]$) and on the localized unpaired spin density (S_i) from measurement of multiplet splitting.

Figure 27 demonstrated how S_i can be obtained from measured ΔE_{ns} despite large correlation effects. The integral in (4) should be dominated by the atomic core region and be relatively insensitive to bonding effects outside the atomic core. Thus for an atom in various environments, ΔE_{ns} should still be proportional to $2S_i + 1$. By plotting measured ΔE_{ns} vs. $2S_i + 1$ of ionic systems, where S is well defined, one obtains in effect a "calibration curve" on which one can place an observed ΔE_{ns} of a metal or an atom in an alloy or a compound and get a value for $2S_i + 1$ or the localized moment. Using this calibration procedure for Fe with an observed $\Delta E_{3s} = 4.5$ eV, we obtain a magnetic moment $\mu = 2.2 \mu_B$ which agrees quite well with the generally accepted value of $2.22 \mu_B$.¹⁰⁰ This agreement suggests the correlation factor is roughly constant for Fe atoms in different surroundings. Our α -Mn measurements implied a localized moment with an average value of $\sim 2.5 \mu_B$. This was discussed in detail in section E.

The "calibration curve" of Fig. 27 has in fact now been used by Pomerantz and Pollak¹¹³ in studying the spin state of the transition metal ions in very thin films. In particular, for the case of manganese arachidate, they were able to conclude that Mn was in the high-spin state ($S = 5/2$) and thus demonstrating that the liquid fields are not "strong" in $MnAr_2$ soap films.

In section F-1, the 4s and 5s splittings demonstrated the divalent character of the ionic core in Eu and Yb as opposed to the trivalent character for the rest of the metals of the lanthanide series.

Also the 4d spectra (section F-2) often have very complicated multiplet structure, which can serve as a spin or valency fingerprint. Fig. 53 shows $\text{La}(4f^0)$ and $\text{Ce } 4d(4f^1)4d$ spectra, which are very different. Ce has rather unique properties, and it can be either tetravalent or trivalent. The spectra of Fig. 53 indicate that it is trivalent in its room temperature phase. The 4s and 5s splittings and the characteristic 4d spectra may be especially important in studying the interesting rare earth compounds which possess mixed valency.* Below we will give some examples of multiplet splitting in rare-earth intermetallic alloys.

We will first discuss the rare earth dialuminides (La, Ce, Sm, Gd and Sm dialuminides were studied). Figs. 54-62 show the rare earth 4d and 3d spectra from the dialuminides. These should be compared with the rare earth metal spectra shown in sections F-2 and F-3. The dialuminide spectra are all quite similar to the corresponding spectra from the pure metal, indicating that the dialuminides we have studied are all trivalent. It would be particularly interesting to extend these studies to YbAl_2 and YbAl_3 where there are some questions.¹¹⁴ The LaAl_2 results are of interest because of the calculations of Switendick¹¹⁵ which predicted

*Recent studies emphasize the great care which must be taken in sample preparation because of the surface sensitivity of PES and the reactivity of many of these materials. The observation of several species may not be due to mixed valency but to surface oxide species. (R. Suryanarayanan, G. Güntherodt, J. L. Freeouf, and F. Holtzberg, Phys. Rev. B 12, 4215 (1975).

occupied 4f bands. This would give rise to multiplet splitting in the 4d spectrum but none is observed (see Fig. 54).

The 4d spectrum from YbZn_2 is shown in Fig. 63. Susceptibility data suggested that there was some Yb^{+3} involved in Yb Zn_2 , with Yb^{+3} predominating at low temperatures.¹¹⁶ The 4d spectrum yields just a simple spin-orbit doublet structure similar to the metal which indicates that at room temperature Yb is divalent in this intermetallic. It would be informative, possibly, to carry these measurements out at a lower temperature to see if any changes occur.

The last case which we will discuss is CePd_3 . The valency of this intermetallic has been the center of much controversy, as can be seen from Table XI.¹²²⁻¹²⁵

Table XI.

<u>Proposed Valency</u>	<u>Configuration</u>	<u>Method</u>
Ce^{+4}	$4f^0$	Heat Capacity Hutchens, <u>et al.</u> (1972)
Ce^{+3}	$4f^1$	Lattice Constant Harris & Raynor (1965)
$\text{Ce}^{+3.45}$	$4f^{0.55}$	Lattice Constant & Mag. Suscep. Gardner, <u>et al.</u> (1972)

Ce has been proposed to be tetravalent, trivalent, or mixed valence. XPS should be able to distinguish among these alternatives. If Ce was tetravalent, no multiplet splitting should be observed. In this case the 4d spectrum should be similar to that of La metal -- i.e., just a spin-orbit split doublet. However, if Ce was trivalent, the Ce peaks should look similar to the Ce peaks in Ce metal or CeAl₂. In the third possibility -- mixed valency -- we have no a priori expectation of what the spectrum should look like, but expect that it should be demonstrably different than in the first two alternatives. The Ce 4d spectrum is shown in Fig. 64. The Ce 3d and Pd 3d are shown in Figs. 65 and 66. It is obvious that the Ce 4d spectrum is not a simple spin-orbit split doublet as expected from a 4f⁰ configuration, nor is it similar to the spectra of Ce (Fig. 35) and CeAl₂ (Fig. 56) which are trivalent. The 4d spectrum of CePd₃ is significantly different from what would be expected in trivalent or tetravalent cases, which supports the hypothesis of a large valency fluctuation as suggested by Gardner, et al.¹²⁰ However, there are two other possibilities: 1) Oxide contamination, and 2) a final-state effect. While, even with in situ cleaning and a vacuum < 9 x 10⁻¹⁰ torr, we never obtained a perfectly clean surface, but inspection of other core-levels suggest this was not a factor. However, a final-state effect such as the mechanism proposed by Kotani and Toyozawa^{25,26,122,123} may be responsible for the observed effect. The 3d and 4d spectra in the Ce halides change with the ligand.^{42,121}

This latter alternative cannot be ruled out at this point, but appears to be unlikely from consideration of the variation of the structure in the halides with ligand electronegativity.

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Table 1. Summary of the Mn 3s and 2s photoelectron results and comparison with theoretical predictions.

Manganese 3s final state	Binding energies (eV) ^a				Intensity ratios ^b				
	² S	² S(1)	² S(2)	² S(3)	² S/ ² S(1)	² S(1)/ ² S(2) ^c	² S(2)/ ² S(3) ^c	² S(1)/ ² S(2'') ^c	² S(2'')/ ² S(2''') ^c
Experiment	0.00	6.62 ± 0.01	20.7 ± 0.1	37.8 ± 0.7	2.3 ± 0.1	2.1 ± 0.1	2.5 ± 0.1	...	...
Theory ^d	1. Freeman, Bagus, and Mellow (MT) ⁹	0.00	14.3	...	1.4	...	...	...	...
	2. Sasaki and Bagus (CI) ⁷	0.00	4.71	22.53 23.75	43.06	...	2.87	1.58	3.58
	3. Sasaki and Bagus (CI) ⁷	0.00	7.83	25.19 27.58	...	2.2	4.1	...	4.48
		0.00							4.47
Manganese 2s final state		² S				² S			² S/ ² S
Experiment		0.00				5.86 ± 0.05			1.4 ± 0.1
Theory	Freeman, Bagus, and Mellow (MT) ⁹	0.00				6.10			1.4

^aThe binding energies are given relative to the ²S peak and are the result of analytically least squares fitting the experimental spectrum with Lorentzian line shapes. The Mn 3s results are the average of two runs on different single crystals.

^bThe intensity ratios for the Mn 3s peaks were arrived at by measuring the areas of the peaks with a planimeter. The Mn 2s ratios were the result of areas derived from a least-squares fit to Lorentzian peak shapes.

^c²S(2) refers to the total intensity due to two neighboring theoretical eigenstates (which could not be experimentally resolved), while ²S(2') and ²S(2'') refer, respectively, to the intensity due to the first and the second of the two neighboring eigenstates.

^dTheory 1 is a multiplet hole theory-optimized orbital calculation. Theories 2 and 3 are configuration-interaction calculations. Theory 2 takes only internal correlations into account, while theory 3 also includes semi-internal correlations.

TABLE II. Separation of $2p_{3/2}$ and $2p_{1/2}$ peaks in XPS spectra of some transition-metal ions and metals (in eV).

Compound	$\Delta E(2p)$
Mn (MnF_2)	12.07(10) ^a (centroid separation) 13.00(1) ^a (maximum separation)
Mn (metal) ^c	11.18(25) ^b
Co (CoO)	15.8(1) ^c
Co (metal)	15.35(20) ^b
Ni (NiO)	15.16(20) ^c
Ni (metal)	17.25(10) ^b
Zn (ZnF_2)	23.22(26) ^b
Zn (metal)	23.15(5) ^b

^aThis work.

^cReference 70.

^bUnpublished work of the authors.

TABLE III. Energy separations of components of the 2p spectrum of Mn in MnF_2 (in eV).

Group	Level	E (GS) ^a	E (XPS) ^b	E (XES) ^c	E (XLS) ^d
$2p_{3/2}$	P1	(0)	(0)	(0)	(0)
$2p_{3/2}$	P2	1.3	1.2	1.2	0.7
$2p_{3/2}$	P3	2.5	2.1	2.1	2.3
$2p_{3/2}$	P4	3.1	3.2	3.1	4.7
$2p_{1/2}$	P5	7.9	7.8	...	8.1
$2p_{1/2}$	P6	10.4	10.8	...	...
$2p_{1/2}$	P7	12.4	11.8	...	12.1
$2p_{1/2}$	P8	14.2	13.1	...	12.7

^aReference 51.

^bThis work, with intensities constrained in GS values.

^cRef. 61.

^dRef. 63.

TABLE IV. Values of ΔE_{ex}^a for $13 < Z \leq 42$ (in eV).

Z	$F(KC_{\text{ex}}) + F(KC_{\text{ex}})^{1/2}$	ΔE_{ex}^b	$E_{\text{ex}}^{\text{HFS}}/E_{\text{ex}}^{\text{H}}^c$	$E_{\text{ex}}^{\text{H}}^d$
13	0.43		0.90	0.60
14	0.60		0.95	0.59
15	1		...	...
16	1.26		0.99	1.06
17	1.61		0.99	1.68
18	2.07		0.93	1.69
19	2.7		0.90	1.46
20	3.50		0.94	1.46
21	4.5	1.92	1.04	1.32
22	5.98	1.13	1.07	1.24
23	7.56	1.82	1.04	1.51
24	9.21	9.31	1.03	1.35
25	11.10	1.15	1.03	1.35
26	13.00	12.10	1.01	1.34
27	15.02	15.35	1.09	1.32
28	17.26	17.25	0.90	1.26
29	19.95	18.8	0.94	1.27
30	23.12	23.13	0.94	1.25
31	26.92		0.95	1.29
32	31.10		0.95	1.31
33	35.73			1.32
34	41.0			1.33
35	46.6			1.34
36	52.5			1.34
37	59.5			1.35
38	67.1			1.34
39	75.5			1.37
40	84.2			1.37
41	94.1			1.39
42	105.0			1.40
MnF ₂ (F)	12.1			1.47
MnF ₂ (max)	13.0			1.58
CoO	15.6			1.37
NiO	18.16			1.46
ZnF ₂	23.22			1.23

^aFrom J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).^bPreliminary data from this laboratory.^cRelativistic Hartree-Fock-State (RHFS) values from Ref. 63.^dSee Eq. (7). The value 0.4 eV has been used for M_1 .

TABLE V. Summary of the observed splitting and relative intensities of the Mn 3p levels in MnF_7 .

Mn 3p final state	1P	$^3P(1)$	$^3P(2)$	$^3P(3)$	$^3P(4)$	$^3P(5)$
Energy (eV) ^a	0.0	2.75(5)	7.6(5)	12.75(30)	17.5(2)	21.8(1)
Relative intensity ^b	1.0	0.19		~0.28 ^c	~0.21	~0.26

^aThe energies are given relative to the 1P state.

^bThe intensities are relative to 1P level.

^cThis is the sum of the $^3P(2)$ and $^3P(3)$ intensities.

Table VI. 3s splittings in and intensity ratios in Mn, Fe, Co, Ni, and Zn compounds. Theoretical values are given in brackets.

Compound	$2s + 2L$	Energies ^a $2L(1)$	$2L(2)^b$	$2L(3)^b$	Intensity ratio $2s + 2L/2sL$	$\frac{s+1}{s}$
MnF ₂	0 (⁷ S)	6.6 (⁵ S)	20.7	37.8	2.3	1.4
	[0]	[4.7 ^d , 4.3 ^e]	[22.5, 23.8 ^d , 20.4, 23.8 ^e]	[42.7 ^e]	[2.2 ^d , 2.1 ^e]	
FeF ₂	0 (⁶ D)	5.9 (⁴ D)	22	39	2.2	1.5
	[0]	[4.5 ^e , 5.6 ^e]	[18.9, 22.8, 24.5 ^e]	[33.6, 44.7 ^e]	[2.2 ^e]	
CoF ₂	0 (⁵ F)	4.9 (³ F)	11	25	2.1	1.7
	[0]	[5.6, 8.2 ^e]		[26.2, 34.8 ^e]	[1.8 ^e]	
NiF ₂	0 (⁴ F)	5.0 (² F)	13	30	2.8	2.0
	[0]	[3.9 ^e]		[30.4, 45.8 ^e]	[2.4 ^e]	
ZnF ₂	0 (² S)	--	--	--	--	--
CoO ^f	0 (³ F)	5.9 (³ F)	11.1	25	1.7	1.7
NiO ^f	0 (³ F)	5.5 (² F)	10.5	25	1.8	2.0
ZnO	0 (² S)	--	--	--	--	--

^aEnergies given relative to the $2s + 2L$ state.

^bCorrelation states.

Multiplicity ratio.

^dRef. 47. Multi Configuration Hartree-Fock (MCHF)

L. -K. Viinikka and Y. Öhrn, Phys. Rev. 11, 4168 (1975).

^eRef. 70. CI Calculations.

Table VII. Calculated 3s and 2s multiplet splittings from various one-electron models for the 3d metal ions. (all energies in eV).

	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Number of unpaired 3d electrons	0	1	2	3	4	5	4	3	2	1	0
K ^a	0	2/5	3/5	4/5	5/5	6/5	5/5	4/5	3/5	2/5	0
G ² (3s,3d) ^b	—	7.45	8.40	9.23	9.0	10.65	11.32	11.94	12.55	12.43	13.74
ΔE_{3s}^{HF}	—	2.98	5.04	7.38	9.0	12.78	11.32	9.55	7.53	4.97	0
RHF + perturbation ^c	—	1.61	3.58	5.83	8.33	11.09	9.29	7.31	5.10	2.66	0
SUHF ^d	—	1.60	3.60	5.89	8.44	11.27	9.70	7.0	5.42	2.87	0
MITT(froz) ^e	—	3.22	5.38	7.77	10.41	13.31	11.61	9.75	7.65	5.32	0
MITT(opt) ^f	—	3.69	6.01	8.54	11.29	14.32	12.40	10.34	8.06	5.66	0
MSX ^g	—	—	—	—	4.2	6.2	—	—	—	—	—
MSX ^h	—	—	—	—	4.9	7.3	—	—	—	—	—
MSX ⁱ	—	—	—	—	6.5	7.3	—	—	—	—	—
UHF ^j	—	1.58	—	7.36	—	13.25	—	—	—	5.42	—
UHF ^k	—	—	—	7.81	—	13.55	—	—	—	5.64	—
C ^l	—	—	—	—	—	4.3	4.55	5.6	3.9	—	—
2s levels											
G ² (2s,3d) ^b	—	0.74	2.18	2.72	2.72	3.54	3.94	4.35	4.75	4.71	5.54
ΔE_{2s}^{HF}	—	0.30	1.31	2.18	2.72	4.25	3.94	3.48	2.85	1.88	0
SUHF ^d	—	0.37	0.94	1.68	2.58	3.67	3.36	2.81	2.07	1.15	—
MITT(froz)	—	0.78	1.45	2.28	3.27	4.43	4.06	3.55	2.90	2.08	—
MITT(opt)	—	—	—	—	—	6.10	5.40	—	—	—	—
Exp.	—	—	—	—	—	5.85 ^m	4.8 ⁿ , 4.3 ^p	—	—	—	—

^aK = (2s + 1)/(2l + 1).

^bRef. 32.

^cEqn. (4).

^dRestricted Hartree-Fock, Ref. 30.

^eSpin Unrestricted Hartree-Fock, Ref. 30.

^fMultiplet Hole Theory, frozen orbitals, Ref. 30.

^gMultiplet Hole Theory, optimized orbitals, Ref. 30.

^hMultiplet Scattering X α , orbital difference in the ground state, E. -K. Viinikka and S. Larssen, J. Electron Spectrosc., 163 (1975).

ⁱMultiplet Scattering X α , orbital difference in transition state, E. -K. Viinikka and S. Larssen, J. Electron Spectrosc., 163 (1975).

^jMultiplet Scattering X α , E. -K. Viinikka and S. Larssen, ibid 163 (1975) their Eqn. (4) for Cr and Eqn. (5) for Mn.

^kUnrestricted Hartree-Fock for difluorides, H. Basch, J. Electron Spectrosc., 3, 463 (1974).

^lUnrestricted Hartree-Fock, free ions, H. Basch, ibid 3, 463 (1974).

^mE. -K. Viinikka and Y. Öhm, Phys. Rev. B11, 4168 (1975).

ⁿRef. 46.

^pRef. 41.

^qRef. 73.

Table VIII. Comparison of empirically correlated values with results from experiments and CI calculations. Energies in eV.

	ΔE_{3s}^{VV-a}	ΔE_{3s}^{MHT-b}	ΔE_{3s}^{CI-c}	ΔE_{3s}^{exp}
Mn ⁺²	6.6	6.6	4.3	6.6 ^d
Fe ⁺²	5.9	5.7	4.5	5.8 ^d
Co ⁺²	4.9	4.8	5.5	4.9 ^d
Ni ⁺²	3.9	3.7	3.9	5.0 ^d , 4.0 ^e , 3.1 ^f

^aFrom equation (4) multiplied by correlation factor

$$[\Delta E_{3s}^{exp} (Mn^{+2})]/[\Delta E_{3s}^{VV} (Mn^{+2})].$$

^bFrom Multiple Hole Theory Value, optimized orbital (Ref. 30)

multiplied by correlation factor $[\Delta E_{3s}^{exp} (Mn^{+2})]/[\Delta E_{3s}^{MHT} (Mn^{+2})]$.

^cFrom C. I. calculation of E.-K. Viinikka and Y. Öhrn, Phys. Rev.

B 11, 4168 (1975).

^dThis work, difluorides.

^eRef. 40.

^fRef. 73.

Table IX
Experimental and calculated 4s and 5s splittings (ev) of the rare earth metals and trifluorides

	2S+1	$\Delta E(4s)^a$	$\Delta E(4s)^b$	$\Delta E_{VV}(4s)^c$ Full	$X_{0,ss}$	$\Delta E(5s)^a$	$\Delta E(5s)^b$	$\Delta E_{VV}(5s)^c$
La	—	0.0(2)	—	0.00	0.00	0.0(2)	—	0.00
Ce	2	1.4(3)	—	2.85	1.56	1.0(3)	0.0	0.93
Pr	3	2.0(3)	—	4.14	2.26	1.4(2)	1.2	1.46
Nd	4	2.7(3)	—	5.78	3.16	1.6(2)	1.7	1.92
Pm	5	—	—	7.52	4.11	—	—	2.38
Sm	6	5.4(3)	—	9.35	5.10	2.9(2)	2.8	2.83
Eu	8,7	7.4(3)	—	12.88, 11.27	7.03, 6.15	3.8(3)	—	3.76, 3.29
Gd	8	7.8(2)	8.2	13.91	7.59	3.6(2)	3.7	3.62
Tb	7	d	7.5	12.17	6.64	3.2(3)	3.4	3.16
Dy	6	d	6.4	10.51	5.74	2.8(2)	2.7	2.78
Ho	5	d	5.6	8.98	4.90	2.4(2)	—	2.32
Er	4	d	4.3	7.35	4.01	d	—	1.85
Tm	3	d	3.4	5.51	3.01	d	—	1.39
Yb	1,2	0.0(3)	—	0.0, 3.84	0.0, 2.10	0.0(1)	—	0.0, 0.93
Lu	—	0.0(2)	—	0.00	0.00	0.0(1)	0.00	0.00

^a This work.

^b Ref. [38].

^c Eq. (11).

^d These values could not be obtained due to intense Auger transitions in the energy region of interest.

Table X
The $4d^9 4f^7; ^9D$ multiplet energies in Eu metal (in eV)

Level	$E(\text{exp})$	$E(\text{fitted})^a)$
9D_6 b)	0	0.1
9D_5	0.78(04)	0.8
9D_4	1.52(04)	1.4
9D_3	2.22(04)	2.2
9D_2	2.85(08)	2.9
7D c)	6.33(10)	6.3

a) After ref. [105]

b) The binding energy of 9D_6 relative to the Fermi energy is 127.70 (15) eV.

c) Mean energy only.

FIGURE CAPTIONS

- Fig. 1. Li 1s spectrum from an Li metal sample. The 1s level exhibits no multiplet splitting. Feature P_s is a surface plasmon, while P_1 and P_2 are bulk plasmons.
- Fig. 2. Manganese 3s spectrum with the energy scale referenced to the Au $4f_{7/2}$ (84.00 ± 0.01 eV) peak.
- Fig. 3. Upper panel: Mn 3s final states in the one-electron (Koopmans' Theorem) picture.
Lower panel: Mn 3s final states with electron correlation (Configuration Interaction) considered.
Note that the 5S states obey a sum rule.
 5S 's are correlation satellites.
- Fig. 4. Manganese 2s spectrum (referenced to Au 4f level).
- Fig. 5. Raw XPS spectrum of the 2p region of MnF_2 , taken under electron flood-gun conditions. The binding energy reference is the top of the valence bands of MnF_2 .
- Fig. 6. Corrected Mn 2p spectrum (points) and spectrum calculated by GS (bars) for MnF_2 . The energy scale of the calculated spectrum has been reduced by a factor of 0.96. The six strong peaks are labelled P1, P2, P3, P4, P7, and P8 from right for purposes of comparison with Table III. The triplet and doublet of small peaks between P4 and P7 are considered as two groups, labelled P5 and P6, respectively. Reference level is the top of the valence bands, as in Fig. 5.

Fig. 7. The $K\alpha_1$ X-ray profile of Mn in MnF_2 , after Nevedov (Ref. 61).

Bars indicate states calculated by Gupta and Sen. Each division on the abscissa is 1 eV. (Compare with Ref. 63.)

Fig. 8. Reduced 2p spin-orbit splitting of the elements,

$\Delta E_r = [(Z-2)^3/Z^4][\Delta E(2p)_Z/\Delta E(2p)(Al)]$. The filled circles denote the compounds in Table II, while the x represents separation of peak maxima in MnF_2 . The open circles are for the elements in their elemental form. The results for $Z = 21-30$ were obtained by XPS and for $Z = 13-20$ and $Z = 31-42$ were obtained from X-ray work. The values are summarized in Table IV. Dashed and solid curves are drawn in only to guide the eye.

Fig. 9. Mn 3p XPS spectrum in MnF_2 , together with fitted peaks.

The very broad peaks probably represent several states.

The binding energy of the $7P$ peak is 46.76 eV relative to the top of the valence bands.

Fig. 10. Fe 3s and 3p spectrum from FeF_2 .

Fig. 11. Co 3s spectrum from CoF_2 .

Fig. 12. Ni 3s spectrum from NiF_2 .

Fig. 13. Zn 3s and 3p spectrum from ZnF_2 .

Fig. 14. Co 3s3p spectrum from CoO and Ni 3s3p spectrum from NiO (after R. A. Pollak, Ref. 70).

Fig. 15. Zn 3s3p spectrum from ZnO .

Fig. 16. The exchange integral $G^2(3s, 3d)$ for scandium through Cu from Ref. 32.

- Fig. 17. Plot of $2 S_1 + 1$ (x) vs. number of 3d electrons (right ordinate). Also plotted is the 3s splitting ($\square$) predicted by Van Vleck's Theorem, Eqn. 4 (left ordinate). Several experimental values ($\cdot$) are shown (right ordinate).
- Fig. 18 Ni 3p spectrum from NiO (after Pollak, Ref. 70). Solid bars represent results from calculations by Bagus and Wahlgren (Ref. 54). D and Q stand for doublet and quartet respectively.
- Fig. 19. Fe 2p spectrum from FeF_2 .
- Fig. 20. Co 2p spectrum from CoF_2 .
- Fig. 21. Ni 2p spectrum from NiF_2 .
- Fig. 22. Zn 2p spectrum from ZnF_2 .
- Fig. 23. Co and Ni 2p spectra from CoO and NiO respectively.
- Fig. 24. 3s spectra of Sc, Ti, and V metals.
- Fig. 25. 5s spectra of Cr and Mn metals.
- Fig. 26. 3s and 2s spectra from Mn metal.
- Fig. 27. Calibration curves for Fe and Mn.
- Fig. 28. 3s spectra of Fe, Co, and Ni metals.
- Fig. 29. 3s spectra of Cu and Zn metals.
- Fig. 30. 4s spectra of Nd, Sm, and Gd metals.
- Fig. 31. 5s spectra of Nd and Sm metals.
- Fig. 32. 5s spectrum of Gd metal.
- Fig. 33. Comparison of the experimental values of the 4s and 5s multiplet splitting with the Van Vleck theorem values (Eqn. 4). Filled circles are for the metals (this work), while open circles are trifluoride values (Ref. 38).

Fig. 34. XPS spectra of the 4d levels of La, Yb, and Lu metals, showing only spin-orbit doublets.

Fig. 35. XPS spectra of the 4d regions of Ce, Sm, and Eu metals exhibiting structure due to final-state coupling. The Eu spectrum has been analyzed as discussed in text.

Fig. 36. Eu 4d spectrum.

Fig. 37. Gd 4d spectrum (narrow scan).

Fig. 38. Gd 4d spectrum (wide scan). Note satellite, probably due to correlations in the $7D$ multiplet.

Fig. 39. 4d spectra of Nd and Pr.

Fig. 40. 4d spectra of Tb, Dy, and Ho.

Fig. 41. 4d spectra of Tm and Er.

Fig. 42. Levels of the configuration f^7d^9 that derive from the core $8S_{7/2}$. The axes are labelled as follows:

$$\eta = [E(J) - \frac{35}{80} G] [G^2 + (\frac{5}{2} \rho)^2]^{-1/2}; \quad \xi = \frac{\chi}{1 + |\chi|}, \quad \text{where}$$

$$\chi = \frac{5}{2} / G. \quad \text{The matrix elements were calculated for the}$$

f^7d configuration so, for our case, $\zeta \leq 0$, $G \geq 0$, therefore $-1 \leq \xi \leq 0$. The LS extreme is given for $\xi = 0$ on the left, and the Jj extreme is given for $\xi = -1.0$ on the right.

Fig. 43. 3d spectrum from La.

Fig. 44. 3d spectrum from Ce.

Fig. 45. 3d spectrum from Pr.

Fig. 46. 3d spectrum from Nd.

Fig. 47. 3d spectrum from Sm.

- Fig. 48. 3d spectrum from Eu.
- Fig. 49. 3d spectrum from Gd.
- Fig. 50. 3d spectrum from Tb.
- Fig. 51. 3d spectrum from Dy.
- Fig. 52. 3s spectra from Sc (a Pauli paramagnet), α -Mn (an anti-ferromagnet), and Fe (a ferromagnet).
- Fig. 53. Comparison of 4d spectra from a metal without unpaired 4f electrons (La) and a metal with one 4f electron.
- Fig. 54. La 4d spectrum from La Al₂.
- Fig. 55. La 3d spectrum from La Al₂.
- Fig. 56. Ce 4d spectrum from Ce Al₂.
- Fig. 57. Ce 3d spectrum from Ce Al₂.
- Fig. 58. Sm 4d spectrum from Sm Al₂.
- Fig. 59. Sm 3d spectrum from Sm Al₂.
- Fig. 60. Gd 4d spectrum from Gd Al₂.
- Fig. 61. Gd 3d spectrum from Gd Al₂.
- Fig. 62. Dy 4d spectrum from Dy Al₂.
- Fig. 63. Yb 4d spectrum from Yb Zn₂.
- Fig. 64. Ce 4d spectrum from Ce Pd₃.
- Fig. 65. Ce 3d spectrum from Ce Pd₃.
- Fig. 66. Pd 3d spectrum from Ce Pd₃.

Fig. 1

XBL745- 3136

Fig. 2

XBL753-2532

Fig. 3

Fig. 4

XBL7210-4221

Fig. 5

XB1 74P-4.05"

Fig. 6

XBL 748-4058

Fig. 7

XBL 748-4055

Fig. 8

XBI.748-4054

Fig. 9

Fig. 10

XBL 757-3405

Fig. 11

XBL7512 - 3942

Fig. 12

Fig. 13

XBL 763-719

Fig. 14

Fig. 15

XBL 7510-8506

Fig. 16

XBL 763-2457

Fig. 17

XBL 763-2461

Fig. 18

XBL 762-2318

Fig. 19

XBL 7512 - 3938

Fig. 20

XBL 757-3401

XBL757-3402

Fig. 21

Fig. 22

XBL7510-8520

NBL 763-718

Fig. 23

Fig. 24

XBL 747-3642

Fig. 25

XRL 741-251A

Fig. 26

Fig. 27

XBL7410-4429

NBL 747-3652

Fig. 28

XBL 747-3651

Fig. 29

Fig. 30

Fig. 31

Thousands of counts

Binding energy (eV)

Fig. 32

XBL 764-1221

Fig. 33

Fig. 34

Fig. 35

Fig. 36.

XBL 7410-4349

Fig. 37

Fig. 38

NBI, 763-781

Fig. 39

XBL 143-779

Fig. 40

NBL 763-780

Fig. 41

XBL746-3551

Fig. 42

Thousands of counts

Binding energy (eV)

Fig. 43

Alf 70050

Fig. 44

XBL 763-763

Fig. 45

XBL 763-764

Fig. 46

Thousands of counts

Fig. 47

XBL 763-765

XBL 763-766

Fig. 48

XBL 763-767

Fig. 49

Fig. 50

XBL 764-993

XBL 763-761

Fig. 51

Fig. 52

Fig. 53

XBL7510 - 8635

Fig. 54

Fig. 55

XBL7510-4171

XBL 762-2261

Fig. 56

Fig. 57

NBL 762-2262

XBL 762-2263

Fig. 58

XBL 763-2449

Fig. 59

Fig. 60

XBL7510-4151

Fig. 61

XBL7510-4157

Fig. 62

XBL7510-8634

Fig. 63

Fig. 64

XBL7510-4162A

XBL7510-4154

Fig. 65

XBL7510-4176

Fig. 66

V. IONICITY

A. Introduction

In this chapter, we shall discuss the use of the experimentally observed valence band density of state VB DOS, in particular the splitting of the two "s-like" bands, to study the chemical bond in binary semiconductors. First in order to provide the background and justification for using the VB DOS, we will discuss XPS results from the VB DOS of the $A^N B^{8-N}$ crystals in the next section. First the III-V and II-VI semiconductors and then the alkali halides will be discussed. We will then proceed to develop a quantitative spectroscopic scale of ionicity based on XPS VB DOS's.

B. Total Valence-Band Densities of States from X-Ray Photoemission Spectroscopy*

1. III-V and II-VI compounds

Tetrahedrally coordinated semiconductors of the chemical formula $A^N B^{8-N}$ have been extensively studied because of their technical and scientific importance. The electronic band structures and electronic density of states of these materials are among their most fundamental properties. High energy photoemission ($h\nu \geq 50$ eV - 100 eV) is one of the most direct probes of the occupied valence band density of states. In this section, we report high resolution XPS (monochromatized $AlK\alpha_{1,2}$ X-rays) on 14 binary semiconductors (see Table I).

*Based on work done in collaboration with L. Ley, R. A. Pollak, F. R. McFeely, and D. A. Shirley and published in Phys. Rev. B 9, 600 (1974).

All these samples were high purity single crystals, which were cleaved in a dry N_2 inert atmosphere just prior to insertion into spectrometer vacuum chamber. The cleavage was performed with the sample in a glove bag attached to the introduction chamber of the spectrometer vacuum system. The glove bag was repeatedly flushed with N_2 evaporated from LN. Once the crystal was cleaved it was inserted into the vacuum system of the spectrometer without exposure to ambient. During the course of these measurements, the pressure in the electron analyzer was $5 \times 10^{-9} < P < 3 \times 10^{-8}$. The results of in situ chemical analysis of surface contamination is given in Table II. No contamination in the form of oxide formation could be detected for any sample.

The similarity of gross features in the valence-band spectra of the binary tetrahedrally coordinated semiconductors makes identification of the observed peaks straightforward. The valence-band spectrum consists in each case of three peaks originating from the outermost cation and anion s and p electrons. A cation d-level peak is also present in each case between 10- and 20-eV binding energy. All peaks in the indium and gallium compounds are well resolved with the 4d and Ga 3d levels below all valence bands, but the Cd 4d level masks the lowest valence band in the cadmium compounds, and the lowest valence band in the zinc compounds lies below the Zn 3d level. The spin-orbit-split Hg 5d level masks the lowest valence band in HgTe.

A background correction was performed in two steps. First the d peaks were subtracted from the spectra. Second, the contribution from inelastically scattered electrons was subtracted. The shape of the inelastic tail of the valence bands in each case was assumed to be the same as that of the nearby d-level inelastic tail. The uncertainty introduced by the first step in the correction affects the determination of the position of the lowest valence bands to a minor extent; this has been included in the errors quoted.

The uncorrected valence-band spectra $I(E)$ are shown in Figs. 1-5 and the corrected spectra $I(E)$ are displayed in Figs. 6-11. The overall similarity of these spectra makes it easy to extract a number of common features. We shall do so first in a completely empirical way, without any reference to band-structure calculations. Let us consider the generalized spectrum shown in Fig. 12. The valence-band structure is grouped into three peaks, which we label P_I , P_{II} , P_{III} in order of increasing binding energy. P_{II} and P_{III} are separated by a gap of low or zero electron density which widens in proceeding from III-V to II-VI compounds. The width of this gap may be determined by linear extrapolation of the steep edges of the respective peaks to the base line, yielding energies E_{II} and E_{III} . In some cases peak P_I is well-enough resolved from peak P_{II} to permit similar determination of E_I , on the high-binding-energy side of P_I . The energies of the bottom and top of the valence bands are determined by linear extrapolations of the leading and trailing edges of peaks P_I and P_{III} , respectively. The top of the valence bands, so determined, is taken as the zero of energy and the bottom is labeled B. Peak P_I ,

the broadest of the three valence-band peaks, exhibits resolvable fine structure in some cases. This is labeled I_1 and I_2 . A shoulder labeled S_1 on the high-binding-energy side of Peak P_I is resolved in almost all cases. In some cases peak I_1 can be resolved into two components, labeled I_1 and I'_1 . The binding energies of these features are listed in Table III. Also included are the energies at which the peaks reach half their heights, labeled H_{IT} (top of peak P_I), etc.

Our results are compared in Table IV with the UPS results of Eastman, Grobman, Freeouf, and Erbudak,¹ who used 20-90 eV synchrotron radiation to study five of these compounds. Because they also gave results for Ge, these are included in Table IV, along with our values for Ge, reported earlier.² The general appearance of the UPS spectra is quite similar to that of the XPS measurements. They differ mainly in that the UPS curves show steeper leading edges on peak P_I and poorer definition of peak P_{III} . In other respects they are of roughly equal quality, with UPS showing better resolution but a poorer signal-to-background ratio. The position of the peak P_{II} with respect to the top of the valence band is extremely well reproduced by both methods (the absolute average deviation is only 0.16 eV) making P_{II} a reference point of high reliability, as is the top of the valence bands.

Toward higher binding energies the agreement is less satisfying: The absolute average deviations are 0.2 eV for P_{III} and 0.7 eV for the bottom of the valence bands. This disagreement probably results largely from the uncertainty in correcting for the large contribution

inelastically scattered electrons in this region of the lower-energy UPS spectra. The binding energies for I_1 obtained from XPS data are an average of 0.45 eV higher than those obtained by UPS. The reasons for this systematic deviation may be the slightly better resolution of UPS or matrix-element effects which emphasize parts of P_1 close to the top of the valence band more in UPS than in XPS. We note that the former reason alone would not account for the good agreement on the positions of P_{II} . The influence of surface states on the apparent position of I' in the UPS work cannot be excluded.

