MASTER

**DETERMINATION OF MORPHOLOGY AND ELECTRONIC STRUCTURE
IN SOLIDS WITH 20-1000 eV RADIATION**

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ABSTRACT

One of the most versatile probes for spectroscopy is the photon because it is readily tuned through a wide range of frequencies, it is chargeless, and because of the additional information available from its vector nature. With the advent of intense radiation light sources a nearly untouched region of the spectrum has become available for a wide range of new experiments. Two of the main techniques in use are those of absorption and photoemission. This thesis uses these techniques on a variety of different materials for the analysis of their morphology and electronic structure. The principles underlying the techniques of soft-x-ray absorption, bulk-, and surface-photoemission are discussed together with some of the experimental methods and instrumentation.

The absorption in the extended region of the spectra (EXAFS) is discussed as a technique for structural analysis for: the $L_{II,III}$ -edge in Ti; the K-edge in microcrystalline, polycrystalline, and monochromator graphite; and the fluorine K-edge of the polymer polyvinylidene fluoride (PVF₂). The first experiment to use photoyield spectroscopy for an EXAFS structural analysis from a surface is discussed for a surface of oxidized aluminum. The near-threshold absorption spectra for the Ti L-edges, the Ag $M_{IV,V}$, the graphite C

VI

K-edge, and the C K-edge in PVF_2 are discussed with respect to their electronic structure. An attempt to show that the absorption is paralleled in the symmetry-allowed component of the empty density of states is fairly successful. However, additional complications are found to arise from atomic-like matrix element effects, large variations in the hole lifetime, and excitonic effects. Examples from the L-edge photoyield of Fe and Cu are also considered. The electronic structure analysis of surfaces and interfaces is discussed using the system GaAs/Ge. Band discontinuities are measured and the unique power of angle resolved photoemission is used to measure the energies and dispersion of states precursive to the formation of GaAs/Ge heterojunction interface states. Bulk photoemission is exploited in Ag(III) to map the valence band dispersion relations along Λ .

CHAPTER 1. INTRODUCTION

Investigations into the structure and electronic properties of matter have advanced enormously in the past decades, spurred on by a variety of innovations in spectroscopy. One of the most versatile probes for spectroscopy is the photon because it is readily tuned through a wide range of frequencies and because of the additional information