Three points should be emphasized when comparing XPS and UPS VB DOS's. That is the spectra may be modulated by final-state, cross-section, and relaxation effects. These effects were discussed in Chapter II. The third-point -- relaxation in the final state -- is often completely ignored in valence-band photoemission spectroscopy, although early attention was called to the effect.³ We note first that most band-structure calculations do not treat exchange self-consistently. Thus a "Koopmans' Correction"⁴ must be made before it is correct to use Koopmans' Theorem⁵ in estimating binding energies. This is not, however, the only objection to comparing $I'(E)$ and $\rho(E)$ directly. Particularly for the deeper valence bands, which are beginning to take on core-like characteristics, final-state relaxation will tend to move the valence-band features such as P_{III} "up" toward the "top" of the valence bands relative to a $\rho(E)$ calculated self-consistently. This statement is, of course, independent of the method of measurement. We shall make no correction for this effect in the discussion below. Thus when we

discuss energies of symmetry points in the Brillouin zone relative to the top of the valence bands, we are in reality referring to the energies of these symmetry points in the one-hole final-states spectrum, relative to the bottom of the hole-state valence-band spectrum.

Despite these caveats it seems possible to obtain reasonable estimates of the energies of symmetry points. This is done below.

The great expenditures in calculating the band structure throughout an irreducible part of the Brillouin zone has limited the available theoretical densities of states to relatively few compounds. Therefore, in order to compare our experimental data with as wide a range of calculations as possible it was necessary to derive from $I'(E)$ the energies of selected symmetry points. The theoretical densities of states $\rho(E)$ for five cubic binary compounds as calculated by the empirical pseudopotential method (EPM)⁶ have been broadened with a Gaussian of 0.7 eV FWHM at the top and 0.8 eV FWHM at the bottom of the valence band, to account for finite instrumental resolution plus life-time broadening which increases with increasing binding energy. Figure 13 shows as an example the close resemblance of this broadened density of states $\rho'(E)$ with the experimental spectrum of $I'(E)$ for GaP. The positions of characteristic features in the theoretical density of states $\rho(E)$, which are associated with the energies E_i of critical points, can be related to corresponding features in the broadened density of states $\rho'(E)$. Applying the same criteria, which determine E_i in $\rho'(E)$ to $I'(E)$, yields in turn experimental values for E_i . The similarity in the band structure of all the

cubic binary semiconductors allows an extension of this procedure to spectra for which no theoretical densities of states are yet available.

The eight valence electrons per unit cell in the zinc-blende structure occupy four bands which constitute the valence-band density of states. The point of triple degeneracy of bands 1, 2, and 3 (counted from the top of the valence band), Γ_{15} , makes the top of the valence band, and corresponds to the zero of energy in Tables V-XV. Next, $\rho(E)$ rises within about 1 eV to a flat, sloped top between points L_3 and X_5 . This flat top is somewhat rounded in $\rho'(E)$, but the peak at X_5 is well resolved in most spectra. The degeneracy of bands 1 and 2 is lifted along the symmetry line Σ between X_5 and Γ_{15} , and the lowest point $\Sigma_1^{\min}$ of band 2 marks the bottom of peak P_I . In $\rho'(E)$ and $I'(E)$, $\Sigma_1^{\min}$ falls about halfway between the bottom of peak P_I and the shoulder which arises from a small sharp peak associated with the band at W_2 . The near degeneracy of the symmetry points of band 3 over the surface of the Brillouin zone gives rise to the sharp peak P_{II} . The top of this peak, which coincides within 0.2 eV with W_1 is the feature which can most reliably be determined from $I'(E)$. The point X_3 usually marks the bottom of peak P_{III} in $\rho(E)$.

Band 4 forms peak P_{I+I} , which is a distorted mirror image of peak P_{II} . Points X_1 and W_4 on the square face of the Brillouin zone are again almost degenerate. They determine the spike and sharp leading edge [in $\rho(E)$] of peak P_{III} . The otherwise rather flat top breaks at L_1 into a smooth decrease in $\rho(E)$ toward the bottom of the valence band at Γ_1 . After broadening, this richly structured band

appears as a slightly asymmetric peak whose top marks fairly accurately the position of L_1 . The positions of X_1 and W_4 fall at about three quarters of the height of peak P_{III} .

Applying the criteria which determine the position of the symmetry points in $\rho'(E)$ to $I'(E)$ of the cubic compounds we obtain the binding energies of these points with respect to the top of the valence band Γ_{15} . These results are listed and compared with pertinent calculations⁶⁻¹⁶ in Tables V-XV. The results from UPS measurements¹ are also given for comparison, where available.

Among the band-structure calculations we can distinguish two classes: first-principles calculations, such as orthogonalized-plane-wave (OPW) and Korringa-Kohn-Rostoker (KKR) (Green's-function method) calculations, which usually have no adjustable parameters, and empirical calculations, such as EPM and adjusted OPW [OPW (adj)] calculations, which include a reasonable number of adjustable parameters to fit theoretical band structures to appropriately interpreted experimental data. In these latter approaches one can assume that Koopmans' corrections are incorporated in the adjustable parameters. The EPM calculations of Cohen and Bergstrasser¹⁷ on a number of binary semiconductors has shown the success of this approach as far as levels within a few eV around the gap are concerned. The shortcomings of local pseudopotential calculations in describing the energies of deeper-lying valence bands are well known. A recent attempt, however, by Chelikowsky, Chadi, and Cohen⁶ to fit the total valence-band spectra of several semiconductors with an effective electron mass as

an additional free parameter was very successful, as the energies in Tables V, VI, X, XII, and XIV show.

The first-principles calculations show in general surprisingly good agreement with experiment. The self-consistent OPW (SCOPW) calculations of Stukel et al.^{10,13} are clearly an improvement over the OPW calculations, especially when the Kohn-Sham exchange approximation is used (see Tables VI and XII).

The KKR calculations of Eckelt,¹⁴ in general, predict the over-all bandwidth and the position of the lowest band very well for ZnS, ZnSe, and ZnTe. The best over-all agreement with experiment, however, was obtained in most cases by a relativistic OPW approach, with $X_{\alpha\beta}$ exchange (ROPW, $X_{\alpha\beta}$).^{9,16} This approach appeared to possess the ability to bring the features near the top of the band down and also to move the P_{III} features down toward their experimental positions. It will be very interesting to see what a self-consistent version of this ROPW, $X_{\alpha\beta}$ approach can do.

Not included in Tables V through VIII are the results of the $\vec{k} \cdot \vec{p}$ method applied to the calculation of the band structures of GaP, GaAs, GaSb, and InP by Pollak, et al.¹¹ and Higginbotham, et al.¹² because only the positions of L_3 and X_5 can be deduced from their work.

Rather than discussing every symmetry point, we shall concentrate on the important gap $X_3 - X_1$ between P_{II} and P_{III} . This gap is closely related to the ionic character of the compound.¹⁸ Our results are compared with theory and UPS results in Table XVI.

The XPS and UPS results are in quite good agreement where comparison is possible and systematic discrepancy appears to arise mostly from different methods of data reduction. Turning to the theoretical work, the KKR II-VI results disagree erratically with experiment, from 0.8 eV low in ZnTe to 2.0 eV high in ZnS. A similar scatter is found in the OPW results, ranging from -1.4 eV in GaSb to +1.5 eV in InP. The results from self-consistent OPW calculations are too few to assess any improvement in going from a non-self-consistent to a self-consistent theory. The three-parameter scheme that leads to the adjusted OPW calculations contains two parameters,⁴ which adjust the cation and anion core levels, respectively, so as to improve the band structure in terms of optical transitions. This adjustment leads, via the orthogonality condition, to an increase in the gap X_3-X_1 comparable to the antisymmetric part in the pseudopotential in the EPM scheme. An inspection of Table VI reveals, however, that this adjustment in all cases but GaP overemphasizes the X_3-X_1 separation. This suggests that XPS and UPS data should be considered in such adjustments. Finally, the relativistic OPW results are on the whole in quite good agreement with experiment. It will be interesting to learn how self-consistent ROPW results will compare.

A detailed interpretation of these and other X_3-X_1 gaps in terms of ionicity will be given in the next section. The general trend -- an increase from III-V to II-VI compounds -- is clear in Table XVI.

The gross features of the valence-band XPS spectra of the wurtzite-structure compounds CdS, CdSe, and ZnO are similar to those of the semiconductors with the zinc-blende structure. This is not surprising, because the immediate surroundings of each atom are almost identical in the two structures.

Two peaks at the top of the valence bands correspond to peaks P_I and P_{III} , respectively. Peak P_{III} which can in the more ionic II-VI compounds be identified with the anion s level, is shifted in ZnO to 20.7 eV binding energy. The very Lorentzian-like line shape indicates considerable lifetime broadening in this level. The true width of the corresponding band is probably appreciably smaller. Peak P_{III} is presumably masked by the Cd d levels in CdS and CdSe. This determines its binding energy in these compounds as lying between 8 and 12 eV. The mean positions of peak P_I , 1.8 eV in CdS and 1.9 eV in CdSe, are in good agreement with the results of Shay and Spicer.¹⁹

Additional fine structure in peak P_I cannot easily be identified with energies of the uppermost valence bands at particular symmetry points because no theoretical densities of states are available and the correlation of symmetry points in the fcc Brillouin zone with those in the extended hexagonal zone²⁰ is limited to a few cases. We must therefore limit the comparison of our results with calculations to the position of Γ_3 , a point which corresponds to L_1 in the fcc lattice and marks the bottom of peak P_{II} (see Table XVI). The top of the valence band is again the zero of energy. It falls in CdS and CdSe with considerable certainty at the center of the

Brillouin zone at the nearly degenerate (except for crystal-field splittings) points Γ_6 and Γ_1 . The top of the valence band in ZnO differs from all other valence bands in showing a region of small but nonzero density of states, which extends 1.4 eV beyond the steep onset of P_I (Fig. 8). This unique feature is an indication that the top of the valence band in ZnO does not coincide with the triply-degenerate point $\Gamma_{6,1}$, but rather with the energy maximum of a presumably nondegenerate band somewhere in the Brillouin zone. It is interesting to note that a similar result has been obtained in augmented-plane-wave (APW) calculations of the band structure of cubic ZnS by Rössler and Lietz,²¹ in which the top of the valence band is determined by the highest band along Λ . This would correspond to a point near Λ for the hexagonal lattice. It is most likely that an interpretation of the valence-band top along similar lines in ZnO would bear on the discussion of optical measurements²² in this compound.

Inspection of Table XVI shows that the overall width of the upper two valence peaks (P_I and P_{II}) is underestimated in all theoretical approaches. It should, however, be noted that the self-consistent OPW calculation of Ewema, et al.,^{23,24} finds the lowest peak P_{III} in CdS between -10.7 and -11.5 eV, in good agreement with our experimental limits of -10 ± 2 eV. Not included in the discussion of our spectra are the effects of spin-orbit splitting on the densities of states. These effects are no greater than about 0.5 eV at certain

symmetry-points in P_1 for the heaviest compounds and are not clearly resolvable in our spectra. An identification of the splitting $1_1-1'_1$ in GaAs and ZnTe is not possible.

2. The alkali halides^{*}

The alkali halides have been the subject of intense research for many years. Part of the reason for this is that the alkali halides almost comprise a class of compounds by themselves. They are the prototype of the ionic insulator and as such may be considered the simplest of binary crystals, being composed of positive and negative ions bound together by Coulomb attraction. In this section, X-ray photoemission spectroscopy (XPS) is used to determine the valence-band densities of states and core-level binding energies for LiF, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, and KI, all of which crystallize in the rock-salt structure. The spectra of these salts show that, far from being anomalous cases, the alkali halides demonstrate features in their valence-band densities of states which bear a qualitative relation to features found in the spectra of II-VI and III-V compounds, and even group-IV elements. The sample preparation techniques for these samples were similar to those of the previous section.

The spectra obtained for the valence-band and outermost core regions is shown in Fig. 14-16. In light of the well known ionic nature of these crystals, it is not surprising that the uppermost

^{*}Based on work done in collaboration with F. R. McFeely, I. Ley, and D. A. Shirley and published in Phys. Rev. B 9, 3573 (1974).

valence-band peaks strongly resemble core-level peaks. Indeed for many purposes this uppermost valence band may be considered to be the pure anion p level. However, the valence band peaks of LiF, NaCl, NaBr, NaI, KBr, and KI all exhibit definite structure on the low-energy (high- E_g) side, which is similar to that found in the III-V and II-VI binary crystals.

We will first examine how the spectra evolve from group-IV elements to alkali halides. In Fig. 17 the theoretical band structures calculated by Cohen and co-workers²⁵⁻²⁸ by the empirical pseudopotential method, of Ge, GaAs, ZnSe, and NaCl are shown along with the valence-band XPS spectra.²⁹ Ge, GaAs, and ZnSe occur in the zinc-blende structure, for which these calculations were done. The bands are in all cases grouped as would be expected from atomic-structure considerations, in a group of three bands nearest the Fermi level and a single band at lower energy. The lowest level has in all cases Γ_1 symmetry and may be characterized quite unequivocally as an s-like level. The other three bands have Γ_{25} symmetry in the tetrahedral case and Γ_{15} in the octrahedral NaCl lattice. It is therefore quite tempting to classify these bands as p like. It is clear, however, that in the case of Ge, where the s-like band (band 1) and the lowest p-like band (band 2) are degenerate at the X point, this artificial categorization of the bands by labels reflecting their supposed atomic parentage is misleading.

The similarity of band 1 and 2 in the group-IV elements is demonstrated by both experimental and theoretical results. Cavell, et al.,³⁰ studied the variation of the XPS cross sections across the valence bands for diamond, Si, and Ge. These results showed that the XPS cross section of the peaks corresponding to band 2 in each case followed quite closely that of band 1, the s-like band, and was very different from that of bands 3 and 4, the p-like bands. Charge-density calculations were also performed on each of the four bands of Ge by Walter and Cohen.³¹ They showed that the charge distributions of bands 1 and 2 are practically identical, and are very s-like. Bands 3 and 4 were found to be very similar to each other also, and both very p-like. By s-like, we mean that the charge density is concentrated on the atomic sites; and by p-like, we mean that the charge density is concentrated between the atomic sites in bonding regions.

In progressing along this series to GaAs, definite changes are apparent in both the photoemission spectrum and in the calculated band structure. The primary difference in the photoemission spectrum is that the band 1 peak has split off somewhat from the peaks due to bands 2-4 and has moved to higher binding energy. This is reflected as well in the band structure; i.e., the degeneracy of bands 1 and 2 lifted is lifted at the point X. On the basis of these changes, one would expect that band 1 is becoming more s-like and band 2 more p-like. The calculated charge densities bear out this expectation. Band 1 in GaAs is almost completely localized on the As site and is

virtually undistorted from spherical symmetry. Band 2 is less profoundly changed from the case of Ge but is definitely more p-like. In ZnSe the analogous changes are observed, with band 1 becoming almost completely corelike and band 2 showing a high degree of p character. It is evident that the effect of increasing the antisymmetric part of the potential is to progressively unmix the s-p bands 1 and 2 into purer atomic-like states. These changes are due to the increasing anion potential.

In the alkali halides, the description in terms of a band structure has come under question.^{32,33} Band-structure theory operates within the confines of the Hartree-Fock (and usually, in fact, of the Hartree-Fock-Slater approximation), in which the motions of electrons of opposite spin are completely uncorrelated. In this approximation every electron sees a truly periodic potential. Bloch's theorem therefore holds for each one-electron state and the electronic eigenfunctions may be labeled by $\vec{k}$. If correlation effects are introduced, the symmetry of the Hamiltonian will be broken, which can result in the mixing of states of different $\vec{k}$ such that highly correlated Wannier-like states become the true eigenfunctions of the system. These two possible descriptions of the system may, of course, both describe the same real-space electron density distribution in the crystal. For example, in NaCl one would expect to find the eight valence electrons per primitive cell near the Cl sites. This could be described in the local-orbital picture by four localized orbitals on the Cl site made up of linear combinations of a large number of

Bloch states. In the band scheme, the periodic part of each Bloch function $\phi_k(\vec{r})$ would have an equal amplitude on each Cl site in the lattice, and the $\sim 10^{23}$ states thus formed would each contribute to the electron density of the given site. It has been suggested³³ that the local orbital (Heitler-London) description of the alkali halides could be valid since the total calculated bandwidths, and thus the magnitude of the energy gain by delocalization, are smaller in comparison with the correlation energy than in any other case.

The implication of each of these models for the photoemission results is clear. If the localized-state description were valid the XPS spectrum would be that of essentially atomic orbitals in a cubic crystal field. Since p orbitals are not split by a cubic field, the only structure in the alkali-halide "valence bands" would be due to spin-orbit splitting. If the band picture were valid, dispersion in the band structure could give rise to extra structure in the valence-band peaks. The band picture could still be qualitatively valid, however, without giving rise to structure in the photoemission spectrum, provided that the bands are sufficiently flat.

Figures 18 and 19 show expanded drawings of the outermost p bands of each of the nine salts studied in this work. In three of the salts (KF, KCl, NaF) there is only one fairly symmetrical peak nominally corresponding to bands 2-4 as observed in the zinc-blende-structure semiconductors. This indicates, whether the Bloch-state formalism is valid or not, that the p bands retain a good deal of their atomic character in the solid. Band-structure calculations on KCl

by Fong and Cohen,²⁸ Howland³⁴ and De Cicco³⁵ all predict the valence bands to be ~ 1 eV wide. Allowing for the ~ 0.6 eV resolution of our spectrometer, it would be unlikely that we would observe any significant structure in the valence-band peak, even if the Block-state limit were rigorously correct.

In contrast to the above cases, the valence bands of LiF, NaCl, NaBr, NaI, KBr, and KI show definite structure on the high-binding energy side. Since these levels in the solid arise from the outermost p levels of the halogens, one could conceivably attribute this structure to the spin-orbit splitting of localized ionic states. We must reject this interpretation for several reasons. In Table XVIII we compare the atomic spin-orbit splittings³⁶ of the appropriate halogen levels with the splittings of the two features in the alkali-halide valence bands. In every case the separation of the features in the solid is larger than that predicted by spin-orbit splitting. In several cases -- NaCl, NaBr, NaI, and especially LiF -- the features are split much more than could be accounted for by spin-orbit splitting alone. Also, the large effect in the spectra of the change from Na^+ to K^+ in the chlorides argues against the structure being due to localized chlorine states. Table XVIII also shows results from gas phase alkali halides.³⁷

A further strong argument in favor of a band picture is provided by the systematics of the variation in the valence-band photoemission spectra and theoretical band-structure calculations in progressing through the Periodic Table. As we have already discussed, there is

a systematic progression in the character of the photoemission spectra in progressing from group-IV to III-V to II-VI crystals. In going on to the alkali halides, the crystal structure is changed; therefore, in terms of group-theoretical symmetry designations, the band structure is qualitatively different. However, a comparison of the features in the photoemission spectra is still not unreasonable. In the alkali halides, the analog of "band 1" in germanium is surely a bona fide core level, as was the case in ZnSe. In going from Ge to ZnSe the top two peaks merged as bands 2-4 came together to form a partially resolved shoulder on the high-binding-energy side of the valence-band peak. This shoulder arises mainly from band 2, which projects down farthest near the L and X points in the Brillouin zone in all the band-structure calculations for both the rock-salt and the zinc-blende structures.

While it is dangerous to compare different types of band-structure calculations done on different crystals, band structures done by the same method can be compared without too great a risk of systematic errors. Fong and Cohen²⁸ have calculated the band structures of NaCl and KCl by the empirical pseudopotential method. In our spectra NaCl shows distinct valence-band structure splitting while KCl does not. That this should indeed be the case is at least strongly indicated by these calculations. The calculated band structures are quite similar except for the fact that the valence band of NaCl is wider and shows a branch of the p bands forming a high density-of states region near L ~ 1.8 eV below the top of the

valence bands. It is clear from our previous experience that such a feature in the band structure could give rise to just such a feature in the photoemission spectrum as is observed.

Our results therefore indicate strongly that, at least for the less ionic of the alkali halides, a band-structure picture is valid. This agrees with the conclusion reached by Di Stefano and Spicer³⁸ regarding CsI. The agreement is especially interesting since they made their conclusions on the basis that they saw evidence for direct transitions in their uv photoemission spectra, and also because their higher resolution made the separation of band-structure and spin-orbit coupling effects even easier and more complete.

Table XIX lists binding energies of the outer core levels in these salts, both relative to the top of the valence bands. These values agree with the lower-resolution results of Citrin and Thomas.^{39,40} Since those authors discussed these binding energies thoroughly, we simply list our values without further comment. For recent compilations of experimental and theoretical results on the alkali halides see References 41-43. Our observed valence bandwidths are shown in Table XX.

C. An Ionicity Scale Based on X-Ray Photoemission Valence-Band Spectra of $A^N B^{8-N}$ and $A^N B^{10-N}$ Type Crystals*

1. Introduction

For several decades, the concept of ionicity has been of great practical use in the study of the chemical bond. It is therefore desirable to formulate a quantitative definition of ionicity. There have been many attempts to quantify ionicity, but all have possessed shortcomings.⁴⁴ For some time it has been known that the chemical shifts measured by x-ray photoemission spectroscopy (XPS) are related to charge transfer from the cation to the anion in a binary compound; this transfer can of course be related to ionicity.⁴⁵⁻⁴⁷ This approach has been applied to binary solids by Vesely and Langer⁴⁸ and, more recently, by Cardona and co-workers.⁴⁹ The measurement of chemical shifts in core-level binding energies in semiconductors and insulators is suspect for two reasons: sample charging (an experimental problem) and lack of a suitable reference energy (a conceptual problem). These problems may both be soluble, but even so it seems questionable whether core-level shifts will yield decisive ionicity information in view of final-state effects, etc.

In this section, we present an alternate approach, also based on XPS results. We have developed a quantitative scale of ionicity from the observed splitting of the lowest (i.e., most tightly bound) two peaks in the XPS valence-band densities of states (VBDOs) of

* Based on work done in collaboration with L. Ley, F. R. McFeely, and D. A. Shirley and published in J. Chem. Phys. 61, 2850 (1974).

41 binary crystals. This scale is compared in detail with the scale of Phillips-Van Vechten based on the single-gap dielectric model. Our scale is tested on the criteria of its ability to predict fourfold vs. sixfold coordination for the binary A^{N_8-N} and $A^{N_{10-N}}$ crystals.

2. Results

Most of the XPS-VBDOS of the crystals used in the analysis below were discussed in the previous section.

In general, the spectra of the valence band region of A^{N_8-N} and $A^{N_{10-N}}$ crystals show a three-peak structure, occasionally with a sharp core d peak intruding. Figure 20 shows the raw XPS-VBDOS spectra of some typical Group IV and Group V elements, and III-V, II-VI, IA-VII, and IV-VI compounds.

Walter and Cohen^{31,50} calculated electronic charge densities for several diamond and zinc-blende-type semiconductors from pseudo-potential band-structure wavefunctions. These charge densities give the distribution of the valence electrons in each band in real space: they can be related to peaks in our spectra. Peak I(PI) consists of electrons centered around the anion atomic site; i.e., an "s-like" distribution. Peak II(PII) consists of electrons basically centered around the cation and located in the bonding region. Peak III(PIII) results from electrons concentrated between the atomic sites in the bonding region, i.e., a "p-like" distribution. With this in mind, and realizing that the valence-band peaks cannot be truly described with such a simple atomic picture, we shall refer to PI and PII as s-like bands and PIII as p-like. Fuller discussions of the atomic derivation of the valence-band peaks are available in Refs. 30, 51, and 52.

Tables XXI and XXII summarize the compounds that have been studied by XPS and give the s-peak splitting ΔE_S^{XPS} in each case. Also given are nearest neighbor bond distances d and other parameters, discussed below.

3. Discussion

It was noted previously in an XPS study of the VB DOS of the isoelectronic series Ge, GaAs, and ZnSe⁵³ that ΔE_S^{XPS} increased with increasing ionicity. This increasing splitting was attributed mainly to an increasing localization of electrons around the stronger anion potential. The effect is visually demonstrated by the charge density distribution in Figs. 2, 3, 8, 9, 14, and 15 of Ref. 31. It was related to antisymmetric form factors of an empirical pseudopotential method (EPM) calculation.^{31,53} Later Ley, et al.,⁵⁴ and Grobman, et al.,⁵⁵ discussed the splitting at the symmetry point X (the X_3-X_1 gap) in the Brillouin zone. Increase of the X_3-X_1 gap was related to increasing ionicity and to Phillips' ionicity (hetero-polar) parameter C .

Recently, Chadi, et al.,⁵⁶ have studied the various possible relationships between C of the Phillips-Van Vechten theory and atomic pseudopotential in several binary crystals. However, to devise a quantitative scale of ionicity, a covalent fiducial point is necessary. The need to treat ionic and covalent contributions on an equal footing has been cogently put forth in a series of articles by Phillips and Van Vechten.^{44,57-68}

Ley, et al.,⁶⁹ in an XPS-VB DOS study of Groups IV and V covalent elemental crystals, observed a rather simple relationship between the covalent splitting of PI and PII, ΔE_S^C , and the nearest-neighbor distance d. The observed relation is

$$\Delta E_S^C = 8.0 - 2.2d,$$

with ΔE_S^C in eV and d in Å. The measured ΔE_S^C for these crystals, listed in Table XXI, are plotted in Fig. 21.

The splitting between the two s peaks corresponds to a splitting at the $L(L_2' - L_1)$ points in the diamond structure and at the $T(T_2' - T_1)$ point for the A_7 structure of the Group V semimetals. The $X_3' - X_1$ gap vanishes by symmetry in homopolar diamond-type crystals. The fact that ΔE_S^C depends on d in such a simple way for the homopolar crystals suggests that it is a strong function of overlap and could serve as a covalent fiducial point. The fact that the Group V semimetals fall on the "universal curve" of Fig. 21 suggests that the ionicity of the $A_B^{N_{10-N}}$ as well as the $A_B^{N_{8-N}}$ crystals might well be included in an XPS-derived scale of ionicity. The covalent (homopolar) parameter E_h of Phillips' model is a function of d only ($E_h \propto d^{-2.5}$). Grobman, et al.,⁵⁵ have speculated on the possible relationship between E_h and the L gap of homopolar diamond-type crystals.

We are now in a position to decompose our measured splitting of the "s-bands," ΔE_S^{XPS} into an ionic and a covalent contribution. ΔE_S^C is arrived at by simply inserting d(Å) of the crystal under

analysis into Eqn. (1). To obtain the ionic contribution ΔE_S^i , we suggest that the relationship

$$\Delta E_S^i = \Delta E_S^{XPS} - \Delta E_S^C \quad (2)$$

be employed. Now an ionicity number can be simply defined as

$$F_i^{XPS}(AB) \equiv \frac{\Delta E_S^i}{\Delta E_S^{XPS}} \quad (3)$$

For example, let us consider the isoelectronic series Ge, GaAs, and ZnSe, the members of which have nearly constant d . Germanium with $d = 2.44 \text{ \AA}$ is of course purely covalent, and $F_i^{XPS}(\text{Ge}) = 0.0$.

GaAs also has $d = 2.44 \text{ \AA}$ and Eqn. (1) or Fig. 21 yields $\Delta E_S^C = 2.6 \text{ eV}$. ΔE_S^{XPS} was measured to be 4.8 eV, which yields $\Delta E_S^i = 2.2$ and $F_i^{XPS}(\text{GaAs}) = 0.46$. In a similar manner for ZnSe ($d = 2.45 \text{ \AA}$), $\Delta E_S^{XPS} = 7.8$, $\Delta E_S^i = 5.2$, and $F_i^{XPS} = 0.67$. Figure 22 schematically displays what is happening in the Ge-GaAs-ZnSe series.

The antisymmetric gaps obtained from recent EPM calculations for this series are $V_A(\text{Ge}) = 0 \text{ eV}$, $V_A(\text{GaAs}) = 4.5 \text{ eV}$, and $V_A(\text{ZnSe}) = 8.2 \text{ eV}$.⁶ The trend in $V_A(AB)$ nicely follows the trend in $\Delta E_S^i(AB)$ and, since $d \approx \text{constant}$, in $\Delta E_S^{XPS}(AB)$ as well.

Table XXII summarizes the structures, the various parameters used, and the derived $F_i^{XPS}(AB)$ for the crystals used in this study. Before discussing the results in detail, let us compare this empirical ionicity scale with the dielectric-based scale of Phillips. Our ΔE_S^i , ΔE_S^C , and ΔE_S^{XPS} are analogous to the C , E_h and E_g , respectively, of Phillips. His E_g is the gap between bonding the anti-bonding states. Here E_h is the homopolar energy and is equal to E_g for

homopolar crystals and determined by the empirical relationship

$$E_h \propto d^{-2.5}$$

for heteropolar $A^N B^{8-N}$ crystals. C is the ionic contribution to E_g and Phillips has shown it to have the analytic form

$$C(AB) = b[(Z_A/r_A) - (Z_B/r_B)]e^{-K_S R}.$$

This just describes a screened Coulomb interaction and, without the screening factor, is similar to an electro-negativity difference. With d constant, $C(AB) \propto \Delta Z = 8 - 2N$, so $C(\text{ZnSe})/C(\text{GaAs}) \approx 2$, which is close to $\Delta E_S^i(\text{ZnSe})/\Delta E_S^i(\text{GaAs})$. In both scales, the homopolar gaps depend only on d . They do have different parametric dependences on d because of the different bases of the two scales. Phillips' C is related to the $X_3 - X_1$ gap in $A^N B^{8-N}$ tetrahedral crystals. It has been shown that the $X_3 - X_1$ gap can be measured with high resolution ($\leq 0.5 \text{ eV FWHM}$) XPS.⁵⁴ For the purpose of this study, however, we have chosen to use the PI-PII splitting, because (1) it is consistent with our choice for the covalent fiducial point, (2) it is chemically more appealing to take the peak position in the density of states which contains a large number of electrons rather than an edge of the Brillouin zone, (3) most XPS spectrometers do not yet possess high enough resolution to pick out the X_3 and X_1 symmetry points, (4) in many cases, core d peaks occur in the valence region; it is then hard enough to detect PI or PII, let alone symmetry points, and (5) we wish to make our $F_i^{\text{XPS}}(AB)$ apply more generally than just to tetrahedral $A^N B^{8-N}$ binary crystals.

Within the framework of an isotropic one-band model, Phillips showed that the total gap energy E_g may be written as $E_g^2 = E_h^2 + C^2$, where E_h and C are, respectively, the homopolar and ionic contributions to the gap energy. For this definition of ionicity, he employed the relationship

$$F_i^{DT} (AB) \equiv \frac{C^2}{E_h^2 + C^2} \quad (4)$$

While this relationship is physically appealing, it is nonetheless arbitrary.⁷⁰ We have no a priori reason to define $F_i^{XPS} (AB)$ either linearly, as in (3), or as

$$F_i^{XPS} \equiv \frac{(\Delta E_S^{XPS})^2 - (\Delta E_S^C)^2}{(\Delta E_S^{XPS})^2} \quad (5)$$

to be similar to Eqn. (4). Both Eqns. (3) and (5) give basically the same ordering of $F_i^{XPS} (AB)$. The $F_i^{XPS} (AB)$ defined by Eqn. (3) appears to be more useful in that it gives a wider range of ionicities, $0.26 < F_i^{XPS} (AB) < 1.00$ vs. $0.46 < F_i^{XPS} (AB) < 1.00$ for Eqn. (5). A big difference is noted in the $F_i^{XPS} (AB)$ of the alkali halides. The $F_i^{XPS} (AB)$ as defined by Eqn. (5) clusters the alkali halides around a very small range of values.

Phillips has discussed in detail the correspondence between ionicity and coordination for the $A^N B^{8-N}$ crystals.^{44,63,64,68} In his study of 70 $A^N B^{8-N}$ crystals, Phillips found a critical ionicity F_i such that $F_i < F_i$ the crystals are fourfold coordinated, and for $F_i > F_i$ the crystals are sixfold coordinated. With $F_i = 0.785$, Phillips' scale had 100% accuracy in predicting crystal structure,

far superior to any other then available quantitative scale of ionicity. In Fig. 23, we have plotted the ionicities of several $A^{N_8}B^{8-N}$ crystals common to studies for each scale, with the structure noted by symbols. We have added to both scales several $A^{N_{10}}B^{10-N}$ crystals, the lead salts, and SnTe, which have the rocksalt structure. We have also added to our scale several $Pb_xSn_{1-x}Te$ alloys and two ternary semiconductors. If for the dielectric scale we keep $F_i = 0.785$, the F_i^{DT} (AB) scale will make four wrong predictions with the inclusion of the $A^{N_{10}}B^{10-N}$ crystals. If we lowered F_i to 0.71, F_i^{DT} (AB) would make two errors but would no longer have a perfect score for the 70 $A^{N_8}B^{8-N}$ crystals of Ref. 44. The F_i^{XPS} (AB) scale with $F_i = \frac{2}{3}$ is able to predict 100% of the structures correctly. However, within the accuracy of the data, F_i^{XPS} (ZnSe) and F_i^{XPS} (PbS) should be considered equal; thus, F_i^{XPS} (AB) makes one error. Thus F_i^{XPS} (AB) appears to be superior to F_i^{DT} (AB) when IV-VI crystals and ternary alloys are included. The lead salts present an interesting case because they can indicate whether the F_i^{XPS} (AB) scale can be generalized beyond $A^{N_8}B^{8-N}$ crystals and because both ionic and covalent bonding have been proposed for them.⁷¹ F_i^{XPS} (AB) predicts the lead salts to have an ionic structure, which is correct. Recent charge density calculations on $PbTe$ ⁷² strongly support an ionic interpretation.⁷² The inclusion of $A^{N_{10}}B^{10-N}$ compounds in Fig. 23 is not meant to imply that 10-electron substances with F_i^{XPS} (AB) < 2/3 would be tetrahedrally bonded. This critical ionicity simply separates the high- and low-coordination-number compounds.

The cesium halides have the eightfold CsCl structure. Citrin and Thomas⁴⁰ have reported XPS data for several of these compounds.

If we apply our treatment to these data, we obtain

$$F_i^{XPS}(\text{CsF}) = 0.93, F_i^{XPS}(\text{CsCl}) = 0.97, \text{ and } F_i^{XPS}(\text{CsBr}) = 1.00.$$

All these values are in the upper range of the alkali halide data.

This is pleasing, although the ionicities of these three salts are ordered opposite to chemical expectations. Phillips did not treat these crystals. In view of the generality of this scale, it would be very useful to enlarge the XPS study, especially to include more $A^{N-10-N}B$ crystals.

In Fig. 23 we have also plotted data from two $A^{II}B^{IV}C_2^V$ (chalcopyrite-type) crystals. These are ternary analogs of the binary $A^{III}B^V$ crystals, i.e., ZnGeP_2 is the analog of GaP, and CdSnAs_2 of InAs.

In Fig. 24 is plotted the bonding charge, as calculated in Ref. 31, vs. $F_i^{XPS}(\text{AB})$ for the series Ge-GaAs-ZnSe. This shows that the phase transformation from fourfold to sixfold coordination occurs as the bonding charges get very small.

We shall not discuss the other scales of ionicity in detail since this has already been done by Phillips.⁴⁴ The major problems with the other scales, notably Coulson's molecular orbital approach,⁷³ $F_i^{\text{Cl}}(\text{AB})$, and Pauling's thermochemically based scale,⁷⁴ $F_i^{\text{P}}(\text{AB})$, derive from the lack of symmetrical treatment of ionic and covalent contributions. The covalent contribution is neglected in Pauling's definition and is an order of magnitude smaller in Coulson's approach.

As an example let us consider GaAs and InAs. Both $F_i^{\text{CRS}}(\text{AB})$ and $F_i^{\text{P}}(\text{AB})$ predict the same ionicity for each set of crystals $F_i^{\text{CRS}}(\text{GaAs}) = 0.37 = F_i^{\text{CRS}}(\text{InAs})$, $F_i^{\text{P}}(\text{GaAs}) = 0.26 = F_i^{\text{P}}(\text{InAs})$. We can see they both have nearly the same ionic contribution but the covalent contribution is different in both $F_i^{\text{XPS}}(\text{AB})$ and $F_i^{\text{DT}}(\text{AB})$. Hence, the values $F_i^{\text{XPS}}(\text{GaAs}) = 0.46$, $F_i^{\text{XPS}}(\text{InAs}) = 0.51$, $F_i^{\text{DT}}(\text{GaAs}) = 0.31$, $F_i^{\text{DT}}(\text{InAs}) = 0.36$. Coulson's scale is limited only to tetrahedrally coordinated $\text{A}^{\text{N}}\text{B}^{\text{8-N}}$ crystals. Both Pauling's and Coulson's scales tend to bunch groups of crystals with respect to ΔZ ; i.e., III-V crystals are clustered at one value and II-VI at another. Phillips stated that his dispersion theory does not work too well for crystals such as alkali halides with $F_i \geq 0.9$, which is where Pauling's scale is best because the covalent contribution is very small. The Phillips-Van Vechten theory uses optical and dielectric data. Optical data are not always straightforward to interpret and this approach includes some approximations.

Finally, we point out problems with the XPS-derived scale:

- (1) For a series with a given cation, the ordering of $F_i^{\text{XPS}}(\text{AB})$ is not what one would expect from chemical intuition. However, within a series with a given anion the ordering is much better. For isoelectronic series that have d essentially constant, $F_i^{\text{XPS}}(\text{AB})$ works out much better, so there may be a size effect which should be taken into account.
- (2) For the alkali halides of a given cation in particular, the ordering of $F_i^{\text{XPS}}(\text{AB})$ is exactly the inverse of what chemical intuition expects. For a given anion, the ordering is the

expected one. Possible sources of this discrepancy could arise from being at the ionic limit where the anion s peak (PI) is essentially a core peak; the effect of cation core peaks at lower binding energies; or a size effect which would be greatest for the alkali halide series. If we divide $F_i^{XPS}(AB)$ by the anion radius r_a to obtain

$$F_i^{*XPS}(AB) = F_i^{XPS}/r_a, \quad (6)$$

the resulting ordering of $F_i^{*XPS}(AB)$ is the intuitively correct one for both cation series and anion series. This is summarized in Table XXIII. If Eqn. (6) is applied to III-V compounds, one gets mixed results. The size effect should be studied further as more results become available.

4. Conclusions

This has been a first attempt to obtain a quantitative experimental measure of ionicity using XPS. An ionicity parameter $F_i^{XPS}(AB)$ was derived from the splitting of the lowest two s-like valence bands, ΔE_S^{XPS} . First a covalent fiducial line was established from the universal curve of ΔE_S^C vs. d . The energy ΔE_S^{XPS} was then decomposed into an ionic and covalent contribution and an ionicity number F_i^{XPS} was defined. This scale was applied to over 40 crystals. The crystals included not just $A^N B^{8-N}$ binary crystals but also $A^N B^{10-N}$ crystals, ternary alloys and chalcopyrite-type $A^M B^{N 8-(M+N)/2}$ crystals. It was able to predict quite well the transformation from fourfold to sixfold coordination solely on the basis of $F_i^{XPS}(AB)$. The scale was compared to other scales. It was

found superior to Coulson's MO approach and Pauling's thermochemical ionicity because it treated covalent and ionic contributions symmetrically. $F_i^{\text{XPS}}(\text{AB})$ also appeared to have wider applicability than the Phillips' scale, which was limited to $\text{A}^{\text{N}}\text{B}^{8-\text{N}}$ crystals. It appears that $F_i^{\text{XPS}}(\text{AB})$ needs a correction factor for the anion size. The question of d-band mixing with valence bands also requires further attention. There is need for further work, especially in the expansion of classes of crystals studied.⁷⁵ This study shows promise in the application of XPS to study of the problem of the nature of the chemical bond in solids. The approach taken in this work by-passes the difficulties associated with core-level shift studies by measuring splittings rather than shifts.

As mentioned earlier, there are several problems associated with chemical shift studies in solids: 1) charging, 2) reference level, and 3) the fact that observed binding energy shifts are composed of initial-state (chemical) effects and final-state (relaxation or polarization) effects. The approach used above circumvented this problem by measuring valence band splittings. There are two other ways of using PES data to obtain ionicity information and not be plagued with the above three problems. One approach is to use the concept of differential extra-atomic relaxation⁷⁶ in Auger transitions, using a core level as a fiducial point. Thus these differential shifts are independent of reference levels or charging. Extra-atomic relaxation is related to the ease of response of outer electrons on neighboring atoms to screen the increased positive charge in the

hole-state. It is easy to see that this ease of response is related to the concept of ionicity. Thus in metal where there is a common sea of conduction electron, these electrons should easily respond to the excess positive charge. On the other hand, going to compounds, as these electrons become more tightly bound to an atomic core (i.e., more ionic), they can respond less easily to the created hole. This is illustrated in Fig. 7 of Chapter II. This differential shift decreases from Na metal to sodium fluoride.

The concept of extra-atomic relaxation⁷⁶⁻⁷⁸ gives a theoretical basis to the concept of the Auger parameter recently introduced by C. D. Wagner.⁷⁹ Wagner has shown that there are suitable Auger transitions throughout most of the Periodic Table using conventional photon sources.⁷⁹ Wagner recently reported a compilation of the Auger parameter for a large set of compounds dispersed through a large range of the Periodic Table. (Note: We have found it important experimentally when doing such measurements on highly insulating compounds to obtain the Auger transition and the reference core-level within the same spectrum to obviate effects of changes in charging with time.)

Another way of obtaining information on ionicity, is through the use of multiplet splitting in compounds which have unpaired spin. This was noted in the very first investigation of this phenomena (Fadley and Shirley,⁸⁰ T. A. Carlson, et al.⁸¹). These authors suggested that the delocalization of d electrons in transition metal compounds could be studied with multiplet splitting. However, the

splittings are not easily observable in the 2p or 2s levels.⁸² The 3s and 3p levels are complicated by intra-shell correlation.⁸² However, the conversion of a "CI spectrum" into a "Koopmans' Theorem spectrum" by a sum rule could provide a way around this problem as discussed in Chapter IV. One must be leary of the problem of the spin distribution being different in the final-state from that in the initial state as pointed out by D. W. Davis, et al.,⁸³ Shirley,⁸⁴ and Larson, et al.⁸⁶ So far multiplet splitting has not been very useful for detailed studies of spin delocalization in solids.

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TABLE I. Structures of materials studied in this work.

Group	Compound	Structure ^a	Lattice constant $a(\text{\AA})^b$
III-V	GaP	<i>z</i>	5.448
	GaAs	<i>z</i>	5.6534
	GaSb	<i>z</i>	6.095
	InP	<i>z</i>	5.869
	InAs	<i>z</i>	6.053
	InSb	<i>z</i>	6.478
II-VI	ZnO	<i>w</i> (1.60)	3.249
	ZnS	<i>z</i>	5.406
	ZnSe	<i>z</i>	5.667
	ZnTe	<i>z</i>	6.1026
	CdS	<i>w</i> (1.62)	4.136
	CdSe	<i>w</i> (1.63)	4.299
	CdTe	<i>z</i>	6.481
	HgTe	<i>z</i>	6.453

^a*z* = zinc blende, *w* = wurtzite (*c/a* in parenthesis).

^bFrom *Powder Diffraction File* (Joint Committee on Powder Diffraction Standards, Swarthmore, Pennsylvania, 19081, 1972).

TABLE II. Surface contaminations of semiconductor samples as measured *in situ*.

Monolayers of oxygen ^a		$\frac{OK^b}{CA}$
CaP	<0.1	...
GaAs	0.2	1
GaSb	0.2	large
InP	0.2	1.9
InAs	<0.1	...
InSb	0.6	0.8
CdS	<0.1	...
CdSe	<0.1	...
CdTe	0.4	0.4
ZnS	<0.1	...
ZnSe	0.5	0
ZnTe	0.6	0.2
HgTe	0.4	0.6

^aDeduced from comparison with oxygen signal from ZnO; estimated error 100%.

^bRatio of O 1s to C 1s peak intensities.

TABLE III. Binding energies of characteristic valence-band features from top of valence bands (in eV). (See Fig. 12 and text for definition of points. Accuracy is ± 0.1 eV.)

Material	H_{1T}	I_2	I_1	I'	S_1	H_{1B}	E_1	H_{11T}	P_{11}	H_{11B}	E_{11}	E_{111}	H_{111T}	P_{111}	H_{111B}	B
GaP	0.7	1.7	2.4	***	3.5	4.0	***	5.4	6.5	7.0	7.4	8.2	9.1	10.3	12.2	13.4
GaAs	1.0	1.8	2.4	2.9	3.8	***	***	***	6.6	7.5	8.1	9.0	10.0	11.4	13.3	14.4
GaSb	0.8	1.7	2.1	***	3.4	3.7	4.4	5.5	6.4	7.1	7.4	8.5	9.2	10.0	11.1	11.9
InP	0.7	***	1.8	***	2.7	3.6	***	***	5.4	6.2	6.9	7.8	8.6	9.7	10.8	11.0
InAs	0.6	1.7	2.1	***	3.0	3.5	***	***	5.8	6.3	6.9	8.5	9.4	10.5	11.6	12.6
InSb	1.0	2.0	2.5	***	3.2	3.5	4.2	***	5.9	6.5	7.2	8.4	8.9	10.0	11.1	12.0
ZnO	2.1	***	2.9	***	3.8	***	***	***	5.9	6.6	7.0	~18	19.8	20.7	23.1	24.8
ZnS	0.8	2.0	2.6	***	3.2	4.0	***	***	4.9	5.9	6.4	11.4	11.8	12.4	13.3	13.8
ZnSe	0.8	1.6	1.9	***	2.6	3.5	***	***	5.2	5.8	6.0	11.6	12.1	13.1	14.6	15.8
ZnTe	0.7	1.2	1.7	2.2	2.8	3.4	***	***	5.1	5.8	6.3	11.3	11.5	11.9	12.7	13.4
CdS	0.8	1.3	1.6	***	2.1	3.1	***	***	4.1	4.8	5.5	***	***	***	***	***
CdSe	0.8	1.5	1.9	***	***	***	***	***	4.3	5.1	5.5	***	***	***	***	***
CdTe	0.6	1.5	1.8	***	2.5	2.9	(3.6)	***	4.5	5.2	5.6	***	***	***	***	***
HgTe	0.7	1.5	2.1	***	***	3.3	***	***	5.3	6.0	6.4	***	***	***	***	***

TABLE IV. Comparison of characteristic features in valence-band spectra from XPS (this work) and UPS (Ref. 1) in eV. (Relative to top of valence bands. Quoted values were obtained graphically from both sets of spectra.)

Material	I_1		S_1		P_{II}		P_{III}		B	
	XPS	UPS	XPS	UPS	XPS	UPS	XPS	UPS	XPS	UPS
GaP	2.4	1.6	3.5	3.6	6.5	6.5	10.3	10.2	13.4	12.3
GaAs	2.4	1.7	3.8	3.6	6.6	6.4	11.4	11.2	14.4	13.6
InSb	2.5	1.9	3.2	3.4	5.9	6.0	10.0	9.9	12.0	11.7
ZnSe	1.9	1.3	2.6	2.7	5.2	4.9	13.1	13.7	15.8	...
CdTe	1.7	1.5	2.5	2.5	4.5	4.4	...	...	...	...
Ge	2.6	2.6	3.8	3.8	7.4	7.7	10.5	10.6	13.2	12.8

TABLE V. Valence-band energies in GaP (in eV with respect to the top of the valence band).

Method	I_3	X_2	W_2	Σ_1^{mla}	W_1	$X_3(I_1)$	X_1	I_1	Γ_1	Ref.
XPS	1.2(3)	2.7(2)	3.6(2)	4.0(2)	6.5(2)	6.9(2)	9.6(3)	10.6(3)	13.2(4)	this work
UPS	0.8	...	...	4.1	...	6.9	9.7	...	11.8	1
EPM (adj)	1.0	2.5	3.7	4.1	6.6	6.9	10.9	11.7	13.6	6
OPW (adj)	0.9	2.3	...	...	...	6.1	9.2	10.0	11.8	7
OPW ^a	0.9	2.3	...	...	...	6.1	9.4	10.1	11.9	8
ROPW, X_{OS}	0.9	2.2	...	...	...	6.1	9.5	10.3	12.0	9

^aKohn-Sham exchange.

TABLE VI. Valence-band energies in GaAs (in eV with respect to the top of the valence band).

Method	L_2	X_2	W_2	Σ_1^{mla}	W_1	$X_2(L_1)$	X_1	L_1	L'_1	Ref.
XPS	1.4(3)	2.5(3)	4.0(2)	4.4(2)	6.6(1)	7.1(2)	10.7(3)	12.0(5)	13.8(4)	this work
UPS	0.8	...	...	4.1	...	6.9	10.0	...	12.9	1
EPM (adj)	0.9	2.5	3.5	3.9	6.6	6.8	11.4	...	13.8	6
OPW (adj)	0.9	2.3	...	...	...	5.6	10.7	11.1	12.4	7
OPW ^a	1.0	2.3	...	...	...	6.3	9.7	10.4	12.0	8
ROPW, X_{as}	1.1	2.4	...	...	...	6.4	10.2	10.9	12.4	9
SCOPW ^a	1.0	2.5	3.4	4.0	6.2	6.6	9.2	10.1	11.9	10
SCOPW ^b	1.0	2.3	3.0	3.3	6.0	6.3	9.5	10.2	11.8	10

^aKohn-Sham exchange.^bSlater exchange.

TABLE VII. Valence-band energies in GaSb (in eV with respect to the top of the valence band).

Method	L_3	X_3	W_2	Σ_1^{min}	W_1	$X_3(L_1)$	X_1	L_1	Γ_1	Ref.
XPS	1.3(2)	2.7(2)	2.6(2)	3.8(2)	6.4(1)	6.9(3)	9.4(2)	10.3(3)	11.6(3)	this work
OPW (adj)	0.9	2.3	...	...	...	5.5	9.8	9.9	11.1	7
OPW ^a	1.1	2.4	...	...	...	6.3	7.9	9.0	10.7	8
ROPW, X_{as}	1.2	2.5	...	...	...	6.9	8.9	9.7	11.3	9

^aKohn-Sham exchange.

TABLE VIII. Valence-band energies in hP (in eV with respect to the top of the valence band).

Method	L_3	X_5	W_2	Σ_1^{min}	W_1	$X_3(L_1)$	X_1	L_1	Γ_1	Ref.
XPS	1.0(3)	2.0(2)	2.5(2)	3.2(2)	5.4(2)	5.9(2)	8.9(3)	10.0(3)	11.0(4)	this work
OPW (adj)	0.6	1.7	...	...	...	4.6	9.7	10.1	11.1	4
OPW ^a	0.6	1.7	...	...	...	4.5	9.0	9.4	10.6	4
ROPW, X_{ss}	0.7	1.6	...	...	...	4.6	9.2	9.7	10.8	9

^aKohn-Sham exchange.

TABLE IX. Valence-band energies in InAs (in eV with respect to the top of the valence band).

Method	L_3	X_5	W_2	Σ_1^{min}	W_1	$X_3(L_1)$	X_1	L_1	Γ_1	Ref.
XPS	0.9(3)	2.4(3)	2.7(3)	3.3(2)	5.8(2)	6.3(2)	9.8(3)	10.6(3)	12.3(4)	this work
OPW (adj)	0.6	1.7	***	***	***	4.7	10.3	10.6	11.5	4
OPW*	0.7	1.8	***	***	***	4.7	9.4	9.8	10.8	4
ROPW, X_{OS}	0.8	1.9	***	***	***	5.1	10.0	10.4	11.4	9

*Kohn-Sham exchange.

TABLE X. Valence-band energies in InSb (in eV with respect to the top of the valence band).

Method	L_7	X_5	W_2	Σ_1^{ma}	W_1	$X_3(L_1)$	X_1	L_1	Γ_1	Ref.
XPS	1.4(3)	2.4(4)	3.1(2)	3.4(2)	5.9(2)	6.4(2)	9.5(2)	10.5(3)	11.7(3)	this work
UPS	1.05	...	...	3.65	...	6.5	9.0	...	11.2	1
EPM (adj)	1.2	2.1	2.8	3.2	5.7	6.2	9.5	10.1	11.3	6
OPW (adj)	0.7	1.8	...	...	...	4.7	9.0	9.3	10.2	4
OPW ^a	0.8	1.9	...	...	...	5.0	7.7	8.3	9.6	4
ROPW, $X_{\alpha\beta}$	1.1	2.1	...	...	...	5.7	8.8	9.3	10.5	9

^aKohn-Sham exchange.

TABLE XI. Valence-band energies of ZnS (in eV with respect to the top of the valence band).

Method	L_3	X_5	W_2	Σ_1^{ma}	W_1	$X_3(L_1)$	X_1	L_1	Γ_1	Ref.
XPS	1.4(4)	2.5(3)	3.0(2)	3.4(3)	4.9(2)	5.5(2)	12.0(3)	12.4(3)	13.5(4)	this work
OPW (adj)	0.3	1.1	...	...	...	3.5	...	...	...	13
OPW ^a	0.4	1.2	...	...	...	3.5	...	...	...	13
ROPW, X_{as}	0.5	1.3	...	...	...	3.8	11.2	11.5	12.2	16
SCOPW	0.6	1.6	2.0	2.1	3.7	4.2	10.0	10.6	11.7	13
KKR	0.6	1.4	...	2.1	...	3.3	11.9	12.1	12.6	14
APW	0.9	1.7	...	...	...	3.4	13.4	13.4	14.0	15

^aSlater exchange.

TABLE XII. Valence-band energies of ZnSe (in eV with respect to the top of the valence band).

Method	L_3	X_3	W_2	Σ_1^{min}	W_1	$X_3(L_1)$	X_1	L_1	Γ_1	Ref.
XPS	1.3(3)	2.1(3)	2.6(2)	3.4(2)	5.2(2)	5.6(3)	12.5(4)	13.1(3)	15.2(6)	this work
UPS	0.7	...	...	3.4	...	5.3	...	...	...	1
EPM (adj)	0.9	2.1	3.3	3.8	5.3	5.9	14.2	14.5	15.8	6
OPW (adj)	0.4	1.4	...	...	...	3.7	...	...	...	7
OPW ^a	0.4	1.3	...	...	...	3.8	...	...	...	8
ROPW, $X_{\text{ex},A}$	0.7	1.6	...	...	...	4.2	11.6	11.9	12.6	16
SCOPW ^b	0.7	2.0	2.7	3.1	4.5	4.7	10.4	10.8	11.8	10
SCOPW ^c	0.7	1.6	2.3	4.5	4.2	4.4	10.5	10.9	11.8	10
KKR	0.6	1.3	...	2.2	...	3.6	12.0	12.2	12.6	14

^aSlater exchange.^bKohn-Sham exchange.

TABLE XIII. Valence-band energies of ZnTe (in eV with respect to the top of the valence band).

Method	L_3	X_3	W_2	Σ_1^{min}	W_1	$X_3(L_1)$	X_1	L_1	Γ_1	Ref.
XPS	1.1(3)	2.4(2)	2.7(2)	3.2(3)	5.1(2)	5.5(2)	11.6(3)	12.0(3)	13.0(4)	this work
OPW (adj)	0.5	1.4	...	...	...	3.7	...	...	...	7
OPW ^a	0.6	1.5	...	...	...	4.4	...	...	...	8
ROPW, X_{as}	1.0	2.0	...	...	...	5.0	10.2	10.6	11.5	16
KKR	0.6	1.6	...	2.8	...	4.3	9.6	9.7	10.5	14

^aSlater exchange.

TABLE XIV. Valence-band energies of CdTe (in eV with respect to the top of the valence band).

Method	L_3	X_5	W_2	Σ_1^{da}	W_1	$X_3(L_1)$	X_1	L_1	Γ_1	Ref.
XPS	9.9(3)	1.8(2)	2.2(3)	2.7(3)	4.5(2)	5.1(2)	...	...	...	this work
UPS	0.7	...	...	2.8	...	4.7	8.8	...	...	1
EPM (adj)	1.6	1.5	2.0	2.7	4.3	4.6	10.6	...	11.8	6
OPW (adj)	0.4	1.1	...	...	...	3.0	...	...	...	7
OPW ^a	0.4	1.1	...	...	...	3.1	...	...	...	8
ROPW, X_{ad}	0.8	1.6	...	...	...	3.9	10.1	10.3	10.8	16
KKR	0.6	1.4	...	2.1	...	3.5	8.7	9.2	10.3	14

^aSlater exchange.

TABLE XV. Valence-band energies of HgTe (in eV with respect to the top of valence band).

Method	L_3	X_3	Σ_{val}	W_i	$X_3(L_3)$	X_1	Γ_1	Ref.
XPS	1.2(2)	2.5(3)	3.2(3)	5.3(2)	5.7(3)	...	...	this work
ROPW, X_{val}	0.8	1.6	...	...	4.8	10.2	10.9	16

TABLE XVI. X_2-X_1 Gap (eV).

Material	KKR (Ref. 14)	OPW (Ref. 8) ^a	OPW (adj) (Ref. 7)	SCOPW (Ref. 10) ^a	SCOPW (Ref. 10) ^b	ROPW, X_{sp} (Refs. 9, 16)	XPS ^c	UPS (Refs. 1, 18)
GaP		3.3	3.1			3.4	2.7	2.8
GaAs		3.4	5.1	2.6	3.2	3.8	3.6	3.1
GaSb		1.1	4.3			2.0	2.6	
InP		4.5	5.1			4.6	3.0	
InAs		4.7	5.6			4.9	3.5	
InSb		2.7	4.3			3.1	3.1	2.5
ZnS	8.6				5.8 ^d	7.1	6.5	
ZnSe	8.4			5.7	6.1	7.4	6.9	
ZnTe	5.3					5.2	6.1	
CdTe	5.2					6.2	***	4.1

^aWith Kohn-Sham exchange.^bWith Slater exchange.^cThis work.^dReference 13.

TABLE XVII. Energy of point Γ_3 in the Brillouin zone with respect to Γ_{1c} for hexagonal CdS, CdSe, and ZnO (in eV).

	XPS	KKR ^a	OPW ^b	SCOPW ^c	EPM ^d
CdS	5.0 ± 0.4		3.4	3.6	2.8
CdSe	5.2 ± 0.3				2.5
ZnO ^e	5.2 ± 0.3	3.8			

^aReference 20.

^bReference 23.

^cReference 24.

^dReference 17.

^e $\Gamma_{6,1}$ is assumed to be the zero intercept of the linear extrapolation of the maximum slope at the leading edge of peak I.

TABLE XVIII. Comparison of atomic spin-orbit splitting of outermost halogen level with splitting of observed features in valence bands of the alkali halides of this study.

	Atomic spin-orbit splitting ^a	LiX ^b	NaX ^b	NaX ^c	KX ^b	KX ^c
F	0.05	1.68	...	...	...	...
Cl	0.11	...	1.13	0.46	...	...
Br	0.46	...	1.28	0.65	...	0.48
I	0.94	...	1.48	1.07	1.08	0.98

^aReference 36.

^bThis work.

^cReference 37, gas phase data.

TABLE XIX. Binding energies (eV) of the outer core levels of the sodium and potassium halides. Energies are relative to the top of the valence band and are given to ± 0.1 eV. VB stands for valence band.

LiF							
		VB(1)		3.34			
		VB(2)		5.22			
F 2s		24.90					
Li 1s		59.77					
NaF		NaCl		NaBr		NaI	
VB	2.06	VB(1)	1.47	VB(1)	1.67	VB(1)	1.67
F 2s	23.20	VB(2)	2.60	VB(2)	2.95	VB(2)	3.15
Na 2p	24.77	Cl 3s	12.58	Br 4s	12.59	I 5s	11.21
Na 2s	37.46	Na 2p	27.03	Na 2p	29.21	Na 2p	29.29
		Na 2s	59.77	Na 2s	61.00	1 4d _{3/2}	47.68
				Br 3d	66.21	1 4d _{5/2}	49.35
						Na 2s	61.96
KF		KCl		KBr		KI	
VB	1.38	VB	1.87	VB	1.27	VB(1)	1.48
K 3p	13.01	K 3p	14.07	K 3p	14.17	VB(2)	2.56
F 2s	22.24	K 3s	30.11	Br 4s	16.24	I 5s	10.82
K 3s	27.73			K 4s	30.21	K 3p	15.55
				Br 3d	65.69	K 3s	31.59
						1 4d _{3/2}	47.48
						1 4d _{5/2}	49.10

Table XX. Valence Bandwidths (eV) of the Alkali Halides.

	W(XPS) ^a	W(UPS) ^b	W(ETBM) ^c
LiF	5.6(2)	6.1	5.9
NaF	4.5(3)	4.9	4.4
NaCl	4.0(2)	4.1	3.0
NaBr	4.0(2)	3.8	2.7
NaI	4.2(3)	--	2.3
KF	3.3(2)	3.7	3.3
KCl	4.5(2)	2.7	2.4
KBr	3.2(2)	2.6	2.2
KI	3.7(3)	2.8	1.9

^aThis work.

^bRef. 43.

^cRef. 42, calculated using the empirical tight-binding method.
See Ref. 41 and 43 for summary of theoretical results from other methods.

TALBE XXI. Nearest-neighbor distance and ΔE_S^C splitting for Group IV and Group V elemental crystals.

Crystal	Structure ^a	$d(\text{\AA})^a$	$\Delta E_S^C(\text{eV})$	Reference
C	diamond	1.54	4.7	30
Si	diamond	2.34	2.6	2
Ge	diamond	2.44	3.1	2
α -Sn	diamond	2.80	1.8 ^b	...
As	A7	2.50	2.6	69
Sb	A7	2.86	1.7	69
Bi	A7	3.10	1.2	69

^aR. W. G. Wyckoff, *Crystal Structures* (Wiley-Interscience, New York, 1963).

^bPredicted value from Eq. (1).

^cF. R. McFeely, S. P. Kowalczyk, R. Pollak, and D. A. Shirley, *Phys. Rev. B* **8**, 641 (1973).

TABLE XXII. Nearest-neighbor distances, energy of XPS splitting of lowest two valence bands ΔE_S^{XPS} , the covalent splittings ΔE_S^C , ionic splittings ΔE_S^I , and ionicity number $\gamma_S^{XPS}(AB)$. These parameters are explained in the text. All energies are given in electron volts.

Crystal	$d(\text{\AA})^a$	Structure ^b	ΔE_S^{XPS}	ΔE_S^C	ΔE_S^I	$\gamma_S^{XPS}(AB)^d$	Reference
GaAs	2.44	Z	4.8	2.6	2.2	0.46	54
ZnSe	2.45	Z	7.8	2.6	5.2	0.67	54
InSb	2.81	Z	4.1	1.8	2.3	0.56	54
CdTe	2.81	Z	~5.2	1.8	~3.4	~0.65	54
GaSb	2.65	Z	3.6	2.2	1.4	0.39	54
ZnTe	2.64	Z	6.5	2.2	4.3	0.66	54
KI	3.53	R	8.3	0.2	8.1	0.97	51
InAs	2.61	Z	4.7	2.3	2.4	0.51	54
CdSe	2.63	W	~5.7	2.2	~3.5	0.61	54
InP	2.54	Z	4.3	2.4	1.9	0.44	54
CdS	2.53	W	~5.5	2.4	~3.1	~0.56	54
RbCl	3.29	R	10.7	0.7	10.0	0.94	g
AlSb	2.66	Z	4.3	2.2	2.1	0.49	h
NaI	3.24	R	8.1	0.9	7.2	0.89	51
NaBr	2.99	R	9.9	1.4	8.5	0.86	51
GaP	2.36	Z	3.8	2.8	1.0	0.26	54
ZnS	2.34	Z	7.5	2.9	4.6	0.61	54
KCl	3.15	R	11.8	1.1	10.7	0.91	51
ZnO	1.95	W	9.1	3.7	5.4	0.59	54
KF	2.67	R	20.9	2.1	18.7	0.90	51
MgO	2.10	R	13.5	3.4	10.1	0.75	h
NaF	2.32	R	21.1	2.9	18.3	0.86	51
PbS	2.97	R	4.4	1.5	2.9	0.67	i
PbSe	3.06	R	4.3	1.3	3.0	0.70	i
PbTe	3.25	R	3.5	0.9	2.6	0.74	i
SnTe	3.14	R	4.4	1.1	3.3	0.75	h
Pb _{0.8} Sn _{0.2} Te	3.23	R	3.1	0.9	2.2	0.70	h
Pb _{0.8} Sn _{0.2} Te	3.18	R	3.5	1.0	2.5	0.71	h
Pb _{0.8} Sn _{0.2} Te	3.16	R	4.3	1.1	3.2	0.74	h
LiF	2.01	R	19.7	3.6	16.1	0.82	51
KBr	3.30	R	12.9	0.7	12.2	0.95	51
NaCl	2.82	R	10.0	1.8	8.2	0.62	51
CdSnAs ₂	2.64 ^e	Z ^f	~5	2.2	~2.8	~0.56	j
ZnGeP ₂	2.37 ^e	Z ^f	4.8	2.8	2.0	0.42	j
CsCl	3.51	CsCl	10.6	0.3	10.3	0.97	40
CsF	3.00	R	20.9	1.4	19.5	0.93	40
CsBr	3.71	CsCl	9.6	-0.2	9.6	1.00	40
HgTe	2.76	Z	~3.5	1.9	1.6	~0.46	54
SrO	2.57	R	~13	2.4	10.6	~0.82	h

^aR. W. G. Wyckoff, *Crystal Structures* (Wiley-Interscience, New York, 1963).

^bZ—zincblende; R—rocksalt; W—wurtzite; CsCl—cesium chloride.

^cFrom Eq. (1).

^dFrom Eq. (3).

^eA. S. Borschevskii, N. A. Goryunova, and F. P. Kesamanly, *Phys. Status Solidi B* 21, 9 (1967).

^fChalcopyrite structure is analogous to zincblende structure with the cation site being occupied alternately by Group II and Group IV cation.

^gC. J. Veseley, D. L. Kingston, and D. W. Langer, *Phys. Lett. A* 41, 137 (1973).

^hUnpublished work of this laboratory.

ⁱF. R. McFeely, S. P. Kowalczyk, L. Ley, R. A. Pollak, and D. A. Shirley, *Phys. Rev. B* 7, 5228 (1973).

^jC. Varea de Alvarez, M. L. Cohen, L. Ley, S. P. Kowalczyk, F. R. McFeely, D. A. Shirley, and R. W. Grant, *Phys. Rev. B* 10, 596 (1974).

TABLE XXIII. Anion size correction applied to alkali halide crystals.^a

Crystal	$\Delta E_S^{\text{XPS}}^b$	ΔE_S^c	$\Delta E_S^{f,2}$	$\tau^{\text{XPS}}(\text{AB})^d$	$\tau^{\text{XPS}}(\text{AB})^e$	$r_e(\text{\AA})$
LiF	19.65	3.57	16.11	0.919	1.14	0.72
NaF	21.14	2.90	18.24	0.863	1.26	0.72
NaCl	9.99	1.60	8.39	0.820	0.83	0.99
NaBr	9.88	1.42	8.46	0.856	0.75	1.14
NaI	8.06	0.87	7.19	0.892	0.69	1.33
KF	20.86	2.13	18.73	0.898	1.25	0.72
KCl	11.8	1.07	10.73	0.909	0.92	0.99
KBr	14.97	0.74	14.23	0.951	0.83	1.14
KI	8.26	0.23	8.03	0.972	0.73	1.33

^aEnergies in eV.^bFrom Ref. 51.^cFrom Eq. (1).^dFrom Eq. (2).^eFrom Eq. (3).^fFrom Eq. (5).

FIGURE CAPTIONS

- Fig. 1. X-ray photoelectron spectra from GaP, GaAs, and GaSb.
- Fig. 2. X-ray photoelectron spectra from InP, InAs, and InSb.
- Fig. 3. X-ray photoelectron spectra from ZnO, ZnS, ZnSe, and ZnTe.
- Fig. 4. X-ray photoelectron spectra from CdS, CdSe, and CdTe.
- Fig. 5. X-ray photoelectron spectrum from HgTe.
- Fig. 6. The corrected valence-band spectra, $I'(E)$, of GaP, GaAs, and GaSb.
- Fig. 7. The corrected valence-band spectra, $I'(E)$, of InP, InAs, and InSb.
- Fig. 8. The corrected valence-band spectrum, $I'(E)$, of ZnO.
- Fig. 9. The corrected valence-band spectra, $I'(E)$, of ZnS, ZnSe, and ZnTe.
- Fig. 10. The corrected valence-band spectra, $I'(E)$, of CdS, CdSe, and CdTe.
- Fig. 11. The corrected valence-band spectrum, $I'(E)$, of HgTe.
- Fig. 12. Generalized photoelectron spectrum for the binary semiconductors.
For an explanation of the labeled features see text.
- Fig. 13. Band structure, density of states $\rho(E)$, broadened density of states $\rho'(E)$, and corrected valence-band spectrum $I'(E)$ for GaP. Band structure and $\rho(E)$ are taken from Ref. 6.
- Fig. 14. X-ray photoemission spectrum of the valence band region of LiF.
- Fig. 15. X-ray photoemission spectra of the valence band region of the sodium halides.

- Fig. 16. X-ray photoemission spectra of the valence band region of the potassium halides.
- Fig. 17. X-ray photoemission spectra and band structures of Ge, GaAs, ZnSe, and NaCl. The upper row shows the uncorrected experimental spectra. The lower row shows the corresponding band structure of EPM calculations of Refs. 25-28.
- Fig. 18. The outermost p band of LiF.
- Fig. 19. The outermost p band of the sodium and potassium halides.
- Fig. 20. (a) X-ray photoemission valence band spectra of several typical A^{N-8}_B type crystals, Ge, GaAs, ZnSe, and KBr; and (b) A^{N-10}_B type crystals, Sb and PbS.
- Fig. 21. Plot of ΔE_S^C (eV) vs. $d(A)$ for group IV and V crystals which yields Eqn. (1). Figure is taken from Ref. 69.
- Fig. 22. Schematic display of the ΔE_S^{XPS} splitting of the isoelectronic series Ge, GaAs, and ZnSe. The relevant parameters in determining $F_i^{XPS}(AB)$ are denoted.
- Fig. 23. Comparison of the XPS-derived scale of ionicity, $F_i^{XPS}(AB)$ from Table XX and the Phillips-VanVechten ionicity, $F_i^{DT}(AB)$ (Ref. 44) illustrating the ability to predict structural phase transformation. $F_i^{DT}(AB)$ for crystalline materials of average V valence was obtained from P. J. Stiles, Solid State Commun. 11, 1063 (1972). Vertical line indicates critical ionicity, F_i . Dashed vertical line for $F_i^{DT}(AB)$ is the F_i derived in Ref. 44. Crystals with diamond, zinc-blende or chalcopyrite structure are indicated by $\blacktriangle$, wurtzite structure by Δ and rocksalt structure by $\circ$.
- Fig. 24. Plot of bonding charge determined as in Ref. 31 vs. $F_i^{XPS}(AB)$ for the series Ge, GaAs, and ZnSe.

XBL 7210-5822

Fig. 1

Fig. 2

REL 7210-5824

Fig. 3

XBL 7210-5823

Fig. 4

Fig. 5

XBL 7210-5807

XBL 733-2505

Fig. 6

XBL733-2506

Fig. 7

XBL733-2504

Fig. 8

XBL733-2507

Fig. 9

Fig. 10

XBL733-2508

XBL 733-2503

Fig. 11

XBL735 - 2813

Fig. 12

Fig. 13

XBL738-3763

Fig. 14

XBL736-3234

Fig. 15

XBL736-3233

Fig. 16

Fig. 17

XBL738-3762A

Fig. 18

Fig. 19

Fig. 20a

Fig. 20b

XBL 744-2886

Fig. 21

XBL 744-2888

Fig. 22

Fig. 23

XBL 744-2867

Fig. 24

VI. Valence Band Density of States of Metals and Alloys

A. Introduction

The results from the valence band density of states (VB DOS) overview of binary semiconductors and insulators (Chapter V, section B) demonstrated the great wealth of information which can be obtained from PES VB DOS studies. For the case of Au metal, Shirley¹ demonstrated that detailed information about $N(E)$ could be obtained by XPS from metals. In this chapter, we shall present high resolution total XPS VB DOS results for a large number of metals, representative of the various classes of metals and several alloys. The free-electron-like metals Na, Mg, and Al will be discussed first. Next we will deal in some detail with the 3d transition metals, scandium through zinc. Then results from the rare earth metals lanthanum through lutetium will be briefly summarized. Finally, a study of several alloys which included β -NiAl, several rare earth dialuminides and YbZn_2 and CePd_3 will be given as examples of the application of XPS to the study of the electronic structure of alloys.

All of the specimens reported in this chapter were prepared in situ and under UHV conditions. These precautions were necessary because most of these metals are extremely reactive. For the most part, evaporation by resistive heating onto polished substrates (stainless steel or tantalum) was found to be the most convenient and reliable technique of preparing specimens clean on an atomic scale. Some metals were also prepared by means of sputter deposition.

This technique may, however, yield samples with disordered surfaces which can lead to subtle changes in the electronic structure.^{2,3} For the few cases where we prepared samples in this manner and by the evaporation method, no discernible difference in the two spectra were observed. In Chapter III, we discussed the problems associated with the in situ preparation of multicomponent specimens. Thus for the study of alloys reported in this chapter, we employed the mechanical cleaning device described in Chapter III for preparing fresh, clean alloy specimens. References 4 through 9 review earlier PES investigations of metals.

B. The Nearly Free-Electron-Like Metals:

Na, Mg, and Al

These metals have the simplest electronic structure and many of their electronic properties may be successfully described by the nearly free-electron model. Thus these metals are good systems to study. The XPS spectra for the valence region of Na, Mg, and Al are shown in Figs. 1-3. The valence bandwidths, observed X-ray emission bandwidths and theoretical bandwidths are summarized in Table I.

Sodium ($[Ne]3s^1$) is monovalent and one of the most free-electron-like metals. The valence band spectrum of Fig. 1 agrees roughly in shape and width with the X-ray emission spectrum.¹⁰⁻¹³ An approximate free-electron $E^{1/2}$ dependence on energy is observed. The observed valence bandwidth is 3.1 ± 0.1 eV if measured from the low energy edge or 2.5 ± 0.1 eV if measured from the gold Fermi level. This latter value agrees well with X-ray emission data of Crisp and

Williams.¹¹ It must be remembered (Chapter II, section C) that XPS and XES (and X-ray absorption) are different processes and the various spectra are not necessarily identical. The spectrum of Fig. 1 does not exhibit the excitonic structure which has been observed in X-ray emission^{11,13} and attributed to the Mahan-Nozières-DeDominicis (MND) singularity.^{14,15} The spectrum is, however, unusual both in the position of the valence band relative to $E_F(\text{Au})$ and in the gradual slope of the VB edge.

Divalent Mg has a free-electron configuration $[\text{Ne}] 3s^2$ and has the hcp crystal structure. Since Mg is metallic, the occupied electron states overlap Brillouin zone boundaries. This should introduce structure due to Van Hove singularities. Again as in the Na case, a sharp Fermi edge is not observed. Also, there is clearly structure in the VB DOS (0.8, 2.0, 2.8, and 5.2 eV). As mentioned in Chapter II (section C-7), a comparison of the K_β and L X-ray emission results of Neddermeyer suggest that the p-states are concentrated at the top of the bands and the s-states are concentrated in the lower part of the bands. The steep sharp peak observed at the Fermi edge in the L emission is not present in the XPS spectra which suggest that this feature in the XES experiment is not a density of states effect but probably a collective effect. The features in the XPS spectrum correspond roughly to features in the recent DOS of Chatterjee and Sinha.¹⁶ Detailed analysis, however, must await the publication of partial density of states which when weighted by the photoemission cross-section and added should yield a direct comparison with the PES VB DOS.

The XPS valence band spectrum of trivalent aluminum ([Ne] $3s^2 3p^1$) is shown in Fig. 3. Al has a sharp Fermi edge, which is limited by our experimental resolution of 0.55 eV, and a free-electron-like profile. Theoretical calculations¹⁷⁻¹⁹ predict three features in the DOS at about 1.0, 3.0, and 5.0 eV. Our spectra show features in fair agreement at about 1.0, 3.3, and 4.3 eV. There is some uncertainty in these features because this spectrum was obtained before the non-random noise in the data system was eliminated (see Chapter III). Our spectrum is also similar to that of Baer and Busch.²⁰ Neddermeyer has obtained K β and L $_{2,3}$ emission band spectra of Al²¹ which indicate that the p-states are centered near the top of the valence band and the s-states are centered lower in the band. Thus as in the case of Mg, detailed comparison with theoretical calculation must wait for partial s- and p-densities of states to be calculated.

C. X-Ray Photoemission Study of the Electronic Structure of the 3d Transition Metals Sc to Zn^{*}

1. Introduction

The 3d transition elements comprise an interesting group of metals, exhibiting a wide variety of structural and electromagnetic properties. A key factor in the understanding of these metals is the peculiar nature of their electronic band structures. The valence bands may be considered to arise from two nearly degenerate atomic

* Based on work done in collaboration with L. Ley, F. R. McFeely, and D. A. Shirley.

levels, the 3d and 4s. These levels, however, have very different spatial distributions, with the 4s electrons extending considerably beyond the average radius of the 3d shell. Thus the valence bands are of two distinct types, a wide band of predominantly 4s character resembling the valence bands of simple metals, and a set of narrow, more correlated d-like bands. The s-like electrons are believed to be the primary source of bonding in the metals,²² while the narrow atomic-like d bands give rise to such phenomena as ferromagnetism.²³

Because many theories of the magnetic properties of the transition metals take d-bandwidth, total bandwidth and density of states at the Fermi level as essential one-electron properties responsible for the magnetic behavior, it is clear that a detailed and quantitative knowledge of the valence-band density of states $N(E)$ is essential. Electronic specific heat data, conductivity measurements, and the de Haas-van Alphen effect, to mention only a few, sample the electronic properties only within $\sim kT$ of the Fermi energy; thus information on the more tightly bound states is necessarily indirect. Spectroscopic methods such as soft X-ray emission spectroscopy (SXS),²⁴⁻²⁸ ultraviolet and X-ray photoemission (UPS, XPS)²⁹⁻³⁸ and optical reflectivity measurements are free of these limitations and have contributed valuable information about the overall features of $N(E)$ for most of the materials under consideration here.

As discussed earlier (see Chapter II), a straightforward interpretation of SXS and low-energy ($h\nu \lesssim 40$ eV) UPS data in terms of only the initial density of states is not possible in most cases.

In SXS, the initial-state core vacancy may distort the valence-band density of states severely. Examples of such distortions are well documented in the emission spectra of the alkali metals.³⁹ Low-energy UV photoemission spectra are commonly interpreted in one of two ways; the direct transition model,⁴⁰ in which $\vec{k}$ -conservation is an important selection rule and the non-direct-transition model.⁴¹ In either case the measured spectrum will contain features reflecting both the initial electron state and the final electron state subject to the restriction of energy conservation. Starting with a reliable band-structure calculation, an interpretation of the UPS spectrum in terms of initial- and final-state properties is possible, and it can yield very detailed results.⁴² The method is, however, very involved, and it has so far been applied in a rigorous way to only a few cases.

With increasing excitation energy $h\nu$, the $\vec{k}$ selection rule is readily fulfilled without introducing additional structure. This is expected from the high and uniform density of available states over the whole range of $\vec{k}$ -space at energies large compared to the energy variations of the lattice potential. Experimental evidence for this fact is well documented,⁴³ and an interpretation of high energy ($h\nu \gtrsim 100$ eV) spectra in terms of initial state density has been highly successful.⁴⁴ It is our objective in this section to present a systematic XPS study of the density of states of the first row transition metals from Sc to Zn. Some of these elements (Fe, Co, Ni, Cu) have been studied earlier by XPS,³⁶⁻³⁸ but the improvements in resolution and vacuum conditions obtained in the present study yield new results even for these cases.

The XPS spectra $I(E)$ of the valence electron region of the transition metals scandium through zinc are shown in Figs. 4-6. These spectra have had smooth background contributions from inelastically scattered electrons subtracted under the assumption that each point in $I(E)$ contributes to the inelastic tail in proportion to its initial intensity. The solid curves are meant only to guide the eye and indicate the real structure in $I(E)$.

Structural features (i.e., characteristic peaks, shoulders and edges) of the XPS valence band spectra $I(E)$ of each element are denoted by letters in Figs. 4-6 and the energies (referred to the Fermi level E_F) are given in Table II. Sharp decreases of intensity at E_F in Sc, V, Co, and Ni define E_F to ± 0.05 eV. This standard allows us to fix the position of the Fermi level in the remaining spectra. At the other end of the valence bands -- the "bottom" or high binding energy limit -- it is more difficult to establish exactly where the bands end, although XPS spectra tend to be more readily interpretable in this respect than either SXS or UPS data. Most of our spectra show some tailing at the "bottom" of the valence bands. This tailing may be a real physical effect or it may result from imperfect correction for scattering. In any case some interpretation is necessary to assign the positions of the bottoms of the valence bands. In zinc, the low energy limit of the 3d bands, and presumably of the valence bands, is defined by the sharp decrease in the d-band peak intensity. The bottom of the valence bands is well defined for Sc, Fe, and Ni by the negative curvature of $I(E)$ in this

region. The spectra of Ti through Mn exhibit a slight kink as $I(E)$ joins the essentially flat background. In Co and Cu, the determination of the bottom of the valence band is more difficult because in this region $I(E)$ connects smoothly with the background.

2. Comparison with other experimental results

As mentioned earlier (section 1), the interpretation of low energy UPS, SXS, and XPS spectra in strictly comparable terms is not possible. That being true, a direct comparison of the original experimental spectra should be equally limited. This is clearly indicated when we compare, as an example, the valence band spectra of Cr obtained by the three different methods (Fig. 7). The soft X-ray spectrum (SXS) is taken from Fischer;²⁵ it represents the Cr (2p-hole) $\rightarrow$ Cr (VB-hole) transition. The UPS spectrum is from Ref. 34 and the XPS spectrum is from this work. We see immediately that the three spectra hardly resemble each other except for having a region of high electron intensity around -2.0 eV with similar widths, of 4.9 eV (XPS), 4.6 eV (UPS), and 4.5 eV (SXS) measured as the full width at half maximum (FWHM). The energies of the fine structure vary considerably from spectrum to spectrum in Fig. 7.

The reasons for these discrepancies have been mentioned before. They are methodical rather than experimental in nature. The recently measured SXS spectrum of Ti²⁸ similarly shows disagreement with the XPS data, whereas UPS and XPS spectra exhibit quite detailed agreement in this case.

The conclusion to be drawn is that a direct comparison of low-energy UV and our XPS spectra is, in principle, meaningless. The degree of actual correspondence can, however, be interpreted as a measure of the structure introduced into the UV spectrum by the final states, together with differences in cross-section modulation between XPS and UPS.

Agreement of the present results with earlier XPS data³⁶⁻³⁸ on Fe, Co, Ni, and Cu is very good. Individual cases are discussed below.

3. Comparison with theory

Let us compare these spectra with band-structure calculations and theoretical densities of states $N(E)$. In doing so, we shall make the important assumption that the "density of ionization potentials," our measured $I(E)$, does indeed resemble the density of energy eigenvalues $N(E)$ as obtained from band-structure calculations. The implications of this assumption have been discussed elsewhere^{36,44} and will not be repeated here. The real justification of this procedure until now has been derived from its success, notably in the almost one-to-one correspondence of $N(E)$ and $I(E)$ for semiconductors (see Chapter V). We shall follow this example here. At the same time, we note that any attempt to interpret $I(E)$ in terms of $N(E)$ may be regarded as a test for the applicability of the procedure.

The transition metal valence bands are derived from 3d and 4s atomic orbitals. The X-ray photoionization probabilities for these orbitals differ,⁴⁵ and the difference is conserved in the solid phase to the extent that Bloch states resemble the atomic wavefunctions near

the nucleus, the region that determines the transition probability for $h\nu \sim 1500$ eV.^{46,47} An estimate for the cross section ratio $\sigma(4s)/\sigma(3d)$ can be deduced from the areas under the sharp 3d peak (10 electrons) at $E_B \sim 10$ eV and the extensive 4s-derived valence region (2 electrons) at E_B between 10 eV and E_F in Zn (Fig. 6).

We obtain:

$$\frac{\sigma(4s)}{\sigma(3d)} = \frac{I("4s\text{-band"})}{I("3d\text{-peak"})} \cdot \frac{10}{2} = 1.5.$$

This ratio will presumably increase somewhat in lighter elements, making the relative accentuation of s-derived bands in $I(E)$ more pronounced. We will now compare the XPS spectra with theoretical results for each of the 3d metals.

a. Scandium and titanium

Scandium and titanium start the 3d transition metal series with atomic configurations $3d^1 4s^2$ and $3d^2 4s^2$ respectively. They both crystallize in a hexagonal lattice with a c/a ratio of 1.59.

This structural identity introduces an element of rigidity into the band structure, which is borne out quite clearly in the high energy part of $I(E)$, if we line up the peaks labeled B in $I(E)$ for scandium and titanium (compare Fig. 4). Between peak B and the Fermi level E_F , $I(E)$ rises in both elements to form a second peak. In scandium, E_F intersects $I(E)$ before the peak is reached and the finite resolution moves the break in intensity to a point 0.4 eV below E_F . The titanium valence bands have to accommodate one more electron, and E_F is accordingly shifted up 0.5 eV. Thus the second peak A in the density of states is occupied beyond its maximum and

E_F intersects a region of comparatively lower density with the break in $I(E)$ again shifted down 0.4 eV due to finite resolution.

Toward lower energy, $I(E)$ tails off in a superficially similar way for both metals. The bottom of the valence bands is, in each case, well marked by a distinctive kink E which occurs at $(E_F - 7.8)$ eV for Sc and at $(E_F - 8.1)$ eV for Ti. These points also coincide to within experimental error, if peak B is lined up in the two spectra.

A closer inspection reveals some important differences in detail. Between peak B and edge D, the scandium spectrum tails off in an s-like shape with an inflection point C around -3.8 eV. Beyond D, $I(E)$ falls off to zero in a form resembling that of a free electron band. In titanium, we can just distinguish a discontinuity in slope marked C in Fig. 4.

The density of states $N(E)$ for scandium and titanium has been calculated by Altmann and Bradley^{48,49} using the cellular method. We compare their results with our spectra in Fig. 8. The energies of characteristic features are set out in Table III.

The agreement in the overall shape of $N(E)$ and $I(E)$ is excellent for both metals. Notice especially the two peaks A and B and the change in position of E_F relative to peak A from scandium to titanium. The repeated changes in the curvature of $I(E)$ between B and E in scandium as opposed to the essentially smooth decrease of $I(E)$ in the same region in titanium agrees also quite well with the Altmann and Bradley calculation. The lack of resolution

in their $N(E)$ histograms, however, makes the identification of feature C in the titanium spectrum difficult.

This quite satisfactory overall picture is marred by considerable discrepancies in the energies of characteristic features between $N(E)$ and $I(E)$, the exception being the total bandwidth of titanium (compare Table III). The different directions in which the upper and lower parts of $N(E)$ deviate from their experimental counterparts reflect the different origins of these regions in terms of atomic orbitals. These differences make it somewhat arbitrary to match features C and D in $I(E)$ for scandium with similar ones in $N(E)$.

Mattheiss⁵⁰ has calculated the band structure of titanium along the Γ -K symmetry direction using the augmented plane wave method (APW). His total bandwidth of 6.3 eV falls considerably short of the 8.0 eV measured in this experiment. Hygh and Welch have also done several APW calculations on Ti. Their bandwidths also fall short of experiment but their density of states does show a two-peak structure.⁵¹

The APW bands calculated for Sc by Fleming and Loucks are likewise considerably narrower than observed.⁵² S. G. Das, et al.,⁵³ have recently performed an RAPW calculation on Sc. Their density of states compares qualitatively with our XPS results but again are much too narrow.

b. Vanadium and chromium

Vanadium and chromium with 5 and 6 valence electrons, respectively, crystallize in the relatively open body-centered cubic (bcc) structure.

Chromium is an antiferromagnet at room temperature with a spin arrangement in the form of a spin-density wave. The wavelength of this spin-density wave is slightly less than twice the periodicity of the chemical lattice. Disregarding this difference, Asano and Yamashita⁵⁴ have treated the band structure of an idealized antiferromagnetic chromium by invoking the concept of a magnetic superlattice with twice the ordinary lattice constant. This reduces the Brillouin Zone (BZ) of the bcc lattice and introduces gaps of the order of 0.4 eV at points where bands cross the new zone boundaries. Though the occurrence of these gaps at the Fermi energy is essential for the stabilization of the antiferromagnetic order⁵⁵ in Cr, we do not expect them to alter the overall density of states strongly because they occur at different energies for different bands. This explains the great similarity in the densities of states derived by Connolly⁵⁶ from the band-structure calculation of paramagnetic and antiferromagnetic Cr by Asano and Yamashita.⁵⁴ It is therefore reasonable to compare our measurements with calculations on the paramagnetic state of bcc chromium. Densities of states $N(E)$ have been calculated by several authors. The best qualitative and quantitative agreement between theory and experiment is found in the APW calculations by Gupta and Sinha,⁵⁷ as shown in Fig. 9. The two peaks at 2.0 and 3.9 eV in $N(E)$ agree excellently in position and intensity with the corresponding peaks C and D in $I(E)$. The edge at 4.9 eV in $N(E)$ marks the position of the symmetry points H_{12} and N_1 and therefore the bottom of the d bands.

The peak closest to E_F in $N(E)$ has two sharp spikes. The lower one at 2.4 eV arises from the flat bands connecting P_1 and N_2 along the P-N edge of the bcc Brillouin zone. The higher spike is not readily attributable to any particular regions in the BZ. The shoulder B is well reproduced in $N(E)$ by a comparable shoulder at 0.8 eV. The edge of this shoulder toward E_F marks the position of E_{25} . The region of very low electron density between this point in $I(E)$ and the Fermi energy can be readily distinguished from the background and E_F itself is marked by a well-defined edge in $I(E)$. The excellent agreement of $I(E)$ and $N(E)$ in this region provides dramatic confirmation of the essential correctness of the band structure calculation in predicting low values of $N(E)$ near E_F . Neither the UPS nor the SXS spectra showed this feature.

A tail due mainly to a 4s-derived band extends down to 8.5 eV in $N(E)$. This agrees reasonably well with the value 9.4 ± 0.5 eV determined for the total valence bandwidth of chromium from our spectrum. The d-band densities of states calculated by Asdente and Friedel⁵⁸ using a tight-binding scheme agrees in general shape with our spectrum, as does the APW calculation of Snow and Kaber.⁵⁹ Energies of symmetry points from four recent calculations^{57,60,61} are compared with values deduced from our spectrum in Table IV. It is clear from this Table that only the APW calculation of Gupta and Sinha⁵⁷ yields energies that agree with the XPS spectrum of chromium. This is surprising because the calculation was not self-consistent and it used an exchange parameter $\alpha = 1$. The tight-

binding calculations^{60,61} give bands that are generally too narrow. Furthermore, they both give $N(E)$ profiles that are definitely incompatible with our spectrum for the peak marked C in Fig. 9. For example, in both the $N(E)$ calculated⁵⁶ from the band structure of Asano and Yamashita and in the $N(E)$ given by Rath and Callaway,⁶¹ the splitting of peak A is 1.1 eV and the two parts are well separated by a valley, a feature that would show up in the UPS spectrum. We must therefore conclude that the earlier interpretation⁵⁴ of structure on the UV photoemission ODS in terms of this density of states is not valid.

The valence-band spectrum of vanadium is very similar to that of chromium. Allowing for a shift in the Fermi level E_F due to the reduction by one in the number of valence electrons, we find a one-to-one correspondence in the characteristic features of the two spectra. In vanadium, E_F has moved down toward the higher peak by about 1 eV and the shoulder (B in Fig. 9) presumably lies above E_F . The separation between the two main peaks is slightly reduced from 1.8 eV in Cr to 1.6 eV in V. In addition, both peaks appear narrower. This reduction in d-band dispersion is presumably due to the slightly increased atomic spacing of vanadium as compared to chromium. In Fig. 9, we compare the Cr density of states of Gupta and Sinha,⁵⁷ shifted toward E_F , with our vanadium spectrum. Peak A marks the maximum near symmetry points P_4 and N_2 . The energies of H_{12} and N_1 at the bottom of the d bands are well defined in the vanadium spectrum at (3.5 ± 0.3) eV below E_F .

The detailed picture that we have obtained for the density of states of Cr and V will aid us later in interpretation of the Fe spectrum.

c. Manganese

Manganese crystallizes in a distorted cubic lattice with 29 atoms per primitive cell. No band structure has therefore as yet been calculated. The VB-spectrum (see Fig. 5) shows a broad hump with a total width of 8.6 ± 0.3 eV. A peak A at ($E_F - 1.1$) eV and a shoulder B at ($E_F - 2.4$) eV can be distinguished in $I(E)$. Judging from the steep slope at E_F , the density at E_F is probably close to its maximum value.

d. Copper and zinc

Copper and zinc have closed 3d shells with atomic configurations $3d^{10}4s^1$ and $3d^{10}4s^2$ respectively. Copper crystallizes in a face centered cubic lattice and zinc in a hexagonal lattice.

The band structure of copper has been thoroughly studied, both theoretically and experimentally. Our spectrum agrees very well with earlier XPS work,³⁶⁻³⁸ especially the high resolution spectrum of Hüfner, et al.³⁸ A comparison of our spectrum with a density of states obtained by Fong and Cohen⁶² in a pseudopotential calculation allows the experimental determination of key energies (compare Fig. 10). The Fermi level intersects a region of low density derived from the remnants of the free-electron-like sp band. The steep rise at 2.0 eV in $I(E)$ marks the top (X_5) of the completely filled d-bands. Two distinct peaks in $N(E)$ around 2.2 eV and 3.4 eV are well reproduced

in $I(E)$ by a peak centered at 2.7 eV and a shoulder at 3.6 eV. The latter peak is derived from flat bands along $\Gamma \rightarrow L \rightarrow W$ and its maximum marks the position of Γ'_{25} .

A broader hump at 4.8 eV in $N(E)$ derives its density from bands along the hexagonal edge $W-K$ in the Brillouin zone of Cu. It finds its counterpart in a just visible shoulder at the same energy in $I(E)$. The bottom of the d-bands is marked by the edge E in $I(E)$ at $(E_F - 5.3 \pm 0.2)$ eV in excellent agreement with the 5.3 eV calculated by Fong and Cohen. Beyond the edge E, $I(E)$ joins smoothly with the background of inelastically scattered electrons and it is not possible to assign an energy to Γ_1 , the bottom of the valence bands from our spectrum. Krolikowski and Spicer⁴¹ obtained a value for Γ_1 of 8.0 eV from their UPS data on Cu and Dobbyn, et al.²⁶ deduced a slightly higher value of 9.0 eV from the $M_{2,3}$ soft x-ray emission spectrum. We shall therefore adopt an average value of 8.5 ± 0.5 eV for the position of Γ_1 below E_F .

Table V compares the energies of certain symmetry points as obtained by the preceding analysis with some pertinent calculations, using X_5 as a fiducial point. The table is arranged to facilitate a comparison of the salient features in the band structure: the width of the d-bands ($X_5 - X_1$) and their position relative to the bottom of the sp band ($X_5 - \Gamma_1$). The latter is characterized by the energy separation $X'_4 - \Gamma_1$ and the position of the Fermi level E_F relative to the bottom of the sp band $\Gamma_1 + X'_4 - \Gamma_1$ has been inferred from $X_5 - \Gamma_1$ (from our spectrum) and the energy of the optical transition

$X_5 \rightarrow X_4^-$ at 4.50 eV.⁶³ The close agreement between the experimental and calculated values for the energies of the sp band (columns 2 and 3 in Table V) is not surprising in view of the essentially free-electron-like character of the sp band that makes its shape insensitive to the potentials chosen in the calculation.

The parameters that characterize the width and position of the d bands varies considerably. The APW calculations by Chodrow⁶⁹ and Burdick⁶⁵ and the KKR calculation by Segall⁶⁶ employ the same potential and give consistent results in excellent agreement with experiment. Mattheiss⁵⁰ APW band structure yields a width ($X_5 - X_1$) for the d-bands in good agreement with our value; the relative position is, however, high by about 1.4 eV.

The calculation by Segall⁶⁶ employing a ℓ -dependent potential improved the position of E_F and the d-bands relative to Γ_1 slightly, but yielded d bands about 0.8 eV too wide. The next two entries in Table V are examples of self-consistent calculations. A comparison of the results by Wakoh⁶⁷ (KKR) and Snow and Weber^{59,68} (APW) employing the same full Slater exchange approximation illustrates the differences that can be encountered even in a self-consistent calculation. Whereas Wakoh's results agree excellently with our values, the $X_5 - X_1$ separation obtained by Snow is ~ 0.7 eV too small and the position of X_5 is 1.5 eV too low. In the light of these results it is not too surprising that eigenvalues obtained from different starting potentials in non-self-consistent calculations show very substantial variations, as the next three entries in Table V prove.

It is interesting to note that the calculations, which give poor agreement with data relating to the Fermi surface, are the ones that disagree with our XPS results; namely the calculations by Snow⁶⁸ using full Slater exchange and the calculation by Ballinger and Marshall⁶⁹ employing a potential derived from Hermann-Skillman wavefunctions for atomic copper. This lends some additional support to our treating an eigenvalue spectrum as representative of a spectrum of ionization potentials. The last entry in Table V is an example for an empirical pseudopotential band structure calculation using earlier UPS,⁴⁰ XPS,³⁶ and optical data⁶³ on Cu as input information for the proper choice of parameters. The agreement with experiment is excellent as expected.

Let us now turn to the valence bands of zinc. The Zn spectrum is shown on the right side of Fig. 6. We find an intense 3d peak (A in Fig. 6) centered at 10.18 ± 0.10 eV below E_F . The width of this peak is 1.45 ± 0.02 eV (full width at half maximum, FWHM). Emission from the 4s 4p bands is relatively less intense and extends from the well defined Fermi edge all the way down to the d-peak. The interference from the intense d-peak makes an accurate location of the bottom of the sp band impossible.

Recent UPS and SXS studies on Zn give values of 10.01(3) (UPS Ref. 70) and 10.36(15) (SXS Ref. 71) for the position of the 3d emission relative to E_F that are in good agreement with our value. The higher resolution UPS results determine the spin-orbit splitting of the 3d peak in Zn to be 0.54 eV. Taking this splitting and a

spectrometer resolution of 0.6 eV into account we deduced a component line width of not more than 0.8 eV from our spectrum. This sets an upper limit for the amount of energy dispersion in the d-bands of Zn, which is presumably even smaller since lifetime broadening of the 3d hole-states can well account for much of this width.

The picture that we have gained for the valence bands of Zn seems to favor the first-principles calculation of Juras, et al.⁷² employing the Green's function method over the results of Mattheiss,⁵⁰ APW calculation.

Juras, et al.⁷² obtain an essentially free-electron-like sp band with a total occupied width of 10.6 eV and d-bands centered at ($E_F - 8.5$) eV. The total width of the d-bands is about 1.6 eV. Mattheiss' calculation arrived at a seemingly unrealistic position of the d-bands about 7 eV below the bottom of the sp band.

Ley, et al.⁷³ have discussed in detail the relationship between eigenvalue spectrum (band structure calculation) and the spectrum of ionization potentials as measured in photoelectron spectroscopy considering the relaxation screening of the hole-state by the passive electrons. On the basis of a simple model for the relaxation process, they arrive at the conclusion that the relaxation energy of the d-electrons in Zn is ~ 5 eV bigger than that for the sp electrons. That would mean that the d-states lie about 5 eV below the bottom of the sp bands in the initial state which should be compared with the pertinent calculations. Thus the claim of Juras, et al. that photoemission (and X-ray emission) experiments supported their

results on the position of the d-bands may be wrong because relaxation effects must be accounted for.⁷³ The difference in relaxation energy between sp and d-electrons is a consequence of the difference in the atomic origin of these electrons, which in Zn is rather undisturbed by hybridization.

This view is supported by the observation of Gelatt and Ehrenreich,⁷⁴ that the onset of optical transitions from the d bands in Au and Ag lies about a quarter of an eV higher than the corresponding energy separation between the top of the d bands and E_F in XPS data. The same holds for copper if we compare XPS data with the optical data of Ref. 63.

Screening is presumably more important in the ionization process (XPS) than in the optical excitation. The difference in screening energy in the former is, however, greatly reduced in the noble metals as compared to Zn due to the considerable hybridization between d and sp bands. We take that as an indication that differential relaxation energies need not be considered for the interpretation of the remainder of the 3d transition metals.

e. Iron, cobalt, and nickel

Iron, cobalt, and nickel are ferromagnetic at room temperature. The ferromagnetism of these metals is regarded as itinerant in the sense that the d electrons, which are mainly responsible for the magnetic polarization, also participate in conduction.

The band model of ferromagnetism due to Stoner, Wohlfarth, and Slater (SWS)^{75,76} features spin-polarized bands $\epsilon_n(\vec{k})$ which are split by energies $\Delta E_n(\vec{k})$ due to the exchange interaction. ΔE is a

function of wave vector $\vec{k}$ and band index n but it has usually been treated as a constant for d-derived bands and is set equal to zero for sp-derived bands. Estimates⁷⁷ for the average exchange splitting of the d bands ΔE are about 0.4 eV in Ni, 1.1 eV in Co, and 1.7 eV in Fe.

More recently, band structure calculations of ferromagnetic Fe⁷⁸ and Ni⁷⁹ have derived the exchange splitting $E_n(k)$ self-consistently using an average Hartree-Fock field that is different for the two electron spin directions. These calculations reproduce the observed saturation moments quite satisfactorily.

Schemes different from the SWS-model have been proposed⁸⁰ which emphasize intra-atomic exchange and correlation effects in the formation of spin-ordered structures. However, to our knowledge no explicit calculations have been made which would bear directly on the electronic structure of ferromagnetic transition metals.

Two of the implications of the SWS model have been tested extensively:

(1) The spin polarization of electrons at the Fermi energy E_F is well established^{81,82} and can be explained in sign and magnitude in the framework of the SWS model.⁸³

(2) A number of spectroscopic techniques have been employed to study the changes in the band structure which are supposed to accompany the transition from the ferromagnetic to the paramagnetic state as ΔE goes to zero at the Curie temperature T_C .^{84-87,26,27,29} The effects observed are, however, very small and do not readily lend themselves to a straightforward interpretation in terms of the SWS model.

In this inconclusive situation let us rephrase the question put forward by previous investigators, from: "Does the band structure of a metal change according to the SWS-model if we cross the Curie temperature T_C ?" to, "Does the SWS-model give an appropriate description of the density of states $N(E)$ of a ferromagnetic transition metal like iron below T_C ?"

To do so, let us first consider the $N(E)$ curve for chromium (Fig. 9) which we have found to be in excellent agreement with our XPS spectrum. Since iron and chromium crystallize in the same bcc structure and have only slightly different lattice constants, we may regard this curve as a fair representation of $N(E)$ for iron in the unmagnetized state. The Fermi energy E_F for this state would fall right at the top of the high density peak, as shown in Fig. 11a. The chemical potentials for spin up (λ_+) and spin down (λ_-) can easily be determined by allowing for the appropriate magnetic moment in ferromagnetic iron and assuming a rigid-band exchange splitting ΔE . In the final step, λ_+ and λ_- coincide to form the new Fermi level in the SWS description of the ferromagnetic state. It is clear from Fig. 11 that this new density of states differs drastically from the nonpolarized $N(E)$. Instead of a peak at E_F , we now have a region of very low electron density at E_F and a peak about 1.8 eV below E_F .

These two features are common to all $N(E)$ calculations for Fe employing the SWS model and we find just these features in our XPS spectrum of iron, shown in Fig. 12 together with $N(E)$ derived by Connolly⁵⁶ from the energy bands of Wakoh and Yamashita.⁸⁸

The low intensity of $I(E)$ at E_F and the position of peak A at ($E_F - 1.2$) eV are not artifacts introduced by insufficient resolution. This becomes immediately clear from a comparison of the Fe spectrum with those of cobalt and nickel in Figs. 13 and 14, respectively.

The flat shoulder B in the spectrum of Fig. 12 finds its analog in a wide peak around ($E_F - 2.7$) eV in Connolly's density of states. No such peak occurs in the density of states by Tawil and Callaway.⁷⁸ The bottom of the d bands is marked in both calculations by an edge in $N(E)$ between 4.5 and 5.0 eV. Structure C in $I(E)$ which presumably corresponds to this point lies at least 0.5 eV lower. The bottom of the valence bands is well marked at 9.8 eV by the intercept of the parabolic sp band with the baseline. The calculated values for the same point E_1 again fall short of this value by about 2.0 eV.

A very detailed treatment of the exchange problem in the band structure of ferromagnetic iron has been given by Duff and Das.⁸⁹ As a result they obtained significantly greater exchange splittings throughout the Brillouin zone as compared to other calculations. This increased the overall bandwidth to 13 eV and the d-bandwidth [point C in $I(E)$] to 9.9 eV, which both exceed the experimental values considerably. It is, however, clear from their calculation how assumptions about screening and the localizing effect of correlation influence the exchange and therefore the bandwidths. The input data provided by our spectra can give valuable information about the real magnitude of these many-body effects for the ferromagnetic state.

The valence-band spectra of cobalt and nickel are shown on Figs. 13 and 14. Cobalt shows two narrow peaks separated by 1.2 eV right at the Fermi level. The width of the d-bands is marked by the edge D at $(E_F - 5.5)$ eV. The bottom of the valence bands is poorly defined because the tail joins smoothly into the background. We estimate a value of 9.5 ± 1.0 eV for the total bandwidth.

Densities of states $N(E)$ of paramagnetic cobalt in its hcp structure have been calculated by Wong, Wohlfarth, and Hum,⁹⁰ and by Wakoh and Yamashita.⁹¹ The former is based on a transformation of the Green's function method (KKR) into the form of an interpolation scheme. The latter calculation uses the KKR method self-consistently. The two densities of states are rather similar with two prominent peaks separated by ~ 1.3 eV at the top of $N(E)$ and a shoulder extending toward the bottom of the d-bands, some 4 to 5 eV below the top. The paramagnetic Fermi level intersects the top peak about halfway up the low energy edge.

The rigid exchange splitting ΔE was obtained in both calculations by allowing for the proper difference in spin-up and spin-down electrons. Values for ΔE are 1.35 eV (Ref. 90) and 1.71 eV (Ref. 91) respectively. These values of ΔE would move the upper peak about 0.7 eV below E_F in the ferromagnetic state, a value slightly larger than the 0.5 eV observed in our spectrum. Wohlfarth⁹² discussed ΔE in the light of several experimental data and arrived at a "best" value for ΔE (cobalt) of 1.1 ± 0.3 eV.

Shifting the $N(E)$ curve of Ref. 91 rigidly by 1.1 eV gives excellent agreement with our data for structures A, C, D, and E, lending further support to SWS model for the ferromagnetic transition metals. The position of peak B is, however, off by ~ 0.6 eV. This is not too surprising, since the forced reduction in ΔE necessarily gives a wrong magnetic moment in the original $N(E)$. It appears that a reduction of the peak separation in the paramagnetic density of states together with a more realistic treatment of the exchange splitting would remedy both shortcomings.

The valence band spectrum of nickel is 8.9 ± 0.3 eV wide with a region of high density between E_F and $(E_F - 4.0)$ eV, followed by a rather flat pedestal that turns toward the baseline at $(E_F - 7.0)$ eV. The region of high density exhibits a peak A at 0.5 eV, an unresolved second peak B at 1.4 eV and on the trailing edge a shoulder at about 2.3 eV. Peak A is crucial in the interpretation of $I(E)$ in terms of the numerous band structure calculations on ferromagnetic nickel.⁹³⁻⁹⁹ All these calculations exhibit a peak in $N(E)$ next to E_F , which arises from flat majority spin bands at the top of the d bands between symmetry points X and L in the BZ. The position of this peak relative to E_F depends on the exchange splitting at the top of the d bands, so that the lower limit in ΔE of ~ 0.4 eV gives a position 0.3 eV below E_F and an upper limit in ΔE close to about 0.8 eV would move this peak to the position of peak A in $I(E)$, 0.6 eV below E_F . This is quite in contrast to the position at $(E_F - 0.3)$ eV accepted from UV photoemission data. We remind the reader, however, of the

difficulties encountered in the interpretation of the UPS data in terms of density of states (compare the variations in the positions of characteristic features observed at different excitation energies).¹⁰⁰ As a consequence we have strong indications that ΔE for nickel is between 0.7 and 0.8 eV for a region close to E_F .

In Fig. 14, we compare $I(E)$ with the density of states obtained by J. Callaway and H. M. Zhang⁹⁶ even though their ΔE is 0.4 eV. The general features of this calculation agree, however, quite well with our spectrum: Peaks A and B and the bottom of the d bands (point D) are in almost quantitative agreement. From this figure, it seems reasonable to identify the pedestal around $E_F - 6.5$ eV in $I(E)$ with emission from the sp bands at about the same energy in $N(E)$.

Intensity considerations, however, make it likely that this feature can at least in part be attributed to a multielectron excitation associated with the photoemission from the 3d bands. Such a satellite is observed in the XPS spectrum of NiO¹⁰¹ at a comparable energy below the d bands. We also find satellites associated with the 2p core levels in metallic nickel that are similar to those observed in NiO.¹⁰¹

Let us now return to the question put at the beginning of this section: "Is the SWS model appropriate to describe $N(E)$ for ferromagnetic transition metals?" The answer is clearly yes from all we have seen in the interpretation of our XPS data. But why do the above mentioned experiments fail to detect the collapse of the exchange splitting above the Curie temperature? To qualify this question we

have to consider two things: what has been measured and what does "above T_C " mean. Above T_C means in all these cases not more than $1.07 T_C$. And the quantity measured was closely related to the density of states, which is well known to be already quite well developed for clusters of only 10 to 20 atoms.

The negative results of these experiments then mean that at $1.07 T_C$ there is still a nonvanishing spin density over a region covering a cluster of atoms. This is quite compatible with the loss of any long-range spin order and with the nature of the magnetic transition as a second-order transition.

4. Summary

Briefly, we can make the following general points based on this study of the transition metals.

- 1) The d-bands evolve systematically from highly free-electron-like behavior in Sc and Ti to bona-fide core levels in Zn. This behavior is also paralleled in the systematics of the bulk plasmon behavior in the core levels. (See for example the transition metal 2p spectra in Appendix A-9.)
- 2) A rigid-band model of extrapolation of the theoretical densities of states between isostructural adjacent metals works well, i.e. (Sc and Ti or V and Cr).

- 3) The spectrum of iron can be accounted for by shifting rigidly shifting theoretical non-magnetic $N(E)$'s to align the chemical potential of the spin-up and spin-down sub-bands in strong support of the spin-polarized band model. High resolution studies of Fe and Ni above and below T_c would be helpful in further testing the spin-polarized band model.

D. XPS Investigation of the Electronic Structure of
the 4f and Valence Bands of the Rare Earth
Metals Lanthanum through Lutetium*

1. Introduction

The rare earth metals constitute a very interesting group of elements. These metals are strikingly different than the 3d transition metals in that for the most part their properties are very similar to each other throughout the series and they have the same configuration of outer electrons $[5d6s6p]^3$ (except for Eu and Yb which are $[5d6s6p]^2$). It is the more tightly bound, core-like 4f electrons, systematically changing across the series, which dominate the interesting magnetic and electronic properties of these elements but play a very little role in their chemical bonding. In this section, we present results from a high-resolution XPS study of the 4f and valence levels of the entire series La through Lu (except Pm). These experiments were carried out under UHV conditions on freshly evaporated metal films. Great care was taken to insure

* Based on work done in conjunction with F. R. McFeely and D. A. Shirley and published in Phys. Letters 45A, 227 (1973).

that clean samples were prepared. In situ chemical analysis confirmed that the samples had at most a small fraction of a monolayer contamination and in fact for most of these samples, no oxygen or carbon could be detected.

There have been several previous UPS (with $h\nu = 21.2$ eV) studies of the outermost electrons of several of these metals.¹⁰²⁻¹⁰⁹ The striking feature of the UPS studies was the very low amplitude observed from the 4f states.¹⁰⁴⁻¹⁰⁸ This can be easily understood on the basis of the different partial cross-sections as discussed in Chapter II. The cross-section depends primarily on the overlap matrix element $\langle \psi_{4f} | \chi \rangle$ where ψ_{4f} is the wave function of the 4f electron and χ is a plane wave of the outgoing photoelectron. The radial maximum of the 4f electrons varies from 0.37 Å for Ce to 0.25 Å for Lu.¹¹⁰ The de Broglie wavelength of the photoelectron excited by HeI from E_F is 2.9 Å and by AlK α , it is 0.33 Å, thus the overlap matrix element or photoionization cross-section should be much higher for the 4f levels at XPS energies compared to the cross-section at UPS energies. Thus the 4f electrons are quite readily observed in XPS studies, while being "transparent" in the UPS studies. Hagstrom and co-workers¹¹¹ have previously performed careful XPS measurements on most of these metals, hampered by conditions of low resolution and rather poor vacuum, nonetheless, the salient features of the 4f levels emerged from those studies. Gas phase XPS spectra of Eu have been obtained by Fadley and Shirley.^{112,113} Several recent XPS experiments have been carried out under UHV conditions^{114,115} and have confirmed and added more detail to the earlier observations.

The spectra of the 4f and valence region for the metals Lanthanum through Lutetium are shown in Figs. 15 to 23. The energies of the various spectral features are tabulated in Table VI. Each of these spectra can for the most part be divided into two distinct regions. Near the Fermi level there is a fairly featureless peak due to 3 valence electrons in the 5d6s6p bands. This feature is somewhat similar to that of scandium metal which has 3 electrons in itinerant 3d4s bands. For a review of band-structure calculations of the rare earth metals see Refs. 116 and 117. Table VII lists some results from various band structure calculations. More deeply bound than the valence electrons are the 4f electrons which are very intense and exhibit very complicated structure. These sharp features are due to the various possible final-state multiplets. Yb and Lu which have completely filled 4f shells exhibit only the expected spin-orbit splitting. The possible terms and their relative probabilities can be estimated by evaluating the coefficients of fractional parentage which has been done for the rare earths.^{118,119} The 4f final-state multiplet structure is similar to that of the rare earths in compounds^{118,120-122} demonstrating that the 4f electrons are part of the "ionic core" of these elements. Herbst, et al.¹²³ undertook a systematic investigation of the rare earth metals using the Renormalized-Atom scheme.¹²⁴ They estimated the position of the 4f levels in a one-electron approximation and in a multielectron approximation (screening and relaxation included). The multielectron results agree well with our experimental results.¹²⁵ The multielectron calculations

yield energies about 7 eV lower than the one-electron calculation. This is roughly the amount that the semi-localized exciton model would predict (~ 5 eV).¹²⁶ The relative positions of the 4f multiplets agree well with optical levels¹²⁷ which have been assigned to ~ 5 eV. The XPS multiplets are slightly more widely spaced than the optical levels which is not unexpected as the ionic charge in the $\text{Ce}^{4+}(4f^n)$ XPS final state is one greater than in the $(\text{Ce}-1)^{3+}(4f^n)$ optical ion used in the comparisons. Below we briefly summarize the results.

2. La and Ce Metals

La has the configuration $[\text{Xe}](5d6s6p)^3$. The spectra in the valence region consists of just a peak with its maximum at about 0.9 eV due to the itinerant valence electrons. γ -Ce, the room temperature phase of Ce metal is thought to be "trivalent" and have the configuration $[\text{Xe}](4f)^1(5d6s6p)^3$. The valence band-4f region of γ -Ce is shown in Fig. 15. The spectrum shows that the 4f and the valence electrons overlap considerably. Interpolating the valence band-4f spectrum (normalized to the $5p_{3/2}$) between La, Pr and Nd (Fig. 16), we suggest that the feature at 1.3(1) eV in Ce may be connected with one 4f electron in Ce, and the feature at 0.7 eV is due to the $(5d6s6p)^3$ free-electron-like band. This conclusion is based on the following observations:

- 1) The Ce bandwidth (FWHM), 2.35(15) eV, is considerably wider than the La bandwidth, 1.53(10) eV;
- 2) the increased spectral intensity in Ce compared to La in the 0-3.5 eV region is significantly more than expected from adding one more electron to the dsp band;

- 3) The added spectral intensity in Ce is consistent with one 4f electron if we extrapolate from Nd(4f²) and Pr(4f¹).

Unfortunately, Ce was the most difficult specimen for us to produce and maintain atomically clean samples. (La was also somewhat difficult.) The overlapping of the 4f electrons with the itinerant valence electrons probably is the reason for the very interesting behavior of Ce metal as a function of temperature and pressure and in compounds and alloys. It is well known that γ -Ce undergoes a phase transformation at low temperature and high pressure to the α -Ce phase which is thought to be tetravalent, i.e. (4f)⁰(5d6s6p)⁴ configuration.¹²⁸⁻¹³³ In compounds and alloys, Ce may be trivalent or tetravalent or have interconfiguration fluctuations.¹³⁰ Recently the conventional picture of the electronic configuration of La and γ -Ce have been strongly questioned.¹³⁴⁻¹³⁷ Recent M_{IV} and M_V X-ray emission spectra of La has been interpreted as indicating highly localized occupied 4f states near E_F.¹³⁸ For γ -Ce, it has been proposed that there is considerable f-sd hybridization which increases in the α -phase resulting in increasing the 4f bandwidth and the 4f-states becoming more delocalized. For La, our core spectra lack multiplet structure (Chapter IV, section F) which strongly suggest that there is very little or no localized 4f character in the occupied valence bands. γ -Ce XPS core spectra exhibit multiplet splitting and Ce levels in CeAl₂ exhibit similar spectra which strongly indicate that the γ -Ce configuration is very close to being (4f)¹(5d6s6p)³. As of now, α -Ce has not been studied by means of XPS but that should be a very interesting experiment which

could elucidate the changes in electronic structure in the γ - α phase transition. It would be particularly useful to do these experiments at high and low photon energies to emphasize the 4f states and the valence band states respectively.

3. The light rare earths: Pr, Nd, Sm, and Gd

These elements exhibit spectra (Figs. 16-18) expected of them being trivalent. These spectra are similar to the results of Baer and Busch.¹¹⁴

4. The heavy rare earths: Tb, Dy, Ho, Er, and Tm

The spectra of the 4f and valence region of the heavy rare earths are shown in Figs. 19-21. These show 4f multiplets expected from a trivalent ionic core. The valence region appears to exhibit more structure than the light rare earths.

5. The divalent rare earths: Eu and Yb

These elements are divalent (as opposed to the trivalency of the other rare earths) due to the stability of half filled and completely filled shells. Metallic Eu has the configuration $[\text{Xe}] (4f)^7 (5d6s6p)^2$ and Yb achieves a completely filled 4f shell $[\text{Xe}] (4f)^{14} (5d6s6p)^2$. The 4f levels, as seen from Fig. 22, are very near E_F . The closeness of these levels to E_F is responsible for the known susceptibility of compounds of these elements to undergo inter-configuration fluctuations.¹³⁷

6. Lu metal

This metal completes the rare earth series and has the configuration $[\text{Xe}] (4f)^{14} (5d6s6p)^3$. As in Yb, the 4f spectrum exhibits simply

two spin-orbit split levels (Fig. 23). There is some structure apparent in the valence bands.

F. XPS Investigations of Intermetallic Alloys: β -NiAl, REAl_2 ,
(RE = La, Ce, Sm, Gd and Dy), YbZn_2 and CePd_3

1. Introduction

Theoretical approaches to the understanding of the electronic structure of metals has been fairly successful in accounting for many properties of metals. The electronic structure of alloys however is much less understood. In the past several years there has been much work in developing theoretical approaches for alloys.¹⁴⁰⁻¹⁵⁴ The DOS of alloys is a useful quantity for testing various theoretical descriptions of the electronic structure of alloys. As shown above, PES can fairly directly probe the DOS and has been used extensively in studying all kinds of metals (free-electron-like, transition, and rare earth metals) and compounds, but relatively little work on alloys has been carried out.¹⁵⁵⁻¹⁶⁷ Other techniques such as optical studies and X-ray emission have been used to study alloy electronic structure and have been reviewed.^{168,169}

As discussed in Chapter III, sample preparation is extremely important for PES studies of solids because of the high surface sensitivity of PES. Many methods have been developed for preparing metal specimens (these were reviewed in Chapter III). However, most of these methods are not very suitable for preparation of alloy specimens. Thus clean surfaces of the alloys, studied below, were prepared by using the in situ mechanical cleaning device described in Chapter III.

The bulk alloy samples were prepared by melting stoichiometric amounts of the component metals in an argon arc furnace. Each specimen was remelted at least four times to insure homogeneity. The specimens were then checked for weight loss and the weight loss was less than 0.4% for all the specimens used in the measurements reported below. The samples were also checked by X-ray diffraction to insure that only the right phase was present. The specimens were then machined so that they could be press fitted into a sample platen. The sample platen was loaded on the sample rod and the sample introduction system was then pumped down and baked out (see Chapter III). Once the pressure reached about 5×10^{-10} torr, the specimen surface was mechanically cleaned and then immediately the measurements were undertaken, first with an in situ analysis for possible contamination. First we will describe the results from β -NiAl and then several results from rare earth intermetallics.

2. β -NiAl

β -NiAl crystallizes in the simple-cubic CsCl structure and is one of the simplest types of alloys. It was chosen as one of the first alloy systems to study because 1) being an ordered alloy, it is amenable to the usual band-structure techniques and in fact several band-structure calculations for β -NiAl^{170,171} exist with which we can compare our results; 2) there exists much complimentary data;¹⁷²⁻¹⁷⁷ 3) the fundamental question of the occupancy of the d-bands upon alloying in β -NiAl is open and subject to controversy. This question is vital to the understanding of the electronic structure of this

alloy and XPS results might possibly shed some light on this question.

β -NiAl is a member of the class of alloys which form the β -phases at approximately 50-50 atomic percent. These alloys have the B2 (CsCl) crystal structure and are ordered at room temperature. For the Ni-Al system this phase exists between 40 and 50 atomic percent of Al.

Fig. 24 shows the XPS valence band spectra for β -NiAl. It is compared with the calculated density of states by Connolly and Johnson¹⁷⁰ using the (non-relativistic) Augmented-Plane-Wave (APW) method in conjunction with a LCAO interpolation scheme. The agreement is remarkably good as can be seen from Fig. 24 and Table VIII. The more recent calculation of Moruzzi, et al.¹⁷¹ using the Korringa-Kohn-Rostoker (KKR) method yield similar results. Comparison of the VBDOS of β -NiAl with the VBDOS of pure Ni and Al metals shown earlier in this chapter (Figs. 3 and 5) show that the alloy spectrum is not just a simple superposition of the spectra of the pure metals. The Al VBDOS is very free-electron-like and has a very low photoionization cross-section at the photon energy ($h\nu = 1486.6$) used in these studies. The Ni d-bands are fairly intense at XPS energies and would be only slightly distorted if superimposed on the Al VBDOS.

Moruzzi, et al.¹⁷¹ investigated band narrowing and charge transfer resulting from alloying in six intermetallics with the CsCl structure including NiAl by means of self-consistent band-structure calculations. Band narrowing may result from either 1) a lack of d-density of final states on neighboring atoms onto which electron

tunneling can occur, or 2) mutual d-band repulsion. The second mode of band narrowing is clearly not operative in the β -NiAl case for obvious reasons. Unfortunately, we cannot directly compare the band narrowing calculated by Morruzzi, et al.¹⁷¹ since they used diatomic Ni as a fiducial point. We note a slight narrowing of the Ni d-band as compared to the d-bands in Ni metal. It is somewhat hazardous to derive a d-bandwidth from the XPS VB DOS of Ni metal because of the problem of determining what is the d-band and complications due to multielectron effects which are known to be very important in Ni. We obtain a d-band narrowing N , $0.02 \leq N \leq 0.16$ where N is defined as $(W_m - W_a)/[(W_m + W_a)/2]$, and W_m and W_a are the d-bandwidths of the metal and that component in the alloy respectively. Morruzzi, et al. predict $N = 0.33$.¹⁷¹ We note that if we use the β -Brass results of Wertheim et al.,¹⁷⁸ where the question of d-band width is not complicated by many-electron effects, we get $N = 0.11$ for the Zn 3d bands and for the Cu 3d bands, $N = 0.13$. These compare to $N = 0.82$ and 0.66 respectively predicted by Morruzzi, et al.¹⁷¹ If we use the β -Brass results to scale down the $N = 0.33$ predicted for Ni in NiAl, we get $N = 0.05$, which is in the range observed. Band narrowing has also been observed in other systems.¹⁶¹

By carrying out their calculations to self-consistency, Morruzzi, et al.¹⁷¹ were able to discuss charge transfer on the basis of computed charge densities. Unfortunately their results for β -NiAl are not considered reliable because of size effects. Charge transfer is an important question in alloys¹⁷⁹ and related to the controversy on the

d-band occupancy in β -NiAl. At first it might be thought that this question could be simply answered by determining "chemical shifts" of core levels in β -NiAl compared to the pure metals. As seen from Table IX, no clear conclusions can be drawn. This is not surprising since binding energy shifts are composed of two components -- initial-state charge transfer and final-state relaxation, these can be the same order of magnitude and in opposite directions, which results in the often observed rather small chemical shifts in solids. Furthermore, the results from the Ni levels are ambiguous because of change in multiplet splitting, and many-electron effects may also cause a shift in the spectral distribution.

It has been shown earlier¹⁸⁰ that for a completely filled shell where d-wave screening is no longer possible, there is a large reduction in extra-atomic relaxation compared to the previous element and that Auger transitions are a useful probe of this effect because the two hole final state makes for a larger effect (see Chapter II). A large shift from the metal which might be expected for a filled d-shell in the $L_3M_{45}M_{45}$ transition (Fig. 25) was not observed. Also, the structure in the spectra are superficially the same in the alloy and in the metal. These observations suggest that the d-bands are not completely filled in the alloy.

The effect of the d-band being completely filled should manifest itself on the multiplet structure of the Ni core levels. The Al and Ni core-level spectra are shown in Figs. 26-28. The core-levels are all more symmetric and narrower in the alloy than in the pure metals.

This narrowing may be due to less core-level asymmetry (see Chapter II, section C-4). However, the Ni levels are narrowed very appreciably (see Table X) and such a large narrowing being based solely on a change in the MND singularity¹⁸¹ does not seem plausible. An alternative explanation would be that the amount of unpaired spin in the Ni d-bands is decreased due to the filling of the d-bands and the amount of multiplet splitting is significantly decreased. Further evidence in support of this hypothesis is the change in the splitting of the two major components in the Ni 3p levels. In the alloy, this splitting is 1.88(05) eV as opposed to 1.25(10) eV in the pure metal. The value for Ni in NiAl is a reasonable value for spin-orbit splitting if we extrapolate from the metals with filled d-bands (i.e., metals with no multiplet splitting) Cu and Zn, which have splittings of 2.2 and 2.6 eV respectively. Further support for the filling of the d-bands may be inferred from the Ni 2p levels. In paramagnetic compounds, these levels show intense satellites, which have as much as 50% the intensity of the primary peak, while diamagnetic compounds do not exhibit these satellites.¹⁸²⁻¹⁸⁴ Ni metal 2p levels have such a satellite with about 10% the intensity of the primary peak. In Cu metal which has a filled d-band, the 2p levels are free of these satellites. In β -NiAl, the 2p levels show little or no evidence of these satellites.

One final experimental observation should be considered; that is, a comparison in the alloy of the intensity at the Fermi level relative to a core level with that in the pure metals. In pure Al metal, the intensity of the Al 2p core level relative to the intensity at the Fermi level (from spectrum in which both were observed) is

~ 100 . In Ni metal, the ratio of the Ni 3p core level to the intensity at the Fermi level is ~ 3 in the metal. These intensity ratios partly reflect difference in the photoionization cross-section and thus give information about the Ni 3d and Al 3s3p character at E_F . In the NiAl alloy, the intensity of Al 2p to intensity at E_F was ~ 5 , while the intensity of Ni 3p to the intensity at E_F was also ~ 5 . While these ratios are only meant to be taken roughly, they indicate that there is mostly d-character at E_F with possibly a little s-character which supports conclusions based on Knight shift and electronic specific heat measurement.^{185,186}

In conclusion, we have obtained the density of occupied valence states in β -NiAl. These measurements in conjunction with the measurements of Hagemann, *et al.*,¹⁷⁵ which gave information on the unoccupied density of states, give strong confirmation to the calculation of Connolly and Johnson¹⁷⁰ and Morruzzi, *et al.*¹⁷¹ This adds confidence to Connolly and Johnson's interpretation of the optical data.¹⁷⁰ These results support the concept of the d-band filling up on alloying with Al, but it is not definitely clear that the d-bands are completely filled. Further work which would elucidate this point would include 1) XPS study of β -NiAl throughout its concentration range, 2) XPS studies of FeAl and CoAl systems which have 2 and 1 less d electrons respectively, and 3) PES studies of β -NiAl, Ni, and Al with a variable photon source to use the variation of the partial photoionization cross-section as a function of a photon energy to obtain information about the changes in the band composition upon alloying.

3. Rare earth dialuminides: LaAl_2 , CeAl_2 , SmAl_2 , GdAl_2 , and DyAl_2

XPS results from a study of the valence and 4f region in some rare earth dialuminides are shown in Figs. 29-55. Table XI lists the energies of the characteristic features in the spectra. The rare earth dialuminides all have the cubic Laves phase structure(i.e., MgCu_2 -type structure). Some of their properties are discussed in Refs. 187 through 190. The spectra, especially SmAl_2 , GdAl_2 , and DyAl_2 are reminiscent of the spectra of the rare earth metals themselves (see this chapter, section D). For SmAl_2 , GdAl_2 , and DyAl_2 , we observe the characteristic multiplet structure in the 4f's, which is nearly identical in both structure and energies to the multiplets of the pure metals. Thus the rare earths remain trivalent in these intermetallics. The valence bands are also somewhat similar to the metals. The valence bands appear to be itinerant dsp-like bands such as in the case of Sc or Y. These bands also appear to have a free-electron-like tail due to Al states, but this is hard to tell for certain because of the nearness of the intense 4f bands. The intensity ratio of the valence band maximum to the nearby rare earth core $5p_{3/2}$ peak are nearly the same as this ratio is in the pure metals.

In CeAl_2 as in Ce metal, the 4f and valence bands overlap in energy making a reliable separation impossible (this separation could be achieved in principle by performing this measurement at a much lower photon energy, $h\nu \lesssim 100$ eV and utilizing the difference in cross-section between the 4f level and valence levels.) Using the core-level spectra as a valency fingerprint, we can conclude that Ce is

trivalent in CeAl_2 as the 4d spectrum exhibits structure expected from $4d^9 4f^1$ exchange interaction (see Chapter IV, section F).

The only available calculated density of states for the rare earth dialuminides is the (non-relativistic) APW calculation of Switendick for LaAl_2 .¹⁹¹ Unfortunately, LaAl_2 was very difficult to obtain as a clean sample, even with our in situ mechanical cleaning procedure and to keep clean. The only detectable contamination was oxygen and when it reached about one monolayer, a fresh surface was prepared. For all the other dialuminides, only small fractions of a monolayer of oxygen were detectable and no carbon could be detected. Our results for LaAl_2 indicate a valence band similar to La metal with a width of about 3 eV and maximum at ~ 1 eV but with a fairly pronounced free-electron-like tail which extends to about 9eV. Switendick's band structure yields a bandwidth of about 8.8 eV. One cannot compare the APW total density of states directly with experiment because of cross-section modulation.¹⁹² The aluminium 3s3p states will have a much lower cross-section than the lanthanum 5d6s6p states at AlK α energies. Switendick¹⁹¹ included partial density of states from his calculations which makes comparison with our measurements easier. The APW calculation puts the Al s-like states from about 3.5 to 9 eV above E_F . This probably accounts for the free-electron-like tail we observe in this region. The calculation predicts several features in this region¹⁹¹ and we do see some features in this region. However, we must be cautious here because these features are very sensitive to oxygen coverage (these features tended to be suppressed with increasing oxygen coverage). Due to

the low cross-section of the spectral region and the high sensitivity to oxygen adsorption, good statistics in this region were not obtained. However, several short runs indicate that this structure was intrinsic. The APW calculation places the La d-like states from E_F to about 3-4 eV above E_F in good agreement with our results. Al p-like states were found extending from E_F to ~ 3 eV with high density at E_F . The intensity in this region in the XPS spectrum is probably due mostly to the La d-states because of their higher cross-section. Switendick's calculation suggests that there is a considerable amount of La f character near E_F . Our results do not support the hypothesis of a large amount of occupied La 4f character. This conclusion is drawn on the basis of the La core-level spectra (see Chapter IV, section G) in which there is complete absence of any multiplet splitting, which would be expected from electrons in 4f levels unless they were completely itinerant. It was demonstrated in earlier work by Shirley,¹ that for the 5d6s6p bands of Au, inclusion of relativistic effects were essential. While relativistic effects, which were left out in Switendick's calculation, are not as important as in gold, they may nonetheless be a necessary ingredient for calculation of the La states in LaAl_2 .

4. YbZn_2 and CePd_3

XPS spectra of the valence band and 4f regions of YbZn_2 and CePd_3 are shown in Fig. 34 and 35 respectively. The electronic structure of these intermetallics was discussed in Chapter IV, so we will just briefly describe their valence band spectra here. The YbZn_2 spectrum is very simple. There is just the spin-orbit split 4f bands near

E_F , indicative of Yb being divalent in YbZn_2 at room temperature. The Zn 3d band, which is very core-like, is also seen. In the CePd_3 spectrum (Fig. 35), the valence region is dominated by the Pd d-band and the Ce 4f and valence bands are completely overlapped by the more intense Pd d bands. Thus, Ce core-level spectra must be employed to indirectly obtain information about the valency of Ce in this alloy (see Chapter IV, section G).

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Table 1. Valence Bandwidth (eV) of Na, Mg, and Al from XPS, XES, AES and theory.

	XPS	XES	AES	Theory
Na	3.1 ± 0.1 ^a	2.6 ± 0.3 ^f	--	3.3 ± 0.1 ^p
	2.5 ± 0.1 ^b	2.7 ± 0.2 ^g	4.0 ± 0.2 ^{ff}	3.3 ^q
		3.05 ± 0.15 ^{h,j}	4.0 ± 0.2 ^{gg}	3.2 ^{cc}
	3.0 ± 0.2 ^c			
	3.0 ± 0.2 ^{ee}			
Mg	6.5 ± 0.1 ^a	7.1 ± 0.1 ⁱ	7.5 ^{hh}	6.3 ^r
	$10.$ ^d	6.50 ± 0.2 ^g	8.5 ⁱⁱ	9.3 ^s
		6.4 ^j	7.5 ^{jj}	7.1 ^t
		6.86 ± 0.03 ^k	8.2 ^{kk}	9.4 ^u
		6.81 ± 0.03 ^l		7.1 ^y
		7.0 ⁿ		6.94 ^{bb}
Al	11.5 ± 0.4 ^a	11.67 ± 0.14 ^m	~ 11 ^{ll}	
	12.0 ^e	10.6 ^j		11.0 ^w
		11.30 ± 0.1 ⁿ		11.6 ^x
		11.5 ± 0.2 ^o		11.4 ^z
				11.7 ^{aa}
				17.3 ^{aa}
				11.5 ⁿ
				11.0 ^{dd}

Table I. (continued)

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- ^a This work.
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Table II. Energies of characteristic features in the valence band spectra of the transition metals. Errors are given parenthetically. Entries are in eV.

Element	A	B	C	D	E
Sc	0.4(1)	1.2(1)	3.8(3)	5.3(2)	7.8(2)
Ti	0.8(1)	1.7(2)	4.2(2)	-	8.1(2)
V	0.7(1)	2.5(1)	5.1(3)	-	9.0(2)
Cr	0.6(1)	1.3(1)	2.3(1)	4.1(1)	9.4(3)
Mn	1.1(1)	2.4(2)	-	-	8.6(3)
Fe	1.2(1)	2.9(1)	5.5(5)	-	9.8(2)
Co	0.5(1)	1.7(1)	3.8(3)	5.5(1)	9.5(1.0)
Ni	0.5(1)	1.4(1) (B ¹ = 2.0)	3.5(2)	4.6(3)	8.9(3)
Cu	2.0(1)	2.7(1)	3.6(2)	4.6(2)	5.3(2)
Zn	10.2(1)	-	-	-	-

Table III. A comparison of structural features in the valence band spectrum of scandium and titanium with the corresponding densities of states calculated by Altmann and Bradley.^{48,49} The entries are in eV below the Fermi energy E_F . Errors are given parenthetically.

	Sc		Ti	
	Expt.	Theory	Expt.	Theory
E_F	0	0	0	0
peak A	0.41(1)	0.0	0.8(1)	1.0
peak B	1.2(1)	1.7	1.7(2)	3.4
inflection point C	3.8(3)	2.4	4.2(2)	-
inflection point D	5.3(3)	3.6 ^a	-	-
bottom of VB E	7.8(2)	6.0	8.1(2)	8.0

^a The identification of features C and D in $N(E)$ is ambiguous (see text).

Table IV. Energies of symmetry points in the valence bands of chromium (eV below E_F).

Symmetry Point	Tight-binding plus OPW ^a		Tight-binding, SCF ^b $\mu = 2/3$	APW, $\alpha = 1$ ^c	Expt., this work
	$\alpha = 1$	$\alpha = 0.725$			
r_{25}'	1.0	1.0	1.0	0.7	0.8(1)
P_4	1.6	2.0	2.2	2.5	2.9(2)
N_2	2.3	2.4	2.7	2.4	
H_{12}	3.0	3.3	4.0	4.8	4.6(3)
N_1	3.3	3.9	4.3	4.9	
Γ_1	5.1	6.9	5.9	8.7	9.4(3)

^a Ref. 60. Here α is the exchange parameter

^b Ref. 61.

^c Ref. 57.

Table V. Characteristic energy differences in the valence bands of copper. Values are given in eV, and errors are given parenthetically.

	$X'_4 - \Gamma_1$	$E_F - \Gamma_1$	$X_5 - \Gamma_1$	$X_5 - X_1$	$X_5 - \Gamma'_{25}$
Experiment	11.0(5) ^{a)}	8.5(5) ^{b)}	6.5(5)	3.3(3)	1.6(2)
Theory					
APW, Chodrow Ref. 64	11.2	--	7.0	3.2	1.7
APW, Purdick Ref. 65	10.9	8.8	7.0	3.4	1.5
KKR, Segall Ref. 66	11.1	9.0	7.0	3.5	1.6
KKR, Segall Ref. 66 l-dependent potential	11.0	8.9	6.4	4.1	1.9
Mattheiss, Ref. 50	12.4	--	7.9	3.5	1.5
Wakoh, Ref. 67 self-consistent	--	8.8	6.8	3.3	1.5
Snow, Ref. 68 self-consistent	10.8	8.3	5.0	2.6	1.2
Ballinger and Marshall Ref. 69 (Hermann- Skillman)	8.7	8.0	4.2	2.4	1.2
Ballinger and Marshall Ref. 69, 2/5 Gaspar	11.0	9.0	6.5	3.7	1.9
O'Sullivan <u>et al.</u> Ref. c	11.5	8.9	7.0	3.2	1.4
Fong and Cohen Ref. 62	10.8	8.5	6.7	3.3	1.8

^{a)} Deduced using the value of 4.5 eV obtained for $X'_4 - X_5$ from optical data (Ref. 63) and the value for $(X_5 - \Gamma_1) = 6.5$ eV.

^{b)} Average value from Ref. 41 and Ref. 46.

^{c)} W. J. O'Sullivan, A. C. Switendick, and J. E. Schirber, Phys. Rev. B 1, 1443 (1970).

Table VI. Summary of energies (eV) of characteristic features in the 4f and valence band spectra of the rare earth metals.

	Valence bandwidth	Valence band maximum	4f levels
La	--	0.9	--
Ce	3.0	0.7	1.3
Pr	3.8	0.8	5.4
Nd	3	0.6	4.8
(Pm)	--	--	--
Sm	3.1	1.1	5.1(⁵ F), 6.9(⁵ F), 7.6(⁵ G), 9.4(⁵ D)
Eu	a	a	1.9
Gd	3.2		8.2(⁷ F)
Tb	--	--	2.3, 6.9, 8.7, 9.7
Dy	3	--	4.1(⁷ F), 6.8(⁵ G), 7.8(⁵ L), 9.1(⁵ H, ⁵ I, ⁵ K), 10.3, 12.5
Ho	3.6	0.7	5.2, 5.5, 5.9, 8.4, 9.1, 10.1
Er	3.5	0.6	4.9, 5.7, 7.0, 8.1, 8.8, 9.4
Tm	4	.6, 1.8	4.5, 5.8, 7.3, 8.3, 10.2
Yb	a	a	2.39(4f _{5/2}), 1.14(4f _{7/2})
Lu	~ 4	.6	7.27(4f _{5/2}), 8.72(4f _{7/2})

^a The 4f level is close to the Fermi level and completely conceals the (5d6sp)² valence bands.

Table VII. Calculated bandwidths (eV) of the rare earth metals.

(Scandium and yttrium are given for comparison.

La	3.54 ^a , 3.26 ^b , 3.1 ^m
α - Ce	2.9 ^c , 3.94 ^c
γ - Ce	2.3 ^c , 2.45 ^c , 2.2 ^m
(Pu)	4.1 ^b
Nd	--
Pr	--
Sm	--
Eu	2.7 ^d
Gd	2.99 ^e , 3.40 ^f , 4.67 ^g
Tb	4.90 ^h
Dy	5.10 ^g , 5.45 ^g , 5.44 ⁱ
Ho	--
Er	5.43 ^g , 5.82 ^g
Tm	4.22 ^j
Yb	4.62 ^k
Lu	5.85 ^l , 5.92 ^g
Sc	4.62 ⁿ , 5.98 ^o , 4.49 ^o , 4.49 ^p , 2.72 ^q
Y	4.49 ^r , 4.76 ^o , 3.26 ^o

Table VII. (continued)

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- ^a G. S. Fleming, S. H. Liu and T. L. Loucks, Phys. Rev. Letters 21, 1524 (1968).
- ^b H. W. Myron and S. H. Liu, Phys. Rev. B 1, 2414 (1970).
- ^c G. Mukhopadhyay, J. Phys. F 2, 450 (1972).
- ^d A. J. Freeman and J. O. Dimmock, Bull. Am. Phys. Soc. II, 11, 216 (1966) and unpublished.
- ^e B. N. Harmon and A. J. Freeman, Phys. Rev. B 10, 1979 (1974).
- ^f A. J. Freeman, J. O. Dimmock, and R. E. Watson, in Quantum Theory of Atoms, Molecules, and the Solid State, ed. P. O. Lowden, (Academic Press, New York, 1966), p. 361.
- ^g S. C. Keeton and T. L. Loucks, Phys. Rev. 168, 672 (1968).
- ^h C. Jackson, Phys. Rev. 178, 949 (1969).
- ⁱ W. E. Evenson and S. H. Liu, Phys. Rev. 178, 783 (1969).
- ^j R. E. Watson, A. J. Freeman, and J. O. Dimmock, Phys. Rev. 167, 497 (1968).
- ^k G. Johansen and A. R. Mackintosh, Solid State Commun. 8, 121 (1970).
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- ^m H. H. Hill and E. A. Knetko, J. Phys. F 5, 1119 (1975).
- ⁿ G. S. Fleming and T. L. Loucks, Phys. Rev. 173, 685 (1968).
- ^o S. L. Altman and C. J. Bradley, Proc. Phys. Soc. 92, 764 (1967).
- ^p S. G. Das, A. J. Freeman, D. D. Koelling, and F. Mueller, AIP Conf. Proc. 10, 1304 (1973).
- ^q From Ref. p. The value for the d-bandwidth.
- ^r T. L. Loucks, Phys. Rev. 144, 504 (1966).

Table VIII. Comparison of features in the VBDOS of NiAl obtained by several techniques. (Energies in eV)

	A	B	C	D	E ^h
XPS ^a (β -NiAl)	0.63(08)	1.84(08)	3.17(12)	4.54(12)	9.4(2)
APW ^b (β -NiAl)	0.7	1.9	3.0	4.8	$\sim 11^b$,
UPS ^c (β -NiAl)	0.8	2.1			$\sim 10^g$
SXS-AlK β ^d (β -NiAl)	0.7		3.3	5.5	11.7
SXS-NiL _{III} ^d (β -NiAl)		1.8		4.8	
XPS-Al ^e (metal)	--	--	--	--	~ 10
XPS-Ni ^f (metal)	--	--	--	--	~ 8.9

^a This work.

^b Ref. 170.

^c Ref. 172.

^d Ref. 173.

^e From Chapter VI, section B.

^f From Chapter VI, section C.

^g Ref. 171.

^h Total bandwidth.

Table IX. Core-level binding energies (eV) for Ni metal, Al metal, and β -NiAl.

	Ni Metal	NiAl		Al Metal
	<u>Ni</u>	<u>Ni</u>	<u>Al</u>	<u>Al</u>
2s	1010.03(20)	--	117.72(10)	117.99(10)
2p _{1/2}	871.47(10)	870.51(10)	72.80(05)	72.84(05)
2p _{3/2}	854.22(10)	853.31(10)		
3s	110.97(10)	111.12(10)	--	--
3p _{1/2}	67.87(05)	68.89(05)	--	--
3p _{3/2}	66.54(05)	67.09(05)	--	--

Table X. Comparison of FWHM of core-levels in NiAl, Ni and Al.

	metal	NiAl ^b		metal
	Ni ^a	Ni	Al	Al ^c
2s	--	--	1.17(5)	1.24(5)
2p _{1/2}	1.9	1.6	.86	.95
2p _{3/2}	1.6	1.3		
3s	3.2	2.5	--	--
3p	3.6	3.2	--	--

^a Unpublished data.

^b This work.

^c Unpublished data.

Table XI. Summary of energies (eV) of characteristic features in the 4f and VBDO spectra of several rare earth dialuminides.

REAl ₂	VB Width	VB Maximum	4f Levels
LaAl ₂	3.6(4), 10(1) [*]	0.8(2)	--
CeAl ₂	4.0(5), 9(1) [*]	1.0(4)	2.0(4)
SmAl ₂	3.0(4)	.9	5.2, 6.9, 7.6, 9.1
GdAl ₂	3.2(4)	.6, 1.6	8.0
DyAl ₂	2(1)	--	4.0, 6.7, 7.8, 8.6 9.2, 10.5, 12.5

* Bandwidth due to Al 3s3p states.

FIGURE CAPTIONS

- Fig. 1. Sodium valence band. The data have been treated by adding four channels and then performing a sliding linear fit to three adjacent points. Insert shows a wider unsmoothed scan, with plasmons.
- Fig. 2. Magnesium valence band and first plasmon.
- Fig. 3. Aluminum valence band.
- Fig. 4. X-ray photoemission spectrum $I(E)$ of the valence band region of Sc, Ti, V, and Cr. The background contribution due to inelastically scattered electrons has been subtracted. The features denoted by letters are discussed in the text and the energies are given in Table II.
- Fig. 5. X-ray photoemission spectrum $I(E)$ of the valence band region of Mn, Fe, Co, and Ni. The background contribution due to inelastically scattered electrons has been subtracted. The features denoted by letters are discussed in the text and the energies are given in Table II.
- Fig. 6. X-ray photoemission spectrum $I(E)$ of the valence band region of Cu and Zn. The background due to inelastically scattered electrons has been subtracted. The features denoted by letters are discussed in the text and the energies are given in Table II.
- Fig. 7. A comparison of the valence band spectra of Cr obtained by ultraviolet photoemission (UPS, Ref. 34), soft X-ray spectroscopy (SXS, Ref. 25) and X-ray photoemission (XPS, this work).

Fig. 8. A comparison of the X-ray photoemission valence band spectra $I(E)$ (upper curves) with density of states $N(E)$ (lower curves) calculated by Altmann and Bradley (Ref. 48 and 49) for Sc and Ti. The energies of the characteristic features are given in Table III.

Fig. 9. The X-ray photoemission valence band spectra $I(E)$ of V and Cr are compared with the APW results of Gupta and Sinha (Ref. 57). For V we have used Gupta and Sinha's Cr density of states with the Fermi level shifted corresponding to the reduction by one of the number of valence electron.

Fig. 10. The X-ray photoemission valence band spectrum $I(E)$ of Cu is compared with the density of states $N(E)$ of Fong and Cohen (Ref. 62). A comparison of the energy of features of $I(E)$ with theory is given in Table V.

Fig. 11. a) The bcc chromium density of states of Ref. 57 $\lambda_{\downarrow}$ and $\lambda_{\uparrow}$, the spin up and spin down chemical potentials for bcc Fe are determined from the magnetic moment of Fe under the assumption of a rigid band exchange splitting.
b) The resulting spin-polarized density of states where the chemical potentials $\lambda_{\downarrow}$ and $\lambda_{\uparrow}$ have been made to coincide. This density of states should be representative for that of ferromagnetic iron.

Fig. 12. A comparison of the X-ray photoemission valence band spectrum $I(E)$ of Fe (upper curve) with the $N(E)$ derived by Connolly (Ref. 56) (lower curve).

- Fig. 13. The X-ray photoemission valence band spectrum of Co is compared with the density of states calculated by Wong, et al. (Ref. 90) (middle curve) and by Wakoh and Yamashita (Ref. 91) (histogram).
- Fig. 14. A comparison of the X-ray photoemission valence band spectrum $I(E)$ of Ni (upper curve) with the calculated density of states obtained by Callaway and Zhang (Ref. 96) (lower curve).
- Fig. 15. Valence band and 5s5p spectrum of Lanthanum metal and the valence band-4f and 5s5p spectrum of Cerium metal.
- Fig. 16. Valence band and 4f spectra of Praesodymium and Neodymium metals.
- Fig. 17. Valence band-4f and 5s5p spectrum of Samarium metal.
- Fig. 18. The valence band-4f and 5s5p spectra of Europium and Gadolinium metals.
- Fig. 19. Valence band and 4f spectra of Terbium and Dysprosium metals.
- Fig. 20. Valence band, 4f and 5p spectrum of Holmium.
- Fig. 21. Valence band-4f and 5p spectra of Thulium and Erbium metals.
- Fig. 22. Valence band and 4f spectra of Europium and Ytterbium metals.
- Fig. 23. Valence band and 4f spectra of Ytterbium and Lutetium metals.
- Fig. 24. Valence band density of states for β -NiAl. Points are the experimental XPS results (this work) and the dashed curve is from calculations of Connolly and Johnson (Ref. 170). The solid curve is the theoretical curve broadened to experimental resolution to expedite comparison with experiment.

- Fig. 25. Ni LMM Auger spectrum from β -NiAl.
- Fig. 26. Ni 3s and Al 2s spectrum from β -NiAl.
- Fig. 27. Al 2p and Ni 3p spectrum from β -NiAl.
- Fig. 28. Ni 2p spectrum from β -NiAl.
- Fig. 29. Valence and La 5p region of LaAl_2 .
- Fig. 30. Valence, Ce 4f, and Ce 5p region of CeAl_2 .
- Fig. 31. Valence and 4f spectrum of SmAl_2 .
- Fig. 32. Valence and 4f spectrum of GdAl_2 .
- Fig. 33. Valence and 4f spectrum of DyAl_2 .
- Fig. 34. Valence and 4f spectrum of YbZn_2 . The Zn 3d level is also observed.
- Fig. 35. The valence and Ce 5p region of CePd_3 .

98-134-2629

Fig. 1

Fig. 2

XBL 7311-4433

Fig. 3

XBL7510-3946

Fig. 4

XBL 751-2149

Fig. 5

Fig. 6

XBL 748-4053

Fig. 7

XBL 747-3648

Fig. 8

XBL 747-3647

Fig. 9

XBL 747-3646

Fig. 10

Fig. 11

XBL 751-2147

Fig. 12

XBL 747-3650

Fig. 13

XBL 747-3649

Fig. 14

NBL 763-901

Fig. 15

Fig. 16

Fig. 17

Fig. 18

Fig. 19

NHL 763 897

XBL 763-894

Fig. 20

NBL 763-896

Fig. 21

-591-

Fig. 22

Fig. 23

NBL 763,900

Fig. 24

XBL7510-4150

Fig. 25

XBL7510-4170

Fig. 26

Fig. 27

XBL7510-4156

Fig. 28

Fig. 29

Fig. 30

XBL 763 2450

NBL 762-2264

Fig. 31

Fig. 32

XBL7511-3926

Fig. 33

Fig. 34

XBL7510-8631

XBL 7512- 3929

Fig. 35

VII. TRANSITION METAL COMPOUNDS

Transition metal compounds are of great scientific and technological interest. They possess a wide range of interesting magnetic and electrical properties. XPS valence band densities of states of several transition metal compounds will be discussed in this chapter. Section A deals with the 3d metal difluorides and section B is concerned with several simple oxides.

A. 3d Metal Fluorides: MnF_2 , FeF_2 , CoF_2 , NiF_2 , and ZnF_2

The 3d metal compounds have very localized (spatially) 3d bands near the Fermi level. It is these d electrons which give rise to the interesting and wide range of properties that characterize these compounds.¹⁻⁴ They range from being good metals to being extremely good insulators. Several transition metal compounds undergo metal-insulator transitions. These materials also exhibit many interesting magnetic properties which are also due to the d electrons. Because the electrons in the 3d bands do not have a very large spatial extent beyond their ionic core, they do not get broadened very much by nearest-neighbor overlap. Thus the d bands are very narrow and atomic-like. PES studies of the 3d bands of these materials are of great interest because the usual band theoretic methods which worked so well for other solids (see Chapter V, section E and Chapter VI) fail as a result of the highly localized (correlated) nature of the 3d electrons.^{5,6} However, simple atomic models have not been completely successful in explaining the properties of these materials

either. To study the 3d bands, we carried out XPS measurements of the 3d metal difluorides. As they are the most ionic and simplest compounds, they will serve as a good first step and fiducial point in understanding the 3d bands in more complicated and more covalent compounds. These results will also serve as a stringent test of calculations, in particular, for cluster molecular orbital models (i.e., the central metal atom and its nearest ligands are explicitly considered) which have been suggested as being appropriate for these compounds. If these models are successful for the fluorides, they should be applicable to other 3d metal systems. Refs. 7-20 refer to some previous PES studies of 3d metal compounds.

The XPS measurements, which will be reported below, were carried out on single crystals.²¹ These compounds crystalize in the rutile structure and have D_{4h} symmetry. The specimens were cleaved in situ under UHV conditions²² and analyzed for contamination. No oxygen or carbon was detectable in most cases. An electron flood gun was used in conjunction with the measurements to minimize any line-broadening resulting from inhomogeneous charging (see Chapter III). Figs. 1-8 show the valence region for these compounds and Table I summarize the energies of the characteristic features of the spectra.

MnF_2 is the simplest case. It has a half-filled 3d shell with a $t_{2g}^3 e_g^2$ configuration. The valence region of MnF_2 exhibits two broad peaks. One, extending from 0 to ~ 5 eV, is centered at ~ 3.3 eV from the top of the valence band. The other peak is centered at about 6.6 eV and extends from ~ 5 to ~ 10 eV. With the aid of the alkali fluoride

spectra,²³ we can safely and unambiguously assign the band at 6.6 eV to the F 2p band. This follows from the F2s to F2p separation and intensity ratio being essentially constant in the various alkali fluorides and matching the separation in MnF_2 of the F2s to the 6.6 eV peak and the relative intensity of the F2s to the 6.6 eV peak.²⁴ Fig. 10 shows the MnF_2 spectrum after the F2p contribution has been subtracted from the valence region. This was accomplished by

- 1) normalizing the intensity of F2s spectra in MnF_2 and LiF to each other, 2) aligning the F2s peak in LiF with the F2s peak in MnF_2 , and 3) taking the difference between the two spectra. The result should yield the density of 3d states plus some contribution from multi-electron satellites and differences in the inelastic losses in the two compounds.

Recent UPS results²⁵ at 40.8 eV (Fig. 9) yield essentially identical results as Fig. 2 for the valence region. In the UPS spectrum the band which we have assigned to F2p is more intense than the peak which has been assigned to the d levels. In our XPS spectrum the relative intensities of these two peaks are just reversed. This confirms our interpretation, because the F2p cross-section at 40.8 eV is expected to be favored over the Mn3d cross-section when compared to these cross-sections at 1486.6 eV. Photoionization of a 3d electron in MnF_2 results in either a $^5\text{E}_g$ or a $^5\text{T}_{1g}$ final state with relative intensity of 1 to 1.5. We derive a value of 1.0(1) eV for the $\text{E}_g - \text{T}_{1g}$ splitting with the 1 to 1.5 ratio from our spectrum. A multiple-scattering χ_α (MS χ_α) calculation by Larsson and Connolly²⁶

on a MnF_6^{4-} cluster gives 1.36 eV for the splitting. Recently, Viinikka and Bagus²⁷ have performed calculations on transition metal fluoride clusters using a multiconfigurational Hartree-Fock (MCHF) treatment. This ab initio treatment yields 1.1 eV separation between the $^5\text{E}_g$ and $^5\text{T}_{1g}$ final states of MnF_6^{4-} . In the spectral region to higher binding energy from the Mn 3d and F 2p peaks there is some intensity which is not accounted for by either the p- or d-bands. This intensity is probably due to shake-up, which is well known in core-level spectra of transition-metal compounds.²⁸⁻³³ Shake-up states deriving from ligand-to-metal charge transfer are predicted in this region by the MCHF calculations (see Fig. 10).²⁷ Both calculations^{26,27} predict the p band to be too narrow. The 2p bandwidth is ~ 5.6 eV with a full-width at half-maximum (FWHM) of ~ 3.3 eV. The MCHF calculation gives ~ 3.0 eV for the width, while the MSX α calculation predicts a width of 1.5 eV. The MCHF calculation places the p bands at ~ 4.9 eV below the E_g final state, while the MSX α calculation positions these states at ~ 3.8 eV. The experimental value is ~ 4.4 eV.

The valence spectrum of FeF_2 (Fig. 4) is very similar to MnF_2 except for a new well-resolved feature at the top of the valence band. We can use the procedure that was applied to MnF_2 above to obtain the 3d density of states. This results in the partial density of states spectrum of Fig. 11. Thus the region from 0 to ~ 7 eV is due to the d states and the region from ~ 7 to ~ 11.0 eV are the F2p states. This partitioning into p- and d-regions is further supported by the results of Leckey, et al.²⁵ on the basis of cross-section difference

between their 40.8 eV spectrum and our 1486.6 eV results. The new feature (2.0 eV) is due to final-state multiplets. $Mn^{+2}(3d^5)$ with a half-filled d shell can result only in quintet final states. In Fe^{+2} , the one extra d electron in the d-shell is antiparallel to the other d electrons. Thus, quartet- and sextet- final states are possible. The band centered at 5.1 eV represents the manifold of quartet states, and the peak at 2.0 eV with about 1/5 the intensity (0.23) of the intensity of the quartet states is the 6A_1 final state. A similar conclusion was drawn by Wertheim, et al.,³⁴ from a spectrum in which the 6A_1 state was just barely resolved. This points up the very localized nature of the 3d bands. In the rare earth metals the 4f electrons are well known to be very localized and give identical spectra in their compounds such as the trifluorides.³⁵ We have an analogous case in going from Gd metal with a half-filled (4f) shell to Tb with one electron beyond a half-filled (4f) shell. Photoemission from the Gd 4f states can only yield 7F states, while for Tb photoionization of the 4f electrons produces a manifold of sextet states from the majority spin states plus an 8S state (minority spin state) with $\sim 1/7$ the intensity of the sextet states (see Fig. 12).³⁵ In FeF_2 there are also shake-up states in the higher binding energy region of the valence band. There are no theoretical results available for FeF_2 . The $F2p$ states are about 6 eV below the ${}^6A_{1g}$ state.

The VB DOS of CoF_2 (Fig. 6) is not as simple as MnF_2 or FeF_2 . However, our success of using LiF to decouple the $F2p$ contribution from the 3d states in the simpler cases of MnF_2 and FeF_2 gives us confidence to apply this technique to CoF_2 . The results are shown in

Fig. 13. Also shown in Fig. 13 as lines are the most intense final states predicted by the MCHF calculation of Viinikka and Bagus.²⁷ The agreement is remarkably good. The hatched area represents shake-up and is much more intense than in FeF_2 or MnF_2 . However, Co core levels of CoF_2 exhibit intense shake-up satellites while in MnF_2 and FeF_2 the metal core levels have much weaker satellites.²⁹ The MCHF calculations do predict shake-up in this region as indicated in Fig. 13. Again, the UPS²⁵ results are in good agreement and show the expected cross-section modulation. The p band falls about 4.7 eV below the most intense feature in the d bands. The MCHF calculation predicts this peak to fall at 7.0 eV, far too low.

The XPS VB DOS of NiF_2 , like CoF_2 , is not very simple as there is a large degree of overlapping of the metal 3d bands with F2p bands. Also the NiF_2 spectrum may not be as well resolved as the above-discussed difluorides since it was not a single crystal specimen. We do get good agreement with the XPS spectrum of Wertheim, *et al.*³⁴ Leckey and co-workers²⁵ have also done UPS measurements at $h\nu = 40.8$ eV on NiF_2 . Fig. 14 shows the result of subtracting the F2p contribution out. Again, very reasonable agreement with MCHF calculation for the 3d states is observed. A large amount of shake-up is also observed, in agreement with the large amount of shake-up observed in the Ni core-level spectra in NiF_2 . The p levels are observed to be ~ 5.2 eV below the $^4\text{T}_{1g}$ state, which compares with ~ 6.1 and ~ 3.8 eV predicted by the MCHF and MSX α calculations, respectively. As in the case of MnF_2 , both calculations predict the p-bands to be too narrow. The

MSX α calculation yields a bandwidth of 1.8 eV, while the MCHF calculation is somewhat better with a bandwidth of ~ 3.0 eV. As in the case of MnF_2 , the MSX α calculation tends to suggest about a 1 eV splitting in the p bands which is not observed.

In analyzing the ZnF_2 spectra we found a peculiar peak shape in the $(\text{Zn}3d)\text{--}(\text{F}2p)$ region which cannot be interpreted in terms of two simple peaks: we attribute this peak shape to crystal-field splitting in the final state. In the case at hand (ZnF_2) the evidence for crystal-field splitting is especially compelling, both because the satellite structure on the main 3d peak falls at lower binding energies (thereby precluding alternate interpretations in terms of energy losses or shakeup structure) and because independent cross-section and energy arguments can be invoked. The spectrum is shown in Fig. 8. We list below the arguments for interpreting the $(\text{Zn}3d)\text{--}(\text{F}2p)$ structure in terms of crystal-field splitting (Interpretation A) instead of just a single $\text{Zn}3d$ peak plus a $\text{F}2p$ peak (Interpretation B).

- (i) The spectrum cannot be fitted with only two peaks: the low- E_B pedestal is too broad.
- (ii) The area under the pedestal (a_p) is too large to be attributable to the $\text{F}2p$ shell alone. The area ratio of the $\text{F}(2s)$ peak (not shown) to a_p is 1.3, while the ratio obtained from the alkali fluorides that we have recently studied are $\text{F}(2s)/\text{F}(2p) \sim 4.8$ (LiF and KF).
- (iii) The $\text{F}(2s)\text{--}\text{F}(2p)$ spacing in the above compounds is 20.93(14) eV, while the pedestal in Fig. 15 extends to ~ 23 eV from the 2s peak.

(iv) If only the main peak in Fig.15 were taken as containing all the 3d strength (Interpretation B), the Zn(2p)/Zn(3d) ratio would be 3.3, whereas this ratio is only 2.5 in Zn metal.

(v) Finally, the Zn(2p_{3/2})-Zn(3d) spacing would be anomalously low, by 1 eV, if the 3d strength all lay in the main peak.

While these arguments appear to establish the existence of final-state crystal-field splitting unambiguously, the exact nature of the final-state levels is elusive. The D_{4h} symmetry of ZnF₂ should split the single-hole 3d⁹ final states beyond the t_{2g} and e_g levels expected in an octahedral field. Any estimate of the extent of this distortion would be rather speculative, however. The initial-state geometry is not applicable, and the effective crystal field in the final state is hard to assess, because the speed of the photoemission process implies relaxation of the F(2p) electrons toward the hole state but essentially no nuclear motion. The magnitude of the splitting (4 eV or $3 \times 10^4 \text{ cm}^{-1}$ total) is unusually large for a transition-metal compound. We note, however, that:

(i) even if relaxation were complete, the total splitting should be comparable to optical values of 10Dq from tripositive ions; i.e., $2 \times 10^4 \text{ cm}^{-1}$ rather than $\sim 10^4 \text{ cm}^{-1}$;

(ii) the final-state crystal-field strength should be further increased during the effective sampling time of the XPS experiment ($\sim 10^{-15}$ sec) by the fact that ligand electrons can relax toward the hole state in this time interval while ligand nuclei cannot. This will enhance the effect of the negative charge on the ligands.

Finally, then, we are unable to state whether the 3d structure should be

analyzed, after the F 2p intensity is subtracted out, as two peaks (t_{2g} and e_g) with intensity ratio 3:2, or as three peaks (because of further splitting in the tetragonal field) with intensities 3:1:1. The peak structure shown in Fig. 15 can be analyzed into peaks of relative intensities $\sim 3.5:1$. This may denote extreme tetragonal distortion, which would split one d level out and leave the other four rather close together,²² giving a 4:1 intensity ratio. Since the spectrum does not allow us to decide conclusively among the various possibilities, we simply note here that there is crystal-field splitting present in the final state.

For the difluorides, to a good approximation the 3d metal d bands and the F 2p band are decoupled. In cases where we have MCHF calculations (MnF_2 , CoF_2 , and NiF_2), the calculations appear to give very good agreement with the d bands. In these calculations 1) the 3d electrons are allowed to rearrange among themselves, 2) all the electrons are explicitly treated, and 3) final-state effects are treated. Both the MCHF calculation and the MSX α calculation do not do very well on the F2p bands. They are especially too narrow. The MCHF results are much better. The MCHF calculation also does well in predicting the energy of the shake-up states. It would be particularly useful to obtain spectra over a wide range of photon energies in the cases where there is large overlap between the d- and p-bands (CoF_2 and NiF_2). Such data would be a good test of the usefulness of the technique used above to obtain partial density of states.

B. SrTiO₃, TiO₂, SrO and MgO

This section will deal with the electronic structure of SrTiO₃ and several related oxides. SrTiO₃ crystallizes in the simple cubic perovskite structure. Its properties range from exhibiting ferroelectricity to becoming a superconductor at low temperatures. The perovskites have been studied with a wide range of experimental solid-state techniques.³⁶⁻⁴⁸ We have studied SrTiO₃ with XPS under UV conditions and with high resolution. In order to help understand the valence band density of states of SrTiO₃, we have also studied several simple, related oxides, MgO, ZnO, TiO₂, and SrO which we will discuss first.

These oxides, unlike the 3d halides discussed above, do not have occupied 3d bands (except ZnO, which has a filled, core-like d band). These materials are fairly ionic and their constituents approach a noble gas filled-shell configuration; thus both the band and atomic picture should give reasonable description of their properties.

All the specimens of these materials were high grade single crystals, which were cleaved in a glove bag filled with dry nitrogen and immediately inserted into the spectrometer vacuum without exposure to the ambient. This procedure was demonstrated in Chapter V to yield very satisfactory samples for obtaining representative bulk density of states.

MgO crystallizes in the NaCl structure. Its XPS spectra are shown in Figs. 16 and 17. The valence bands consist of three groups of peaks. One, at about 18 eV from the top of the valence band,

which can be assigned to the O 2s levels on energetic grounds and two bands due to the O 2p-Mg 3s-bands from about 0 to 6.5 eV relative to the top of the valence band. We will refer to this band as the valence band. The other oxides have quite similar spectra (see below). There are several calculations on the electronic structure of MgO. Tossell⁴⁹ has carried out SCF X α Scattered Wave calculations on MgO₆¹⁰⁻ obtaining both energies and charge distributions of the various levels. He finds that the valence levels fall into three sets. There are 5a_{1g}, 4t_{1u}, and 1e_g levels which are O 2s non-bonding orbitals; then comes a set of bonding orbitals which are predominately O 2p (5t_{1u}, 6a_{1g}, and 1t_{2g}) and then a set of non-bonding O 2p orbitals (1t_{2u}, 6t_{1u}, 2e_g, and 1t_{1g}). The oxygen 2s levels are predicted to be about 1 eV wide which agrees well with the observed FWHM of this level. The top two bands, the O 2p bands which we refer to as the valence bands, have an observed bandwidth of 6.5 eV. The calculated bands, ~ 3 eV wide, are, as might be expected from a MO calculation, too narrow. Tossell's calculation gives ~ 1.8 eV for the separation between the two groups of O 2p-bands which compares with our measured separation of 2.5 eV. The separation between the O 2s and the O 2p-bonding band is calculated to be 12.5 eV while our results for the separation of the O 2s band from the more tightly bound valence band is measured to be 14 eV. Thus Tossell's calculation⁴⁹ gives quite reasonable agreement with experiment. There exist several band structure calculations for MgO.⁵⁰⁻⁵⁴ Cohen and collaborators have performed EPM⁵⁰ calculations. We have seen in Chapter V,

that EPM calculations have yielded quite good results for the outer-most valence bands in many compounds. The EPM calculation gives a band width of ~ 5.0 eV and separation of ~ 3 eV for the two peaks in the valence band, both in good agreement with our observations. The oxygen 2s band is placed about 19 eV above the more tightly bound band, much too high. This is undoubtedly due primarily to using a non-local potential (see Chapter V, section B-1). Pantelides, *et al.*,⁵¹ have carried out ab initio self-consistent Hartree-Fock energy-band calculations for MgO, which yield a band width of 10 eV, valence band splitting of ~ 6 eV and the O2s band being 21 eV above the bottom-most band. All those results are far too high. Recently, Pantelides has discussed the use of an empirical tight-binding method (ETBM) for insulating rocksalt-type crystals.⁵² The ETBM calculation predicts a bandwidth of 7.0 eV which agrees quite well with our observations. Finally, Walch and Ellis⁵³ have studied MgO employing both a MO-cluster and an energy-band representation within the Hartree-Fock-Slater scheme. The cluster calculation gave a bandwidth of 4.9 eV and a valence band splitting of a little over 3 eV, while their band structure calculation gave 2.7 and 1.6 eV respectively. Both their calculations give the separation of the O 2s band from the bottom-most band as about 14 eV. Thus all the above calculations more or less reproduce the general features of the occupied density of states, but none do well in predicting all the features of the VBDOS.

Fischer has reported X-ray emission (XES) studies of MgO.⁵⁵ His spectra yield a bandwidth of about 7 eV, (Mg K β), a band splitting of ~ 2 eV (in both Mg K β and OK spectra) and the O 2s levels at 14.5 eV (Mg K β' - Mg K β separation) above the bottom valence band. Thus there is quite good agreement between the XPS and XES results. ZnO, which has filled a 3d band, has been discussed in detail in Chapter V. Its VBDOS (Fig. 18) is very similar to MgO (except for the presence of the Zn 3d level which is very core-like).

SrO has been studied relatively little. We present XPS results in Figs. 19 and 20. The spectra should be qualitatively similar to MgO, which is the case. In SrO, the Sr4p core level overlaps the O 2s band. The bandwidth in SrO is about 10 eV and the splitting is about 4.5 eV, both surprisingly significantly larger than what was observed in MgO. There are no detailed calculations for SrO. ETBM would predict a bandwidth of < 5 eV⁵² which would appear to be in contradiction with our XPS results. The SrO results will be useful primarily in helping to interpret the levels due to Sr in the SrTiO₃ spectra.

We will now briefly discuss the results for TiO₂, which are shown in Figs. 21 and 22. There appear to have been no band-structure calculations for TiO₂, however, Tossell, et al.⁵⁶ have performed MD calculations using the S6F X α method for TiO₆⁸⁻ and there have been several band-structure calculations on TiO₂^{57,58} and one for Ti₂O₃.⁵⁹

The TiO_2 VB DOS is very similar to what was observed for MgO . There are two peaks in the valence band which are separated by 1.9 eV. The total bandwidth is 5.5 eV. There is the more tightly bound O2s level with a FWHM of 2.5 eV and 15.0 eV higher than the lower valence band peak. This agrees pretty well with the MO cluster calculation of Tossell, *et al.*⁵⁶ The X α calculation has a roughly 2 eV wide O2 s non-bonding band ($5a_{1g}$, $4t_{1u}$, and $1e_g$) which is about 11.5 eV more tightly bound than the bonding orbitals ($5t_{1u}$, $6a_{1g}$, and $1t_{2g}$) which are predominantly O2p. These bonding orbitals are separated from the non-bonding orbitals by 3.0 eV. The total valence bandwidth is about 5.5 eV. While we cannot make direct comparison with a TiO_2 band structure, band structure results for TiO and Ti_2O_3 yield bandwidths of ~ 4.5 eV and separation of O2s to O2p of 14 to 14 eV .5 (eV).^{57,59} Low energy UPS investigations of TiO_2 have been performed by Derbenwick. His results give a bandwidth of ~ 5.2 eV and a 1.7 eV splitting which are in excellent agreement with our XPS results. However, due to using low energy photons, the O2s level was mistakenly assigned to be only 2.8 eV above the "bonding" O2 p bands, an assignment which is clearly not supported by our XPS results. Our results are for the most part qualitatively consistent with the XES results of Fischer^{60,62} and Holliday.⁶¹ However, a detailed comparison shows much disagreement. Fischer's TiL_{III} emission spectrum has two features which he labels D and C and assigns to the O2s levels.⁶² C and D are separated by 2.5 eV. Our O2s peak exhibits no sign of such structure. A peak split by 2.5 eV would be readily noticeable. The $\text{TiK}\beta''$ spectrum of

Blokhin and Shuvaev⁶³ falls at about the same energy as feature C in Fischer's TiL_{III} spectrum and is featureless.⁶² The bandwidth obtained from Fischer's TiL_{III} spectrum is 15 eV (features G, A, and F) which is considerably larger than what we obtained. Furthermore the separation between his features A and F is 4.0 eV, far larger than anything possible in the XPS spectrum. Just considering features A and G yields a bandwidth of ~ 9 eV and a separation of features of about 2.3 eV, which would be more consistent with the XPS results. Furthermore the separation of features C and G is about 12.5 eV and between feature D and G is 15.0, suggesting that feature D is the "02s" band and features G and A are the 02p derived valence bands. However, the separation of C from A is 14.8 eV. The oxygen K emission has two features separated by 2.2 eV.⁶² Blokhin and Shuvaev's $\text{TiK}\beta_5$ spectrum had a width of 4.63 eV and ~ 1.7 eV splitting.⁶³ A further examination of the TiL XES results is called for. Our TiO_2 valence band is very similar to the XPS VO_2 valence band reported by Wertheim, *et al*,²⁰ the only difference being a new feature due to the d electron in VO_2 .

It might be expected that the SrTiO_3 VB DOS would be similar to TiO_2 , since in both cases Ti is octahedrally coordinated to oxygen. Optical properties³⁹ and soft X-ray emission⁶¹ of these two materials have been shown to be very similar. Our XPS results shown in Fig. 23 and 24 are similar to the oxides we have discussed above. The 02s band overlaps with the $\text{Sr}4p$ band but from relative intensity arguments, the high binding energy shoulder shown in Fig. 29 is probably the 02s band. The p bands are 6.5 eV wide. There appear to be several

features in the VB DOS but details of these fine features will have to await higher resolution studies.

There are two major features which are resolved in the valence bands. They are separated by 1.9 eV. The O2s band is separated from the 4.5 eV feature by ~ 14.5 eV. There are no detailed experimental results for the total valence bands of SrTiO_3 other than some earlier XPS results which were done under poorer vacuum conditions and obtained with much poorer signal to noise.⁴⁸ Theoretical studies include band-structure calculations by Kahn and Leyendecker⁶⁴ (LCAO-tight binding), Mattheiss⁶⁵ (APW), Soules, et al.⁶⁶ (ab initio-SCF-LCAO, also a cluster calculation was done) and Wolfram, et al.⁶⁷ (LCAO).

On the basis of UPS ($h\nu \leq 11.6$ eV) work, Derbenwick⁴⁷ proposed a density of states for SrTiO_3 . The topmost band is in reasonable agreement with our results. The UPS results yielded a bandwidth of 5.5 eV with two principle features separated by 2.3. However, as in the case of TiO_2 , Derbenwick places the O2s band much too low (3.5 eV above the bottom peak of the 2p band). Blokhin and Shuvaev⁶³ on the basis of $\text{TiK}\beta_5$ X-ray emission spectrum give a bandwidth of 3.55 which is too narrow probably because of different selection rules in XES.⁶⁸

Kahn and Leyendecker⁶⁴ only calculated the p bands for SrTiO_3 . Their calculation determined the bandwidth to be 4.5 eV. The calculations of Wolfram, et al.⁶⁷ yielded a bandwidth of 4 to 4.5 eV. Soules, et al.⁶⁶ calculated the bandwidth to be 5.86 eV, however their calculated

O2s bandwidth of 5.2 eV is much too large. Mattheiss' calculations⁶⁵ give a bandwidth of 3.5-3.8 eV, with about 2.0 separation of the principle features in the density of states. His O2s band is about 1 eV wide and ~ 14.8 above the valence band.

Soules, et al.⁶⁶ also carried out a calculation on an isolated TiO_6^{8-} cluster which gave fairly similar results to their band structure calculation, with the valence band being wider by about 2 eV, (i.e., ~ 8 eV wide). This result, along with the similarity of SrTiO_3 and TiO_2 XPS spectra, suggests that short range order is an important factor in determining the VB DOS of these materials.

These simple oxides appear to be fairly well understood and both the band structure and cluster approaches appear to give adequate description of the electronic structure, although there is room for much improvement in the calculations. Table II summarizes our experimental results and lists the results derived from calculations and other experiments. For the oxides which have d electrons (see for example Fig. 25), a pure band-structure approach will no longer be valid,⁵ at least for the d bands as our study of the simple halides in section A showed.

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Table I. Characteristic features (eV) in transition metal di fluorides (relative to top of the valence band).

	1	2	3	4	5	6	7
MnF ₂	2.2(3)	3.2(3)	4.6(3)	6.6(3)	9.6(4)	--	--
FeF ₂	2.0(2)	2.8(3)	5.1(2)	6.5(2)	8.0(3)	11.0(4)	14.0(4)
CoF ₂	2.5(3)	5.1(3)	7.2(3)	10.4(4)	11.2(3)	13.7(4)	--
NiF ₂	4.0(3)	6.8(3)	8.4(3)	10.0(3)	11.5(3)	14.5(3)	--
ZnF ₂ ^a	--	--	--	--	--	--	--

^aThe valence region of ZnF₂ consists of a broad pedestal ~ 5 eV wide and one sharp feature due to some of the Zn 3d crystal-field split levels at ~ 6.2 eV above the top of the valence band (see Fig. 8 and text for discussion.)

Table 11. Comparison of XPS results for the oxides with calculations and x-ray emission results.

Method	Ref.	Valence Bandwidth (eV)	ΔVB (eV) ^a	$\Delta O2s-VB$ (eV) ^b
<u>MgO</u>				
MSX α	49	3	1.8	12.5
EPM	50	5.0	3	19
SCHF	51	10	6	21
ETBM	52	7.0	--	--
MO-Cluster	53	4.9	3	14
HF band-struct.	53	2.7	1.6	14
XES	55	7	2	14.5
XPS	c	6.5	2.5	14
<u>TiO₂</u>				
MSX α	56	5.5	3.0	11.5
UPS (h ν < 11.6eV)	47	5.2	1.7	2.8
XES (TiL _{III})	62	~ 15	4.0 ^e	16.1 ^f
XES (TiK β_5)	63	4.6	1.7	--
XPS	c	5.5	1.9	15.0
<u>VO₂</u>				
APW	d	5.5	2.0	--
XPS	20	5.6	1.7	
<u>SrTiO₃</u>				
SCF-TB	66	5.9	~ 3	14.5
APW	65	3.7	2.0	14.8
TB	64	4.5	--	--
		4.5	--	--
UPS (h ν < 11.6eV)	47	5.5	2.3	3.5
XES (TiK β_5)	63	3.6	--	--
XPS	c	6.5	1.9	14.5

Table II. (continued)

- ^a Separation between the two major features in the valence band.
- ^b Separation between 02s peak and the more tightly bound feature in the valence band.
- ^c This work.
- ^d E. Caruthers, L. Kleinman, and H. I. Zhang, *Phys. Rev. B* 7, 3753 (1973).
- ^e Separation of features F and A in Ref. 62.
- ^f Separation of feature A from the average position of features C and D in Ref. 62.

FIGURE CAPTIONS

- Fig. 1. MnF_2 : F 2s - valence band (VB) region.
- Fig. 2. MnF_2 : Valence band region.
- Fig. 3. FeF_2 : F 2s - VB spectrum.
- Fig. 4. FeF_2 : VB spectrum.
- Fig. 5. CoF_2 : F 2s - VB spectrum.
- Fig. 6. CoF_2 : VB spectrum.
- Fig. 7. NiF_2 : F 2s - VB spectrum.
- Fig. 8. ZnF_2 : F 2s - VB spectrum.
- Fig. 9. UPS ($h\nu = 40.8$ eV) spectra of several transition metal difluorides. This figure was kindly provided by Prof. Leckey (Ref. 25).
- Fig. 10. MnF_2 : Partial d-density of states (DOS), obtained as discussed in text. The solid vertical bars represent calculated d-states from MCHF calculations of Ref. 27. Hatched area represents mostly shake-up intensity. The horizontal bar represents the region of predicted shake-up from Ref. 27.
- Fig. 11. FeF_2 : Partial d-DOS. See caption for Fig. 10.
- Fig. 12. Spectra from the 4f-valence region of Gd and Tb metals (after Ref. 35). These 4f spectra exhibit changes analogous to changes in the 3d bands in MnF_2 and FeF_2 . In both cases, one goes from a half-filled $d^5(f^7)$ shell to a shell filled with one electron more than half filled, $d^6(f^8)$.
- Fig. 13. CoF_2 : Partial d-DOS. See caption to Fig. 10.

- Fig. 14. NiF_2 : Partial d-DOS. See caption to Fig. 10.
- Fig. 15. ZnF_2 : VB DOS with the estimated F 2p contribution indicated.
- Fig. 16. XPS spectrum of the outermost levels in MgO .
- Fig. 17. MgO : VB region.
- Fig. 18. XPS spectrum of the outermost levels in ZnO .
- Fig. 19. XPS spectrum of outermost levels in SrO . [Note intense satellite ~ 13 eV below the 4s level. It is a correlation satellite (see Chapter II, section C)].
- Fig. 20. SrO : Valence band spectrum.
- Fig. 21. XPS spectrum of the outermost levels in TiO_2 (rutile).
- Fig. 22. TiO_2 : Valence band spectrum.
- Fig. 23. SrTiO_3 : Upper panel - XPS spectrum of the outermost levels.
Lower panel - Valence band spectrum. (Note the intense satellite of the Sr 4s level.)
- Fig. 24. SrTiO_3 : Upper panel - Sr 4p and O 2s spectrum.
Lower panel - O 1s spectrum.
- Fig. 25. XPS valence band-O 2s spectra:
Upper panel - CoO .
Lower panel - NiO .
- These spectra are after R. A. Pollak (Ref. 12).

Fig. 1

XBL7512-3937A

Fig. 2

XBL7512-3935

XBL 7512-3939

Fig. 3

Fig. 4

XBL7512-3941A

XBL 757-3406

Fig. 5

XBL 757-34562

Fig. 6

-639-

XBL 757-3409A

Fig. 7

Fig. 8

XBL 7510 - 4173

Fig. 9

NBL 762-2314

Fig. 10

NBL 762-2315

Fig. 11

NBL 761 38

Fig. 12

NBL 762-2317

Fig. 13

NBL 762-2316

Fig. 14

Fig. 15

XBL736-3134

Fig. 16

XBL 757-3398

Fig. 17

Fig. 18

XBL 7210-5797

XBL 757-3410

Fig. 19

XBL 757-3413

Fig. 20

XBL 757-3400

Fig. 21

Fig. 22

XBL 757-3414

Fig. 23

XBL 757-3412

Fig. 24

XBL 761-212

Fig. 25

VIII. XPS INVESTIGATION OF SURFACES: PRELIMINARY STUDIES

The understanding of the electronic structure of a surface of a pure material or of a surface interacting with an adsorbate is both a challenging fundamental scientific problem as well as a technologically important problem. Much effort is currently underway towards developing theoretical machinery to treat this problem.^{1,2} The surface sensitivity of PES has been apparent from the earliest measurements and necessitated UHV systems and special sample handling techniques for solid-state investigations such as described in Chapter III. Ironically this surface sensitivity was thought of as a drawback by many early workers and except for a few early studies,³⁻⁵ it is only recently that PES is being applied to the study of surfaces.⁶ In this chapter the applicability of PES to the investigation of surface problems will be briefly discussed along with some preliminary results primarily from clean Al and Ni films.

A. Surface Sensitivity Enhancement

The surface sensitivity of PES is determined by the escape depth of the ejected photoelectron Λ_{ee} . Λ_{ee} was shown in Fig. 20 of Chapter III (the "Universal Curve") to be dependent on the electron energy. Inelastic electron scattering can occur through a variety of mechanisms (phonon excitation at less than ~ 50 meV, single electron interactions in the range 1 to 10 eV and plasmon excitation in the range 5 to 30 eV plus multiples). The energy dependence of these processes determines which process is dominant and the shape of the universal curve. It can be seen from the "universal curve" that UPS

samples roughly 5 - 10 Å, while XPS samples more like 15 - 20 Å. It can also be seen from the "universal curve" that the maximum surface sensitivity occurs around the broad minimum at about 100 eV or roughly the energy of $Y\text{M}_{\zeta}$ X-rays (132.3 eV). This would make $Y\text{M}_{\zeta}$ a very useful laboratory source for PES investigations of surfaces. $Y\text{M}_{\zeta}$ and $Z\text{rM}_{\zeta}$ ($h\nu = 151$) have been demonstrated to be feasible PES sources in several gas phase studies⁷ but so far they have not been applied to the study of solids. However, $Y\text{M}_{\zeta}$ and $Z\text{rM}_{\zeta}$ do not allow such important core levels as O1s and Cls to be probed. It is quite handy to be able to measure these levels as they are quite useful for in situ analysis of sample integrity. Alternatively one may obtain a "depth profile" by using a variable photon source such as from a synchrotron, and sampling at a variety of points on the universal curve by changing the photon energy to obtain spectra from different sampling depths.⁸ Another factor which should be considered is that of the cross-section variations. For example, consider an adsorbate containing carbon and/or oxygen on a transition metal surface. At low photon energies, the effective sampling depth may be "high" but the adsorbate levels have a high cross-section and the substrate may be "transparent" due to very low cross-section at low photon energies, resulting in high sensitivity for adsorbate levels. This approach for studying adsorbates has been used by Eastman and co-workers.⁹

Another approach is to perform a depth profiling by the microsectioning technique which has been commonly employed in AES studies. This technique consists of slowly sputtering off controlled amounts of the surface with an ion beam and collecting spectra as a function of

depth spluttered away. Pollak and Bajorek¹⁰ have shown that one can obtain both an elemental and chemical depth profile from XPS by this technique, however, one must worry about surface damage, matrix effects, etc. One very simple means of circumventing these problems is to utilize a low electron takeoff angle, which enhances the surface sensitivity by lowering the "universal curve" by $\sin \phi$ as illustrated in Fig. 1. The effective sampling depth Λ'_{ee} is given by $\Lambda'_{ee} = \Lambda_{ee} \sin \phi$, where ϕ is the angle between the surface plane of the sample and the entrance of the spectrometer. This technique was first used by Fraser, et al.¹¹ and Fadley and co-workers.¹² These latter workers have studied theoretically and experimentally various parameters, which affect the utilization of low electron takeoff angle, in some detail. Table I shows that surface enhancement of the order of 10 is possible. Figs. 2 and 3 show XPS results from evaporated Al metal films. Fig. 2 shows the results of one attempt to prepare a clean film. At the normal measuring angle of the HP 5950A electron spectrometer (51.5°), there appears to be a slight shoulder on the Al 2s level which might be due to oxygen. This is a little ambiguous because core-levels of metals like Al are pronouncedly asymmetric as discussed in Chapter II, section C4. However, taking the spectrum at a lower take-off angle (7.5°), the peak due to Al from aluminum oxide becomes very evident. In changing from 51.5° to 7.5° the surface sensitivity was increased by a factor of 6. The ratio of the oxide to metal peak was about 1 to 8 at the high angle and for the low angle, roughly 1 to 1.3. Assuming $\Lambda_{ee} \approx 15 \text{ \AA}$ for Al, the sampling depths are respectively $\sim 12 \text{ \AA}$ and $\sim 2 \text{ \AA}$ for the high and low angles. Thus the

low angle is sampling practically only one atomic layer. In this particular film, the oxide was essentially concentrated at the surface. We see we can get both an elemental and chemical depth profile by this technique in a non-destructive manner and with extremely good surface sensitivity even at XPS energies.^{13,14} Fig. 3 shows results from a clean Al film at two angles. At the low angle, one can readily see the surface plasmon intensity enhanced. Fig. 4 shows the sample holder which was used to vary the takeoff angle.*

B. Comparison of Surface and Bulk

Core-Level Binding Energies

One conceivably might expect the binding energy of a core level to be different for an atom at the surface compared to an atom in the bulk. The atoms at the surface experience a different potential than the bulk atoms and thus their core levels could be "chemically shifted" from the atoms in the bulk of the solid, reflecting the difference in their ground state electronic distributions. The direction and magnitude of this shift depends on the way the potential changes. As we discussed in Chapter II, in reality a measured core-level binding energy probes both the initial state effect (ground-state potential) and a final-state effect (polarizability via relaxation which is the system's response to the creation of a positive charge). Thus:

*The takeoff angle could be measured to $\pm 1^\circ$.

$$\Delta E_{BE} = \Delta E_i + \Delta E_R \quad (1a)$$

$$\Delta E_R = \Delta E_A + \Delta E_{EA} \quad (1b)$$

where ΔE_{BE} is a measured binding-energy shift, ΔE_i is the "chemical shift" and ΔE_R is the "relaxation shift." Relaxation consists of atomic relaxation (A) and extra-atomic relaxation (EA). Relaxation lowers the observed binding energies (see Fig. 5). Extra-atomic relaxation may be as much as 10 eV in solids.¹⁵ Because of its lower coordination, an atom at the surface might be expected to have less extra-atomic relaxation than a bulk atom. This would tend to increase the binding energy of the surface atoms relative to the bulk atoms. The effect of changing the number of atoms available for extra-atomic relaxation was nicely demonstrated by several calculations by Davis and Shirley,¹⁶ who used the Relaxation Potential Model (RPM) in trying to stimulate graphite and found that the relaxation at a central carbon atom increased with increasing molecular size.

By employing low- and high-electron takeoff angles in XPS, one should be able to investigate changes in core-level binding energies between surface and bulk atoms. We have performed such measurements on freshly evaporated films of a free-electron-like metal, Al, and a transition metal, Ni. In Al, the Al 2s and 2p levels were measured, while for Ni, the 2p_{1/2}, 2p_{3/2}, and 3p levels were studied. Previous work of Houston, Park, and Laramore¹⁷ had found a difference between electron-excited soft-X-ray appearance potential spectroscopy (APS) and photon excited Auger APS binding energies for the metals Ti, Cr, and Ni. It was suggested that the former measured a surface binding

energy and the latter a bulk binding energy.¹⁷ These workers observed that the surface binding energies were lower than the bulk binding energy by about 1 eV.¹⁷ The implications of the results of Ref. 17 are 1) $\Delta E_i > E_{iA}$ (it is assumed that $\Delta E_A \approx 0$, since E_A is a local atomic property and should not change very much) and 2) E_i (bulk) $>$ E_i (surface) $\geq$ 1.0 eV. Our XPS studies of Ni and Al at low (7.5°)- and high (51.5°)- takeoff angles show E_{BE} (bulk) = E_{BE} (surface) to within experimental accuracy (< 0.2 eV). A shift of 1.0 eV would have easily been observed under these conditions especially if the surface was shifted to lower binding energy, since the low binding energy edge of PES core peaks are very sharp. Recent APS results¹⁸ as well as several other XPS measurements^{19,20} confirm these conclusions that there is no observable binding-energy shift between surface and bulk atoms. Other workers have recently reported small shifts of substrate surface levels upon chemisorption.²¹⁻²³

C. Bulk and Surface Density of States

The density of states at the surface is different from the bulk density of states in several ways. One way that the surface DOS is different, is the existence of surface states.²⁴⁻²⁶ These have been observed previously in some semiconductors with UPS measurements.²⁷ Preliminary XPS measurements of the valence region from a clean evaporated Al polycrystalline film at high- and low-electron takeoff angle is shown in Fig. 6 and should be compared to the results from Chapter VI. Much of the structure in the "bulk" spectrum (high angle - 51.5°) appears to be "washed out" in the "surface spectrum" (low angle - 7.1°).

This does not appear to be an instrumental effect because the resolution as determined by measurements of core-levels appears to be very nearly the same at both angles. It is tempting to suggest the valleys in the bulk density of states are filled up by surface states. Recent self-consistent pseudopotential calculations for the (111) surface of Al have identified surface states in this region.^{28,29} Interpretation of the XPS spectrum as confirming the existence of these surface states must be considered extremely tentative at this point. First, the calculations were for a particular face (111) and the experiment was from a polycrystalline surface. Secondly, the surface spectrum is going to be extremely sensitive to any small amount of contamination. These spectra certainly bear repeating. It would be extremely important to carry out these measurements on a particular crystal face rather than on a polycrystalline specimen.

Another primary difference between the bulk and surface density of states is the rms width of the density of states at the surface is reduced for the surface (however, the total bandwidth is the same as the bulk, just the higher moments get reduced).^{21,25,30-33} This reduction of width is proportional to the number of nearest neighbors (the rms width varies as the square root of the number of nearest neighbors).³⁰ Thus for a fcc metal the (110) surface should have its (rms) width narrowed the most and the (111) surface the least compared to the bulk DOS. In experiments on a clean polycrystalline Al film at high (47°) and low (5.0°) takeoff angles, we observe that the bandwidth narrows from 11.4 ± 0.4 eV to 9.6 ± 0.4 eV. We would

predict, based on the number of nearest neighbors, the surface bandwidth to be ~ 0.82 times the bulk bandwidth or 9.4 eV, which is in good agreement with observations. These measurements have a high degree of uncertainty because the Al has very low DOS at the bottom of the valence band.

While the total bandwidth is restrained to be the same for the surface as in the bulk, the states at both extremes (the top and bottom of the bands) are suppressed as discussed by Heine (they decrease as $E_{3/2}$ as opposed to $E_{1/2}$ in the bulk.) This could lead to an observed band narrowing since the density at the band extrema may become very low. Ni metal was also studied but the spectrum being complicated by many-electron effects yields inconclusive results. Cu would be a much better case as the multielectron effects are not as important. Eastman and Grobman have studied thin overlayers of Cu on Ag using low photon energies ($5 \leq h\nu \leq 11.6$ eV) and suggest a narrowing of the bands for very thin films.³⁵ A small narrowing of Ag bands has been observed by Fuggle and Menzel with XPS.³⁶ Ion neutralization results also suggest a band narrowing in Ni.³⁷

We have also studied Ni and Pt with adsorbates such as CO with XPS and used low takeoff angle to enhance the observation of the molecular orbitals of the adsorbate. The preliminary results of CO on Ni confirm the most recent interpretation of the adsorbate level scheme.^{9b,36}

These preliminary results suggest that surface enhanced XPS will become a very powerful surface spectroscopy and that the study of surfaces promises to be one of the most important future applications of PES.

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Table I. Angled Enhanced Surface Sensitivity

ϕ	Relative Depth Sampled	Relative Surface Sensitivity	Effective Sampling Depth (Å) *	Number of monolayers *
90°	1.00	1.00	15.0	6
60°	0.87	1.15	13.1	5.2
30°	0.50	2.00	7.5	3
15°	0.26	3.85	3.9	1.6
10°	0.17	5.88	2.6	~ 1.0
5°	0.09	11.11	1.5	< 1.0

* Assuming λ_{ee} ($h\nu = 1486.6$ eV) = 15 Å

FIGURE CAPTIONS

- Fig. 1. The effect of varying the electron takeoff angle θ on the effective sampling depth λ_{eff} .
- Fig. 2. Al 2s spectra from a evaporated film obtained at a a) low takeoff angle (7.5°) and b) high takeoff angle (51.5°). Note the enhancement of peak due to oxide at the low angle.
- Fig. 3. Al 2s and plasmon spectra from a clean Al film. At the low angle, the relative intensity of the surface plasmon is enhanced compared to the spectrum taken at a high angle.
- Fig. 4. Sample holder for varying the electron takeoff angle. The angle is rotated in situ by means of a probe attached to a linear motion drive. The angle is measured optically to $\pm 1^\circ$.
- Fig. 5. The effect of atomic and extra-atomic relaxation on observed binding energies. [After D. A. Shirley, J. Vac. Sci. Tech., 12, 280 (1975).]
- Fig. 6. Valence band spectrum of Al (polycrystalline film) obtained at a low takeoff angle.

XBL 763-2455

Fig. 1

Fig. 2

XBL7410-4338

XBL 7410-4339

Fig. 3

XBB 756-4249

Fig. 4

XBL748 - 4127

Fig. 5

NBL 762:2267

Fig. 6

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APPENDICES

A-1. CORE-LEVEL BINDING ENERGIES OF THE SOLID ELEMENTS ($Z < 36$) AND SOME MISCELLANEOUS ELEMENTS ($Z > 36$)

There have been several compilations of core-level binding energies, for the most part, without regard to the chemical environment of the element.¹⁻⁵ Recently there has been two compilations of binding energies of core-levels in compounds.^{6,7} Binding energies of an atom in solid-state are different from those of the free atom.⁸ The binding energies of core-levels for the first thirty elements are discussed by Shirley, et al.⁹ In Table A-1a, we tabulate the measured binding energies of the solid elements with $Z < 36$, which were for the most part recorded in the course of these UHV, high resolution studies. Table A-1b lists some miscellaneous binding energies of the solid elements with $Z > 36$.

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Table A-14 Core-level binding energies (relative to the Fermi level) of the solid elements ($Z \leq 36$) in eV

	s^0	1s	2s	2p 1/2	2p 3/2	3s	3p	3d
^1_1H	2.4 ^a	54.8 (1) ^c						
^2_2He	3.9 ^a	111.4 (5) ^d						
^3_3Li	4.5 ^a	187.5 (5) ^e						
^6_6C	4.6 ^a	284.68 (20) ^f						
$^{11}_{11}\text{Na}$	2.3 ^g	1071.7 (1) ^c	63.4 (1) ^c		30.4 (1) ^f			
$^{12}_{12}\text{Mg}$	3.7 ^d	1303.0 (1) ^f	88.55 (10) ^h		49.4 (1) ^h			
$^{13}_{13}\text{Al}$	4.2 ^a	1558.2 (5) ^h	117.99 (20) ^h		72.84 (20) ^h			
$^{14}_{14}\text{Si}$	5.4 ^a	1840.5 (5) ^h	149.8 (5) ^h		98.4 (5) ^h			
$^{15}_{15}\text{P}$		2143.3 (10) ^h	187.2 (7) ^h		130.1 (5) ^h			
$^{16}_{16}\text{S}$		2468.9 (10) ^h	226.9 (10) ^h	163.40 (20) ^h	162.25 (20) ^h			
$^{19}_{19}\text{K}$	2.3 ^a	3618.4 ^h	378.6 (10) ^h	297.3 (10) ^h	294.6 (10) ^h			
$^{20}_{20}\text{Ca}$	3.2 ^a	4037.8 (10) ^h	437.8 (10) ^h	350.4 (10) ^h	346.8 (10) ^h			
$^{21}_{21}\text{Sc}$	3.5 ^h	4489.5 (2)	497.97 (20)	403.58 (20)	398.65 (10)	51.14 (10)	28.34 (10)	0.7 (1)
$^{22}_{22}\text{Ti}$	4.3 ^h	496.5 (2)	561.42 (20)	461.01 (20)	454.88 (20)	58.36 (20)	32.61 (20)	0.8 (1)
$^{23}_{23}\text{V}$	4.3 ^h	5465.06 (10)	627.2 (2)	521.07 (10)	513.41 (10)	66.35 (10)	37.24 (10)	0.7 (1)
$^{24}_{24}\text{Cr}$	4.5 ^h	5990.81 (15)	697.8 (2)	585.35 (20)	576.04 (20)	75.2 (2)	43.1 (2)	2.0 (1)
$^{25}_{25}\text{Mn}$	4.1 ^h	6538.23 (15)	769.4 (2)	650.62 (20)	639.44 (15)	82.4 (2)	47.3 (2)	1.1 (1)
$^{26}_{26}\text{Fe}$	4.5 ^h	7111.44 (20)	848.5 (2)	720.65 (20)	707.55 (20)	91.56 (20)	53.04 (20)	0.8 (1)
$^{27}_{27}\text{Co}$	5.0 ^h	7711.4 (4)	926.6 (2)	796.2 (4)	781.0 (4)	101.4 (10)	59.37 (10)	0.4 (1)
$^{28}_{28}\text{Ni}$	5.2 ^h	8332.4 (14)	1010.35 (50)	871.47 (10)	854.22 (10)	110.92 (20)	66.57 (14)	0.6 (1)
$^{29}_{29}\text{Cu}$	4.7 ^h	8980.5 (3)	1098.6 (5)	952.6 (2)	932.8 (2)	122.45 (10)	77.23 (10) 75.07 (10)	2.8 (1)
$^{30}_{30}\text{Zn}$	4.3 ^h	9660.84 (15)	1196.16 (25)	1045.09 (15)	1021.96 (15)	139.88 (15)	107.3 (2) ⁱ 91.31 (15) 88.70 (15)	10.18 (10)
$^{31}_{31}\text{Ga}$	3.8 ^h	10368.4 (10) ^h	1299.0 (7) ^h	1143.6 (7) ^h	1116.7 (7) ^h	159.4 (2) ⁱ	124.9 (2) ⁱ 120.8 (2)	18.7 (2) ⁱ
$^{32}_{32}\text{Ge}$	4.1 ^a	11103.4 (10) ^h	1414.6 (7) ^h	1248.1 (7) ^h	1217.0 (7) ^h	180.1 (2) ⁱ	146.2 (2) ⁱ 141.2 (2)	29.0 (2) ⁱ
$^{33}_{33}\text{As}$	4.7 ^a	11867.2 (10) ^h	1527.0 (7) ^h	1359.1 (7) ^h	1323.6 (7) ^h	204.7 (2) ⁱ	166.4 ^h 160.7 ^h	41.74 (2) ⁱ
$^{34}_{34}\text{Se}$	5.1 ^a	12655.9 (10) ^h	1652.0 (7) ^h	1474.3 (7) ^h	1433.9 (7) ^h	229.6 ^h	186.4 ^h 180.7 ^h	55.47 ^h 54.64 ^h

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ⁿWork function in eV.

Table A-1b. Core level binding energies (in eV, relative to the Fermi level) of selected outer levels from miscellaneous solid elements with $36 < Z < 86$.^a

	ϕ^b	$3d_{3/2}$	$3d_{5/2}$	$4d_{3/2}$	$4d_{5/2}$	$4f_{5/2}$	$4f_{7/2}$	$5d_{3/2}$	$5d_{5/2}$
⁴⁶ Kr	4.9	312.3 (5)	307.5 (5)						
⁴⁶ Pd	5.6	340.7 (5)	335 (5)						
⁴⁷ Ag	4.0	374.5 (5)	368.5 (5)	6.3 (1)	4.7 (1)				
⁴⁸ Cd	4.1			11.46 (9) ^c	10.47 (9) ^c				
⁴⁸ In	--	451.7 (3)	444.2 (3)	17.64 (9) ^c	16.74 (9) ^c				
⁵⁰ Sn	4.5	493.5 (3)	485.1 (3)	24.76 (9) ^c	23.68 (9) ^c				
⁵¹ Sb	4.6	537.7 (5)	528.2 (5)	33.44 (9) ^c	32.14 (9) ^c				
⁵² Te	5.0	582.2 (5)	572.5 (5)	41.80 (9) ^c	40.31 (9) ^c				
⁷³ Ta	4.1			238.6 (5)	227.1 (5)	24.83 (2)	23.02 (20)		
⁷⁴ W	4.6			255.2 (5)	242.9 (5)	33.6 (20)	31.5 (20)		
⁷⁶ Re	4.8			273.7 (5)	260.2 (5)	42.91 (20)	40.49 (20)		
⁷⁷ Ir	5.3			311.5 (5)	295.8 (5)	63.63 (20)	60.69 (20)	3.85 (10) ^d	1.45 (10) ^d
⁷⁸ Pt	5.7			331.6 (5)	314.8 (5)	74.5 (1)	71.2 (1)	4.35 (10) ^d	1.28 (10) ^d
⁷⁹ Au	5.1					87.58 (10)	83.99 (10)	6.10 (10) ^d	3.10 (10) ^d
⁸¹ Hg	4.5					103.85 (3)	99.8 (3)	9.5 (1) ^d	7.7 (1) ^d
⁸¹ Tl	3.7					123.1 (5)	118.7 (5)	14.53 (5) ^e	12.30 (5) ^e
⁸³ Pb	4.0			434.2 (5)	412.0 (5)	141.2 (3)	136.4 (3)	20.32 (5) ^e	17.70 (5) ^e
⁸³ Bi	4.3			464.2 (5)	440.5 (5)	162.2 (3)	159.3 (3)	26.94 (7) ^e	23.90 (7) ^e

^aThe core levels from the rare earth elements were not included in this tabulation because of their often very complicated structure arising from multiplet effects. The binding energies of the $4d_{3/2}$ and $4d_{5/2}$, respectively 106.55 (10) and 103.70 (10) for ⁸¹La, 109.30 (10) and 181.40 (10) for ⁷⁹Yb, and 206.1 and 196.1 (1) for ⁷¹Lu (S. P. Kowalczyk, N. Edelstein, F. R. McFeely, L. Ley, and D. A. Shirley, Chem. Phys. Letters 29, 491 (1974)). The $4f_{5/2}$ and $4f_{7/2}$ binding energies are 2.39 (20) and 1.14 (20) for Yb and 7.27 (12) and 8.72 (12) for Lu.

^bWork function (in eV). These are taken from Ref. b of Table A-1a where available or from Ref. a of Table A-1a otherwise.

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A-2. LMM AUGER ENERGIES FOR THE 3d TRANSITION ELEMENTS

AND KLL AUGER ENERGIES FOR Na, Mg, and Al

Table A-2a. Kinetic energies of $L_3M_{45}M_{45}$, $L_3M_{23}M_{45}$, and $L_3M_{23}M_{23}$ Augers in the 3d transition metals^{a,b}

	$L_3M_{45}M_{45}$ (eV)	$L_3M_{23}M_{45}$ (eV)	$L_3M_{23}M_{23}$
Sc ^c	--	--	--
T	449.34(94)	416.49(63)	385.95(63)
V	508.38(47)	470.06(31)	436.67(31)
Cr	567.16(15)	523.77(10)	485.86(15)
Mn	634.40(47)	585.76(47)	542.44(47)
Fe	700.57(63)	(644.9)	
Co	771.06(63)	--	654.07(130)
Ni	844.01(63)	772.23(63)	713.42(160)
Cu	917.9(2)	838.2(2)	773.01(60)
Zn	991.8(2)	904.1(2)	883.67(20)

^aThese spectra were obtained by means of X-ray excitation ($h\nu = 1486.6$ eV) and collected digitally.

^bNote that these values are systematically ~ 2 eV lower than tabulated by others (P. W. Palmberg, G. E. Riach, R. E. Weber, and N. C. MacDonald, Handbook of Auger Electron Spectroscopy (Physical Electronics Industries, Edina, Minnesota, 1972); S. Haynes in Proc. Intl. Conf. on Inner Shell Ionization Phenomena AEC Conf. 720404 (1972); T. W. Haas, J. T. Grant, and C. J. Dooley, Phys. Rev. B **1**, 1449 (1970).

^cNot obtained in the course of these measurements.

Table A-2b. KLL Auger energies for Na, Mg, and Al.

<u>Transition</u>	<u>Na</u>		
	<u>E_v^{metal}</u>	<u>E_v^{atom} (eV)</u>	<u>ΔE (eV)</u>
	(a)	(b)	(f)
KL ₁ L ₁ (¹ S)	--	909.1(3)	--
KL ₁ L ₂₃ (¹ P)	952.4(1)	937.6(3)	14.8
KL ₁ L ₂₃ (³ P)	--	948.1(3)	~ 13
KL ₁ L ₂₃ (³ P)	962.1(4)	949.9(3)	
KL ₂₃ L ₂₃ (¹ S)	987.4(4)	972.2(3)	15.2
KL ₂₃ L ₂₃ (¹ D)	991.9(1)	976.7(3)	15.2
<u>Mg</u>			
	(c)	(d)	(f)
KL ₁ L ₁ (¹ S)	1102.2(3)	1088.3	14.0
KL ₁ L ₂ (¹ P ₁)	1136.1(2)	1121.9(7)	14.2
KL ₁ L ₃ (³ P _{0,1,2})	1150.6(6)	1135.9(7)	14.7
KL ₂ L ₂ (¹ S)	1176.1(2)	1162.1(8)	14.0
KL ₂ L ₃ (¹ D)	1181.6(2)	1167.3(6)	14.3
KL ₃ L ₃ (³ P _{0,2})	--	1171.1(8)	--
<u>Al</u>			
	(e)		
KL ₁ L ₁ (¹ S)	1302.3	--	--
KL ₁ L ₂₃ (¹ P)	1341.5	--	--
KL ₁ L ₂₃ (³ P)	1357.2	--	--
KL ₂₃ L ₂₃ (¹ S)	1387.2	--	--
KL ₂₃ L ₂₃ (¹ D)	1393.2	--	--
KL ₂₃ L ₂₃ (³ P)	--	--	--

Table A-2b. (continued)

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- ^a S. P. Kowalczyk, L. Ley, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 8, 3583 (1973).
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- ^d B. Breuckman and V. Schmidt, Z. Phys. 268 335 (1974).
- ^e G. Dufour, J.-M. Mariot, P.-E. Nilsson-Jatko, and R. C. Karnatak, private communication.
- ^f Difference between the atomic and metallic Auger energies. The screening model of extra-atomic relaxation (Chapter II) predicts a difference between the atomic and solids Auger energies of 16.8 and 18.9 eV for Na and Mg respectively. Recently Auger spectra for atomic Zn has been obtained (S. Aksela and H. Aksela, Physics Letters 48 A, 19 (1974). The atomic zinc Augers are ~ 14.8 eV lower than metallic zinc. The screening model would predict 14.4 eV.

A-3. VALENCE BAND DENSITY OF STATES OF AMORPHOUS BINARY COMPOUNDS

The electronic structure of amorphous and disordered materials may be different than in their crystalline or ordered counterparts. Photoemission spectroscopy has proven to be a very valuable and sensitive probe of the electronic structure of amorphous semiconductors.¹⁻⁵ In particular, the "s-bands" are very sensitive to topological disorder, as shown by several studies of elemental semiconductors and semimetals.¹⁻³ Fig. 1 shows the valence spectra of amorphous and crystalline Te as well as the result of a EPM calculation for Te.⁶ Detailed theoretical studies of crystalline and amorphous Te and Se have been carried out by Joanopoulous and co-workers.^{3,6-8} There still remains much controversy and speculation over the structure of amorphous Se and Te.⁷⁻¹² It appears there may be several forms of the amorphous phase depending on how the sample is prepared.³ The amorphous sample of Fig. 1 was prepared by ion bombardment while the specimens of Ref. 9 were prepared by sputter deposition. The spectrum of Fig. 1 exhibits three regions in the valence region. First there is a intense featureless peak at the top of the valence band which is the non-bonding p-band. There is a band in the 2 to 6 eV range which has two features due to the bonding p-like states. The analysis of Refs. 6-8 leads to the conclusion that the lower energy peak is due to intra-chain bonding states and the higher energy peak due to inter-chain bonding levels. The third region is due to s-like states. There is some question about this because some UPS studies of other chalcogens (S and Se)¹³ did not find any evidence for the s-bands. However, there

is much evidence to make Nielsen's position highly untenable.

1) The evolution of the XPS spectra from elements Ag to Xe¹⁴ clearly shows that this feature is due to the 5s electrons, 2) it is well known that s-bands will have much lower cross-section at $h\nu = 21.2$ eV and that the background will be very high in the region of the 5s peak when 21.2 eV photons are used, resulting in great difficulty in observing these states, 3) core-level spectra¹⁵ can be used to rule out that the feature we are interpreting as the "s band" is not due to surface or bulk plasmons, contrary to the suggestion of Nielson,¹³ 4) comparison with spectra from Si, Ge, and III-V and II-VI compounds (see spectra in Chapter V) where the interpretation is on firm footing that these peaks are s-like states, as well as comparison with gas phase data¹⁶ or other atomic data¹⁷ further supports our interpretation. It is thus fairly certain that this band is due to the s-like states. Furthermore, calculations^{6,7} bear this out and show the s-states well below the p bands (~ 10 eV) and that there is little s-p hybridization.

The experimental observations are 1) the lone-pair p band is essentially unchanged on going from trigonal Te to amorphous Te, 2) the relative intensity of the two peak feature in the bonding p region are reversed in the amorphous phase. This suggests on the basis of the calculations of Ref. 7 that there is an increase of intra-chain bonding the amorphous phase of Te and 3) a filling of the "valley" in the s-band is observed on going to the amorphous phase. This is opposite on what is observed in Se and Te specimens prepared by sputter deposition.⁹ These differences may be due to different

structures (e.g., rings or broken chains may be favored under the different preparation conditions). It is not clear what is the cause of the changes in the spectra and further experiments with higher resolution and controlled sample preparations are necessary for further detailed analysis.

While the amorphous elemental Group IV and Group V materials are pretty well understood now, it is of interest to attempt to understand amorphous binary compounds of the A^{N_8-N} and $A^{N_{10-N}}$ type-materials. There are several possible differences in amorphous binary semiconductors from their crystalline counterparts, which could result in observable changes in the XPS VB DOS: 1) Topological disorder, 2) bond-angle and bond-length variations, 3) existence of like-atom ("wrong") bonds (i.e., Ga-Ga and As-As bonds in a GaAs), and 4) clustering. The first two effects are possible in the amorphous elemental semiconductors and semimetals. The s-bands were demonstrated to be very sensitive to topological effects and the p bands shifted due to effect 2).^{1,2} The filling of the "valley" in the s-bands was shown to be related to the existence of odd-membered rings (5 and 7 membered rings) in the Group IV and V amorphous elements.^{1,8,18,19} Since binary amorphous semiconductors have similar radial distribution functions (RDF) as the elemental amorphous materials, it is tempting to speculate that they are structurally similar, i.e., the amorphous binaries would possess significant number of odd-membered rings.²⁰ However, it must be noted that similar RDF's is a necessary but not sufficient condition for the materials to have the same structure,

i.e., RPF's do not uniquely define a structure. If the binary amorphous compounds did have a large number of odd-membered rings, this would result in a significant number of "wrong" bonds. The possibility and effect of like-atom bonds in binary semiconductors on the valence band density of states has been studied in detail by Joanopoulous and Cohen.^{8,21} These workers calculated the VB DOS of various polymorphs of GaAs in which the bond and dihedral angle distributions and the ring statistics were varied.^{8,21} Three effects were predicted by Joanopoulous and Cohen: 1) The appearance of a second s-like peak (~ 3 eV below the lowest s-like peak), 2) peaks due to As-As and Ga-Ga bonding states below and above the p-like band respectively, and 3) a narrowing of the band gap. These authors suggested that there could be approximately 10% "wrong" bonds. Predictions 1) and 2) should be experimentally verifiable by XPS VB DOS. Effects due to "wrong" bonds should also be observed in core-level spectra as indicated by studies of ErCh_x , where Ch = S or Se and $x = 2$ or 3.²² When $x = 2$ in ErCh_x , there are no like-atom bonds and when $x = 3$, there are a considerable number of covalent like-atom bonds.²² In the $x = 2$ cases Jellinek, et al.,²² observed a single peak for each core level but in the $x = 3$ cases, they observed two peaks from the core-levels of the Ch species (see Figs. 3 and 8 of Ref. 22).

Figs. 2 through 5 show preliminary data for a-GaAs, a-GaP, a-InP and a-InSb. The related crystalline spectra were shown in Chapter V. The samples were prepared by RF sputter deposition. The samples were checked for stoichiometry by comparing the relative

intensity of the outermost d level of the cation to that of the anion. The specimens were also checked for contamination and found to be free of detectable oxygen or carbon contamination.

The spectra of Figs. 2-5 are very similar to their crystalline counterparts. No new structure appears in the s-region. The p-bands appear to be broadened somewhat. Neither is any evidence of a chemically shifted component in the core-level spectra apparent. Fig. 5 shows an a-InSb sample which has a gross excess of Sb (~ 160%). In this case we do see extra structure in the s-region probably due to clustering of a Sb metal phase and the p-like region is greatly broadened. These results suggest that there are less than 10% wrong bonds in the stoichiometric amorphous binary semiconductors and that the ionicity of these materials make like-atom bonds and thus odd-membered rings unfavorable. These conclusions agree with those of Shevchik, et al.,²³ on the basis of photoemission results and others from evidence such as heat of crystallization²⁴ and optical data.²⁵

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FIGURE CAPTIONS

- Fig. 1. The upper panel shows a comparison of trigonal Te VBDOS with results of an EPM calculation (after Refs. 3, 6, and 7). Lower panel compares the XPS VBDOS from trigonal Te specimen with an amorphous Te specimen which was prepared by sputter bombardment.
- Fig. 2. Amorphous GaP VBDOS. The specimens in Figs. 2-5 were prepared by RF sputtering onto stainless steel substrate which was at room temperature.
- Fig. 3. Amorphous GaAs VBDOS.
- Fig. 4. Amorphous InP VBDOS.
- Fig. 5. Amorphous InSb VBDOS.
- Fig. 6. Amorphous InSb VBDOS of a specimen with excess Sb.

Fig. 1

XBL 761-39

Fig. 2

XBL7512-3932

Fig. 3

Fig. 4

Fig. 5

XBL7512 - 3933

Fig. 6

XBL 7512-3934

A-4. VALENCE BAND DENSITY OF STATES OF LAYERED COMPOUNDS:

GaSe AND BiI_3^*

Layered compounds have been the subject of much experimental and theoretical activity because of their interesting anisotropic properties and possible application in switching and memory devices.¹ In this appendix we report a high-resolution X-ray photoemission spectroscopy (XPS) investigation of the total valence band density of states (VB DOS) for the semiconducting layered compounds GaSe and BiI_3 . It has been demonstrated previously that XPS can yield rather direct and detailed information on the total occupied density of states for semiconductors,² in particular allowing narrow limits to be placed on the positions of the valence bands (see Chapter V, section B).

The optical properties of both GaSe and BiI_3 have been studied previously, mainly near threshold.³⁻¹⁰ These measurements yield transition energies between the top of valence band and the bottom of the conduction band. Low-energy UPS data,^{11,12} as well as low-resolution XPS data¹³ are available for GaSe. To our knowledge, BiI_3 has not been studied experimentally by any total valence-band probe.

The samples were crystals, which were cleaved in a sample-introduction chamber filled with dry nitrogen. The samples were "cleaved" by the standard method for layer structures: removal of

* Based on work done in collaboration with L. Ley, F. R. McFeely, and D. A. Shirley and published in Solid State Commun. 17, 463 (1975).

adhesive tape. The sample-introduction chamber was then immediately evacuated, and within several minutes the freshly-cleaved surfaces were inserted into the main spectrometer chamber. These measurements were done at a relatively poor vacuum of 5×10^{-9} torr. The samples were analyzed in situ for contamination by scanning 20 eV regions around the oxygen and carbon 1s peaks and by taking a 1280 eV overall scan. For the samples from which the spectra reported here were obtained, no oxygen or carbon could be detected. The BiI₃ analysis indicated the presence of some reduced Bi. After the valence band and outer d-core regions were scanned (approximately 6 hours accumulation time), another in situ analysis was performed on each sample to insure that no contamination had occurred.

Fig. 1 shows our XPS spectrum, to be interpreted in terms of the VB DOS for GaSe. The energies of the characteristic features, along with pertinent UPS results, are given in Table I. Band-structure calculations have been carried out by Kamimura and Nakao¹⁴ (tight-binding, π bands only), Bassani and Parravicini¹⁵ (tight-binding, two-dimensional), denoted hereafter as BP, and Schlüter¹⁶ (empirical pseudopotential method, EPM, three-dimensional). Schlüter's EPM results possessed some qualitative similarities for the valence bands to the BP calculations. This is not surprising because of the weak interaction between the layers, the largely two-dimensional character of the charge density, and the fact that tight-binding calculations do fairly well for valence bands. A very useful feature of Schlüter's work is the calculation of charge

densities, which gives insight to the origin of structure in the density of states and information about the bonding in GaSe. The EPM calculation puts the lowest set of 4 bands in the 12.4-13.6 eV region relative to the top of the valence bands. Bassani and Parravicini obtained a somewhat wider distribution in the two lowest bands from 12.0 to 13.6 eV. (There are twice as many bands in the three-dimensional EPM calculation as in the two-dimensional structure used by BP.) These lowest bands correspond to selenium 4s nonbonding states. Our measurements yield a peak (G) of width 3.8 eV, centered at 14.15 eV. Thus both calculations give bands which are too flat, provided that the experimental width is equivalent to the true band width (i.e., ignoring relaxation broadening). It is well known that EPM calculations must include a non-local potential to obtain agreement with the lowest bands.^{18,19} Pure Se has a broad (~ 9 eV wide) 4s peak centered at ~ 13 eV.²⁰ This peak falls at 11.6 eV in ZnSe,² 12.9 in PbSe,²¹ and 13.4 in ZrSe₂.²²

Next BP found two bands extending from 3.2 to 6.5 eV. The EPM calculation yielded two sets of two bands each, at 6.1 to 6.7 and 3.4 to 5.0, respectively, with a distinct gap between them. The XPS spectrum shows a peak (E) at 7.23 which extends from (D') 6.0 to (F) 8.99 eV. There is no evidence for a gap though peak E may in fact be two peaks, with a splitting of approximately 0.5 eV. These bands derive respectively from Ga-Ga bonding states (lower bands) and Ga-Ga anti-bonding plus some Ga-Se bonding states (higher bands).

Next BP have two sets of bands at the top of the valence band, one (consisting of 4 bands) from 1.8 to 2.8 eV and the other (consisting of one band) from 0.0 to 1.10 eV. For this region, the EPM calculations yield ten bands from 0 to 2.3 eV, with peaks at 0.8 and 2.1 eV. The XPS spectra show an intense peak (B) at 2.89 eV, a well-separated shoulder (C) at 4.38 and a possible shoulder (A) at 1.56 eV. None of these features could be resolved in the earlier low resolution measurements.¹³ Feature C is presumably due in large measure to contributions to the VB DOS from 4 valence electrons involved in the Ga-Ga bond, mixed with some Se px orbitals (π bands). There are 16 remaining electrons which, according to the EPM charge densities^{16,17} results, form GaSe bonds (σ bands). These contribute to features B and A. In summary, both the EPM and BP calculations show qualitative agreement with our XPS results but both still leave much to be desired. Part of the problem may be that the position of the atoms are not known very accurately and better agreement may be expected with improvement of atomic distances within the unit cell.²³ Also the EPM calculation may overestimate inter-layer coupling.

Table I shows qualitative agreement with the earlier XPS¹³ results, the present results allow structure in the top valence band to be resolved. This clears up some confusion which resulted from the low-energy UPS measurements. Earlier low-energy UPS¹¹ attributed two peaks at 0.8 and 2.1 eV and separated by a gap to the density of states and concluded that it supported the BP calculations. More recent UPS work at higher (although still low) photon energies

yield a somewhat different spectrum. These XPS results establish criteria that future calculations will have to meet.

One interesting result of the charge densities obtained by Schluter^{16,17} is that, while they show GaSe to be covalently-bonded, there is an ionic component in the GaSe bond. An upper limit to the effective charge on Se of 0.4 e was derived.^{16,17} Infrared measurements²⁴ have led to an estimate of 0.74 e and X-ray absorption discontinuities²⁵ to 0.5 e as the effective charge on Se. It would be interesting to apply the XPS scale of ionicity proposed by Kowalczyk, et al.,²⁶ to derive an ionicity for GaSe. The formulation of Ref. 26 is not readily applicable to GaSe because of its anisotropic nature and the existence of Ga-Ga bonding states. Using a weighted average of the nearest-neighbor distances to derive the covalent splitting contribution,²⁶ an ionicity of $\sim .60$ was obtained for GaSe. This puts GaSe between the ionicities of GaAs and ZnSe as obtained by Kowalczyk, et al.²⁶ This seems reasonable, considering that the electronegativity of Se is greater than that of As. However, before this approach can be applied with confidence to this class of compounds, measurements on more layered compounds must be made.

We turn briefly to BiI_3 , for which there exists to our knowledge, neither band-structure calculations nor any measurements of the total VB DOS (XPS, UPS, X-ray emission, etc.). Thus we shall simply describe our results and offer a preliminary interpretation.

Figure 2 shows the XPS valence band spectrum, which consists of a three peak structure and Table II lists the energies of the characteristic features. First there is a broad peak (D) centered at 12.1(3) eV. As in the case of GaSe, this should be the anion s-state. Iodine 5s states were observed in NaI at 11.21 eV and in KI at 10.82 eV.²⁷ An EPM calculation²⁸ for the layered compound PbI_2 yielded two very flat bands corresponding to nonbonding iodine 5s states at about 11.5 eV. The XPS spectrum next exhibits a gap (C - C') of about 3 eV. The top of the valence band is a broad doublet (A,B). Feature B is most likely derived from states possessing some bismuth "s-like" character, while feature A corresponds to I 5p levels. In NaI and KI, this feature occurs at 1.67 and 1.48 eV, respectively.²⁷ There is evidence of a slight shoulder A'. The A - A' separation is about 0.4 eV. It may be the origin of the 0.38 eV splitting in absorption measurements that has been attributed to transitions from spin-orbit split iodine 5p valence band to an $n = 1$ exciton level.⁸ As discussed for the alkali halides,²⁷ this uppermost band is probably dominated by band-structure effects rather than spin-orbit splitting. Absorption data for PbI_2 and BiI_3 are similar,⁹ which indicates that their uppermost valence bands are similar. Thus the upper valence band we obtained for BiI_3 is very similar to the XPS PbI_2 results of Ishii, et al.²⁹ (Fig. 3). The EPM calculations for PbI_2 ²⁸ have several bands in the region 1.8 to 4.5 eV, which yield peaks at approximately 2.5 and 3.1 eV. There is also a gap and a narrow peak at 0.8 eV. The broad peak derives from anion p states with bonding between Pb and I. The uppermost narrow peak is a lead

"s-like" state. Except for this uppermost feature, the calculation is in qualitative agreement with our BiI_3 spectrum. Again, the calculated bands are too flat. One special problem in the PbI_2 case is that the calculations were done with no previous knowledge of the iodine form factors.²⁸ Using the XPS ionicity scale with an anion-size correction which proved necessary for the alkali halides,²⁶ an ionicity value of .68 is obtained, making BiI_3 more ionic than GaSe and just over the ionic side of the dividing line between "covalent" and "ionic" compounds.²⁶ As mentioned above, it is not clear whether this model is valid for these anisotropic compounds.

In conclusion, we have used XPS to obtain the total valence band density of states spectrum for GaSe and BiI_3 and to test theoretical studies on layered materials. The calculations were shown to require further refinements if they are to reproduce the experimental results.

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Table 1. Comparison of energies (eV) of characteristic features in the valence band spectra from XPS, UPS, and EPM calculation for GaSe.

Feature	XPS ^a	UPS		XPS ^d	Theory EPM ^c	BP ^f
		b	c			
A	1.56(10)	—	~ 1	—	(~ 0.5)	—
B	2.89(10)	3.0	2.2	2.5	0.8	1.1
C	4.38(10)	4.6	4.3	—	2.1	1.8
D	5.0(3)	—	—	—	2.3	2.8
D'	6.0(3)	—	—	—	~ 3.0	3.2
E	7.23(10)	6.8	7.2	7	6.4	~ 5.5
F	9.0(2)	8.5	—	—	6.7	6.5
G	14.15(15)	—	—	13	~ 13.0	~ 13.0
H	16.0(4)	—	—	—	13.6	13.6
Ga $3d_{3/2,5/2}^k$	19.39(10)	—	—	18.7	—	—
Se $3d_{5/2}^k$	54.19(10)	—	—	—	—	—
Se $3d_{3/2}^k$	54.82(10)	—	—	54	—	—

^a This work (relative to the top of the valence band).

^b Reference 12.

^c Reference 12, Hel.

^d Reference 13.

^e Reference 17.

^f Reference 15.

^k This peak exhibits characteristic energy losses at 7.2(3) and 16.0(2) eV.

Table II. Energies (eV) of characteristic features in the XPS valence band spectrum of BiI₃

Feature	Energy ^a
<i>A</i>	1.68(8)
<i>A'</i>	2.07(8)
<i>B</i>	3.97(14)
<i>C</i>	5.63(8)
<i>C'</i>	8.64(8)
<i>D</i>	12.11(30)
<i>E</i>	14.12(40)
Bi 5 <i>d</i> _{5/2} ^b	24.99(8)
Bi 5 <i>d</i> _{3/2} ^b	28.09(8)
I 4 <i>d</i> _{5/2} ^b	48.43(8)
I 4 <i>d</i> _{3/2} ^b	50.11(8)

^a This work (relative to the top of the valence band).

^b This peak exhibits characteristic energy losses at 6.0(2) and 15.6(2) eV.

FIGURE CAPTIONS

Fig. 1. Valence-band XPS spectrum of GaSe.

Fig. 2. Valence-band XPS spectrum of BiI₃.

Fig. 3. Comparison of the XPS spectrum of BiI₃ (this work) with the spectrum of PbI₂ (Ref. 29).

XBL752-2404

Fig. 1

Fig. 2

XBL752-2403

Fig. 3

XBL 755-3051

A-5. TERNARY SEMICONDUCTORS: II-IV-V₂ CHALCOPYRITES*

We have calculated the valence-band density of states $N(E)$ and measured the X-ray-photoemission (XPS) spectrum $I(E)$ for the chalcopyrite-type semiconductor ZnGeP_2 . $I(E)$ was also measured for ZnSiP_2 and CdSnAs_2 (see Fig. 1). In ZnGeP_2 the shapes of $N(E)$ and $I(E)$ agreed very well, allowing us to correlate structure in $I(E)$ explicitly with Zn-P and Ge-P bonds through contour plots of electron charge densities integrated over selected energy intervals $\rho_{\Delta E}(\vec{r})$. This approach appears promising for a detailed understanding of bonding in chalcopyrite-type compounds and other ternary or more complex materials.

The $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^{\text{V}}$ compounds are ternary analogs of the $\text{B}^{\text{III}}\text{C}^{\text{V}}$ zinc-blende semiconductors (e.g., ZnGeP_2 is the analog of GaP) in which alternate cation sites are occupied by atoms of the group-II and group-IV elements surrounded in tetrahedral coordination by group-V anions.¹ The ternary compounds, therefore, possess an essential complication that is absent in their binary analogs -- two kinds of bonds. The present work represents the first attempt to relate features in $N(E)$ or $I(E)$ to different bonds in a relatively complex material, thereby extending a correlation that is obvious for the diamond and zinc-blende lattices.^{8,9}

*Based on work done in collaboration with C. Varea de Alvarez, M. L. Cohen, L. Ley, F. R. McFeely, R. W. Grant, and D. A. Shirley and published in Phys. Rev. B 10, 596 (1974).

Our approach was to compute the charge density $\rho_{\Delta E}(\vec{r})$ within an energy region ΔE rather than the usual $\rho_n(\vec{r})$, the charge density for band n . The energy region was chosen to correspond to an energy interval in which $N(E)$ contains structure of interest (e.g., a peak). For ZnGeP_2 there appears to be six important regions in $N(E)$. These are labeled A, B, C, D, E, and F in Fig. 2. Figure 3 shows $\rho_{\Delta E}(\vec{r})$ for each region, calculated in the $x = y$ plane, which contains the Zn, Ge, and P ions. The experimental results will be described next, followed by a discussion of the calculation and an analysis of the results.

Single crystals of ZnGeP_2 and CdSnAs_2 were grown by directional solidification of stoichiometric melts synthesized from the elements. The photoelectron spectra were measured in a Hewlett-Packard 5950 ESCA Spectrometer (which uses monochromatized Al K α X-rays) modified to operate at pressures well below 10^{-9} Torr. Samples of the single crystals were fractured inside the spectrometer immediately before the measurements. The freshly exposed surfaces showed no detectable oxygen or carbon contamination even after 12 h. Valence-band spectra $I(E)$ referred to the top of the valence band are shown in Fig. 1. The ZnGeP_2 and CdSnAs_2 spectra have been corrected for contributions from inelastically scattered electrons (Fig. 2).¹⁰ The intense peaks corresponding to emission of core-like Zn 3d and Cd 4d electrons have been truncated to exhibit the valence s and p contributions more clearly. The unperturbed shape of the d peaks is indicated by solid curves in Fig. 2.

We first give a brief description of the spectrum, which we will analyze in detail later. Starting at the top of the valence band, $I(E)$ rises to an intense, broad peak at a binding energy of 2-4 eV. This peak exhibits a wealth of fine structure. After a well-defined minimum at 6.2 eV in ZnGeP_2 , 6.0 in ZnSiAs_2 and 5.7 eV in CdSnAs_2 , the intensity rises again. In CdSnAs_2 a blunt hump is observed around 7.0 eV, with a satellite at 8.3 eV. Beyond 8.5 eV $I(E)$ follows closely the sharp onset of the leading edge of the 4d peak. Valence-band contributions to $I(E)$ cannot be distinguished at higher binding energies.

In ZnGeP_2 a second region of high-valence electron density can be identified around 7.0 eV on the leading edge of the Zn 3d peak. A drop in intensity of peak II beyond 8.0 eV seems likely, but is not certain. ZnSiAs_2 exhibits a well defined peak at 7.4 eV. There is a shoulder on the low-energy (high-binding-energy) side of the Zn 3d peak that cannot be explained by oxidation, plasmon losses, multiplet splitting, or shakeup processes. We therefore interpret that shoulder as due to a third valence-band peak centered at ~ 12.5 eV, with a total width of about 4 eV at its base. This determines the total valence bandwidth in ZnGeP_2 as 14.5 ± 0.5 eV. A corresponding third peak in CdSnAs_2 is presumably masked by the Cd 4d peak. Its position is then limited to a range of between 10.0 and 12.5 eV.

The band-structure calculations for ZnGeP_2 were based on the empirical pseudopotential method.¹¹ No attempt was made to fit the pseudopotential to experiment. The method of choosing the potential and the resulting band structure is given in Ref. 12.

In analyzing the band structure, it is helpful to use the quasicubic model.¹³ In this model, the band structure of the chalcopyrite semiconductor is viewed as a perturbed version of its zinc-blende semiconductor, $N(E)$ exhibits the following prominent structure:⁸ a broad peak (peak I) near the top of the valence band, separated from a second narrower peak (peak II) by a small valley, followed by a gap which separates this structure from the lowest energy peak III. Charge-density calculations⁹ for each of the valence bands separately give some indication of the electron distribution in the zinc-blende case. States in peak I correspond to electrons near the bonding sites, peak II contains electrons which are mostly s-like around the cation and some charge piled up in the bonding region, and peak III contains electrons which are s-like around the anion.

In the chalcopyrites one expects that the overall $N(E)$ should be similar, but that more structure should be present. For example, peak I should contain structure arising from the two types of bonds. Since this calculation was based on a local pseudopotential, one expects the same problems that were encountered with local pseudopotentials for the zinc blends.⁹ In particular, a nonlocal scheme^{9,11} was necessary to obtain the correct width of peak I in the zinc blends. The local potential gives a peak I that is too narrow.

We therefore expect the peak-I region to be too narrow in the chalcopyrite case; however, the basic features of the structure should not be affected.

Figure 2 contains the results for the calculated $N(E)$ for ZnGeP_2 and the measured XPS spectra for ZnGeP_2 and CdSnAs_2 . Critical points in the band structure show up as sharp structure in $N(E)$. To facilitate comparison with experiment, a Gaussian-broadened curve $N'(E)$ is also shown. Figure 2 shows $\rho_{\Delta E}(\vec{r})$. The energy intervals ΔE were chosen through analysis of $N'(E)$; $\rho_{\Delta E}(\vec{r})$ was then calculated for each interval by restricting the band indices and k states to give electron states in the desired energy range ΔE .

Referring to Fig. 2 we see that the highest-energy (lowest-binding-energy) valence-band structure, which corresponds to peak I in the zinc-blende case, is split into two regions, A and B. Using the $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$ of Fig. 3, we see that these regions contain electrons in the Zn-P and Ge-P bonds, respectively. The number of electrons in the energy interval A is 11.4 and there are 5.45 electrons in the B region. Peak I is therefore split by the energy difference in the two bonds. The Ge-P bond appears to be a stronger covalent bond (i.e., it lies lower in energy) than the Zn-P bond, as would be expected on chemical grounds. The theoretical width of peak I is smaller than experiment; this could arise either from the use of the local potential as described before, or from an underestimation of the difference between the potentials of the two cations. The general shape and splitting of peak I, however, shows excellent

agreement between the experimental and theoretical spectra, with four distinct corresponding features present in each.

The peak-II region splits into three peaks C, D, and E. In the binary semiconductors, $\rho(\vec{r})$ shows some concentration around the cation with some charge in the bond. For ZnGeP_2 in the C region (3.15 electrons), charge concentrates on Zn with some charge in the Ge-P bond, while region D (2.05 electrons) and E (1.95 electrons) show charge accumulating on Ge. This order is expected because the Ge potential is deeper than that of Zn. In region D there is some charge in the Zn-P bond, while E shows some charge piled up in the anti-bonding region. In the XPS spectra, peak II is partially hidden by the d peaks. In CdSnAs_2 , by measuring the relative areas under the experimental spectrum and comparing this with the theoretical curve of ZnGeP_2 , we conclude that the structure in the region between 6.5 and 7.5 eV probably corresponds to the D and C unresolved doublet. The satellite at 8.3 eV is interpreted as arising from region E. It is unfortunate that the peak-II region is not easier to discern, as this region is most affected by the differences in the cation potentials.

As discussed before, peak III is observed in the ZnGeP_2 XPS spectrum, but hidden in the CdSnAs_2 spectrum. In the theoretical $N'(E)$ this region is labeled F. There are eight electrons in this region and $\rho_P(\vec{r})$ shows that the electrons are mostly s like around the anion, i.e., the P site. This is the same configuration found in zinc-blende-type semiconductors, as is expected, as the p_{1/2} anionous 3s subshell is tightly enough bound to be nearly corelike.

The above analysis illustrates the advantages of dealing with both $\rho_{\Delta E}(r)$ and $N(E)$. We have concentrated on ZnGeP_2 in this work, but the results should be general for the chalcopyrite-type compounds. The possibility of identifying certain features in $I(E)$ with well-defined charge distributions and specific bonds should be especially useful in the analysis of complex or amorphous materials, which as yet defy a realistic theoretical treatment.

A-5 - References

1. See Refs. 2-7 for examples of the properties and applications of chalcopyrite compounds. For XPS studies of the related I-III-VI₂ compounds see: S. Kono and M. Okusawa, J. Phys. Soc. Japan 37, 1301 (1974); W. Braun, A. Goldman, and M. Cardona, Phys. Rev. B 10, 5069 (1974); M. J. Luciano and C. J. Vesely, Appl. Phys. Letters 23, 60, 453 (1973).
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FIGURE CAPTIONS

Fig. 1. Raw XPS spectra for the valence region of ZnGeP_2 , CdSnAs_2 , and ZnSiP_2 .

Fig. 2. (a) XPS spectrum for CdSnAs_2 ;
(b) spectrum for ZnGeP_2 ;
(c) broadened theoretical density of states for ZnGeP_2 ;
(d) calculated valence-band density of states for ZnGeP_2 .
The XPS spectra have been corrected for background and loss structure.

Fig. 3. Calculated electronic charge-density contour plots for ZnGeP_2 corresponding to density-of-states peaks A, B, C, D, E, and F. The plots are normalized to the number of electrons contained in each peak. This value is given for each plot.

Fig. 1

XBL7310-4205

Fig. 2

XBL7310-4206

Fig. 3

A-6 - TELETYPE CONTROL COMMANDS


```

MULTI-RUN DIGAD          10/27/75
***** STARTING ADDRESS= 2004 *****
*
* NR = # OF RUNS(1 TO 4)
* NR = EV PER SCAN(10*2**N) WHERE N=0 TO 7
* MD = MEMORY DIVISOR(POWER OF 2)
*      TOTAL NC MUST SATISFY SUM(NC).LE.2000
* OK = RESPOND: YES OR NO
* NS = # OF SCANS(FREQUENCY CONTROL)
* DI = DISPLAY
* AC = ACCUMULATE (ONLY FROM GO = AC)
* ST = GO TO START OF DIGAD
* ER = ERASE MCA MEMORY
* PR = PARALLEL OUTPUT ON THE DIGITAL PRINTER
* TI = TELETYPE OUTPUT
* MT = MAG. TAPE OUTPUT
* BE = BINDING ENERGY(999.9EV MAX.)
* VP = VOLT. PRINT(YES OR NO,CONTROL)(SR0=OVERHIDE)
* VT = VIDICON TIME DELAY CONTROL(-100=0.4MS)
* VM = CHANGE DVM MULTIPLIER
* RS = RESTORE MCA MEMORY
* FW = ROUTINE TO IDENTIFY PEAK AND COMPUTE FWHM
* NU = NUMERIC ROUTINE ENTRY
*      1 = ADD A CONSTANT
*      2 = SMOOTH,QUADRATIC,CUBIC,9 POINTS
*      3 = " " " " 17 "
*      4 = DIFFERENTIATE,QUADRATIC, 9 POINTS
*      5 = " " " " 17 "
*      6 = ADD AND MULTIPLY BY A CONSTANT
*
*
* SWITCH REGISTER OPTIONS
SM0 = STOP VP PRINTING
SK1 = DUMP NTH SCAN TO TTY
SK15 = 10 CONTINUE FWHM ROUTINE

```

```

.   AUGER           10/27/75
                        *****STARTING ADDRESS= 2004 *****
*
*   NR = # OF RUNS(1 TO 4)
*   WW = EV PER SCAN (10 TO 2000EV)
*   SM = MEMORY DIVISOR
          TOTAL NC MUST SATISFY SUM(NC).LE.2000
*   OK = RESPOND: YES OR NO
*   NS = # OF SCANS(FREQUENCY CONTROL)
*   TS = TIME PER STEP IN MILLI-SEC.(300=300MS)
*   DI = DISPLAY
*   AC = ACCUMULATE (ONLY FROM GO = AC)
*   ST = GO TO START OF AUGER
*   ER = ERASE MCA MEMORY
*   PR = PARALLEL OUTPUT ON THE DIGITAL PRINTER
*   IT = TELETYPE OUTPUT
*   MT = MAG. TAPE OUTPUT
*   BE = RETARDING VOLTAGE OFFSET
*   VP = VOLT. PRINT(YES OR NO,CONTROL)(SR0=OVERRIDE)
*   VT = VOLTAGE RISE TIME DELAY (100=100MS).
*   VM = CHANGE DVM MULTIPLIER
*   RS = RESTORE MCA MEMORY
*   NU = NUMERIC ROUTINE ENTRY
*   FW = ROUTINE TO IDENTIFY PEAKS AND TO COMPUTE FWHM
          1 = ADD A CONSTANT
          2 = SMOOTH,QUADRATIC,CUBIC,9 POINTS
          3 = " " " " 17 "
          4 = DIFFERENTIATE,QUADRATIC, 9 POINTS
          5 = " " " " 17 "
          6 = ADD AND MULTIPLY BY A CONSTANT
*
*   SWITCH REGISTER OPTIONS
SP0 = STOP VP PRINTING
SK1 = DUMP NTH SCAN TO ITY
SPI3= ONE WAY SWEEP ONLY
SR15= DIAGNOSTIC VOLTAGE PRINTOUT OR CONTINUE FWHM ROUTINE

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-735-

A-7 - SAMPLE INPUT DIALOGUE FOR DIGAD

GO=ST

ERASE ?

BE=0EV V4= -1280.63

NR=4

RUN 1

ENTER ID

CARBON 1S/ALUMINUM

WW=20

NC= 512. AT .04EV/CH

MD=2

NC= 255

OK=YES

BE=280

NS=2

VP=YES

RUN 2

ENTER ID

OXYGEN 1S/ALUMINUM

WW=20

NC= 512. AT .04EV/CH

MD=2

NC= 255

OK=YES

BE=530

NS=2

VP=YES

RUN 3

ENTER ID

ALUMINUM 2P

WW=20

NC= 512. AT .04EV/CH

MD=2

NC= 255

OK=YES

BE=70

NS=10

VP=YES

RUN 4

ENTER ID

ALUMINUM VALENCE BAND

WW=40

NC= 1024. AT .04EV/CH

MD=1

NC= 1023

OK=YES

BE=0

NS=50

VP=YES

A-8 - DATA TREATMENT

As mentioned in Chapter III, DIGAD and AUGER, the system programs for the HP #5950A electron spectrometer, allow for some preliminary on-line data treatment such as smoothing, differentiation and estimation of peak position and width. Once the data is outputted onto magnetic tape, the data can be further analyzed on the CDC 7600 computer at LBL with several programs. The two programs which have been primarily used in data analysis are GAMET and HTUNA. GAMET is a modified version of SUNDER^{1,2} which allows least squares fitting of peaks with Gaussian, Lorentzian, or mixed Gaussian-Lorentzian line shapes. It has been particularly useful in estimating satellite splittings and peak area ratios in cases of multiplet splitting. The program HTUNA³ was used to subtract background and plasmon satellites in a manner similar to that described in Ref. 1 and for adding spectra together. The background and plasmon subtraction was very useful in analyzing valence bands. In any case, one must be careful not to subtract real information. The choice of background is particularly problematic in the case of metals which have asymmetric core-levels and extended tails due to electron-hole interactions. Another useful approach to data analysis but one which was not used in these studies is the deconvolution of the spectrometer line shape from the measured spectrum.⁴⁻⁶

A-8 - References

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A-9. MISCELLANEOUS SPECTRA

In the course of these studies, all of the accessible core-levels and Auger transitions were normally obtained from each material investigated. This appendix is a miscellaneous compilation of some XPS core-level and valence band spectra, as well as, some X-ray excited Auger spectra obtained in these studies.

FIGURE CAPTIONS

Figs. 1 through 10. The 4s4p spectra of the elements: Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, and Te, respectively.

Figs. 11 through 19. The 4p spectral region of the metals: La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, and Lu, respectively.

Figs. 20 through 28. The 4p spectra region from the metals: Ta, W, Re, Ir, Pt, Au, Tl, Pb, and Bi, respectively.

Fig. 29. The 5p spectrum of Au metal.

Fig. 30. The 5p spectrum of Tl metal.

Fig. 31. The 5p spectrum of Pb metal.

Fig. 32. The 5d spectrum of Bi metal.

Figs. 33 through 42. The 3s3p spectra of the transition metals: Sc through Zn, respectively.

Figs. 43 through 49. The 2s2p spectra of the metals: Sc, Ti, V, Cr, Mn, Fe, and Co, respectively. The spectra of Fe and Co also exhibit LMM Augers in this region.

Fig. 50. The Co metal 2s spectrum.

Fig. 51. The Ni metal 2s spectrum.

Figs. 52 through 54. The 2p spectra of Co, Ni, and Cu, respectively.

Figs. 55 through 61. The LMM Auger spectra from Ti, V, Cr, Mn, Ni, Cu, and Zn, respectively.

Fig. 62. Sodium (metal) 2s2p spectrum. Note the surface and bulk plasmons.

Fig. 63. Sodium (metal) and Li (metal) 1s spectra with plasmons.

Fig. 64. Aluminum (metal) 2s2p spectrum with plasmons.

Fig. 65. Si 2s2p spectrum.

Fig. 66. Si 2s spectrum.

Fig. 67. Si 2p spectrum.

Fig. 68. Ga 3s spectrum.

Fig. 69. Ga 3p spectrum.

Fig. 70. Ga 3d spectrum.

Fig. 71. Ge 3s3p spectrum.

Fig. 72. Ge 3d spectrum.

Fig. 73. As 3s3p spectrum.

Fig. 74. As 3d spectrum with plasmons.

Fig. 75. As 3d spectrum.

Fig. 76. Sn 3p spectrum.

Fig. 77. Hg (liquid) 4f spectrum.

Fig. 78. Hg (liquid) 5d spectrum.

Fig. 79. Bi 4f spectrum.

Figs. 80 through 84. The F 1s spectra from LiF , MnF_2 , CoF_2 , NiF_2 , and ZnF_2 , respectively.

Fig. 85. Spectrum of outermost levels in LiF_2 .

Fig. 86. Spectrum of outermost levels in CoF_2 .

Fig. 87. Spectrum of Co 3s3p levels in CoF_2 .

Figs. 88 through 92. Spectra of sodium KLL Augers in Na metal, NaF, NaCl, NaBr, and NaI, respectively.

Fig. 93. Mg metal KLL and KLV Auger spectrum.

Fig. 94. Mg metal KLV Auger spectrum.

Fig. 95. Mg (MgO) KLL Auger spectrum.

Fig. 96. F KLL Auger, Mn LMM Auger, and F 1s spectrum from MnF_2 .

Fig. 97. F KLL (CoF_2) Auger spectrum.

Fig. 98. $L_{5/2} M_{45} M_{45}$ and $L_2 M_{45} M_{45}$ Auger spectra from Zn and Cu metals.

Figs. 99 through 102. Zn LMM Auger spectra from ZnF_2 , ZnS, ZnO, and ZnTe, respectively.

Figs. 103 through 105. LMM Auger spectrum from elemental Ge and As.

Figs. 106 through 109. $M_{5/2} N_{45} N_{45}$, $M_4 N_{45} N_{45}$ Auger spectra from elemental Pd, Sn, Sb, and Te, respectively.

Fig. 110. VBDOS of AlSb.

Fig. 111. VBDOS and outermost d-levels from several $\text{Pb}_x \text{Sn}_{1-x} \text{Te}$ alloys. The Sn Te spectrum is severely distorted due to oxygen.

Fig. 112. VBDOS of several $\text{Pb}_x \text{Sn}_{1-x} \text{Te}$ alloys. The Sn Te spectrum is distorted by oxygen.

Fig. 113. MO and K 2p region of $\text{K}_3\text{Fe}(\text{CN})_6$.

Figs. 114 through 118. The VBDOS of the intermetallics, $\text{Au}_4 \text{V}$, $\text{Sc}_3 \text{In}$, Co Pd (4% Co), α -Brass (30% Zn, 70% Cu), and ZrZn_2 .

Fig. 119. Ga 3d and As 3d spectrum from a heavily oxidized amorphous Ga As sample prepared by sputter deposition. Note the As is preferentially oxidized over Ga, as shown by the oxide to metal ratio for the As and Ga 3d's.

Fig. 120. Ti 2p (TiO_2) spectrum.

Fig. 121. Ti 3s3p and O2s (TiO_2) spectrum.

Fig. 122. Sr 3p (SrTiO_3) spectrum.

Fig. 123. Sr 3d (SrTiO_3) spectrum.

Fig. 124. Ti 2s and Ti 2p (SrTiO_3) spectrum.

XBL 761-2157

Fig. 1

Fig. 2

NBL 762-2268

Fig. 3

Fig. 4

XBL 7510-8524

NBL 762-2266

Fig. 5

Fig. 6

XBL7510-8532

Fig. 7

XBL7510-8632

XBL7510-862

Fig. 8

Fig. 9

XBL 7510-8623

Fig. 10

XBL 7510-8624

Fig. 11

XBL 763-760

Fig. 12

XBL 763-778

Fig. 13

XBL 763-777

Fig. 14

XBL 763-776

XBL 763-775

Fig. 15

XBL 763-774

Fig. 16

Fig. 17

NBL 763-772

Fig. 18

XBL 763-773

Fig. 19

NBL 763-771

Fig. 20

XBL7510-8527

XBL7510-8628

Fig. 21

Fig. 22

Fig. 23

XBL7510-8526

Fig. 24

XBL 7511- 8682

Binding energy (eV)

Fig. 25

Fig. 26

XB_7510-8636

Fig. 27

XBL 7510 - 8622

Fig. 28

XBL7511-8679

Binding energy (eV)

Fig. 29

XBL 764-994

Fig. 30

XBL 7510 - 8625

Fig. 31

XBL7510-8528

XBL7511-8677A

Fig. 32

Fig. 33

XBL758 - 3824

Fig. 34

XBL 758-3823

Fig. 35

XBL758-4043

Fig. 36

Fig. 37

XBL758-3850

X8L758-4040

Fig. 38

Fig. 39

XBL759-3844

XBL758-4044

Fig. 40

Fig. 41

XBL 763-2447

Fig. 42

Fig. 43

XBL 758 - 3825

XBL758-3821

Fig. 44

Fig. 45

Fig. 46

XBL 758-3847

Fig. 47

XBL758-3848

Fig. 48

Fig. 49

XBL758-3846

Fig. 50

Fig. S1

XBL7510-4155

XBL758-3851

Fig. 52

XBL7510-4158

Fig. 53

XBL7510-8640

Fig. 54

XBL 758 - 3820

Fig. 55

Fig. 56

XBL 758-4045

XBL758-4041

Fig. 57

XBL 758-3849

Fig. 58

Fig. 59

XBL7510-4152

Fig. 60

XBL7510-8511

Fig. 61

NBL 734-7752

Fig. 62

Fig. 63

Fig. 64

-808-

NBL 761-2151

Fig. 65

NBL 761-2155

Fig. 66

Fig. 67

NBL 763-720

Fig. 68

XBL7510-8530

Fig. 69

XBL 7511-8680

Fig. 70

NBL 7h2-2270

Fig. 71

XBL7510-8626

Fig. 72

XBL 7510-8629

Fig. 73

Fig. 74

XBL7510-8523

Fig. 75

Fig. 76

XBL7510-8522

XBL7510-8531

Fig. 77

Fig. 78

XBL 761-2152

Fig. 80

Fig. 81

XBL7510-4175

Fig. 82

XBL 757-3408

XBL 757-3407

Fig. 83

XBL7510 - 8509

Fig. 84

XBL757-3403

Fig. 85

XBL7512-3945

Fig. 86

XBL 7512-3943

Fig. 87

Fig. 38

Fig. 89

XBL7510-8508

Fig. 90

XBL7510-8500

Fig. 91

XBL7510-8503

Fig. 92

XBL7311-4436

Fig. 93

Fig. 94

Fig. 95

Fig. 96

XBL7512 - 3944

Fig. 97

XBL7212-4680

Fig. 98

Fig. 99

Fig. 100

XBL7510-8525

Fig. 101

XBL7510-8504

Fig. 102

XBL7510 - 8512

Fig. 103

XBL7510 - 8639

NBL 762-2265

Fig. 104

Fig. 105

XBL 7510-8630

XBL 764-992

Fig. 106

Fig. 107

XBL 764-1223

Binding energy (eV)

Fig. 108

Fig. 109

XBL 764-1224

XBL 757-3456

Fig. 110

XBL 75/7 5594

Fig. 111

Fig. 112

XBL 757-3593

Fig. 113

XBL 757-3416

Fig. 114

Thousands of counts

Binding energy (eV)

Fig. 116

NBL 761 999

Thousands of counts

Fig. 117

NBL 764 1001

Thousands of counts

Fig. 118

Fig. 119

NBS 764 (1984)

-363-

Fig. 120

XBL 757-3411A

XBL 757-3397

Fig. 121

XBL 757-3457

Fig. 122

XBL 757-3399

Fig. 123

XBL 757-3404

Fig. 124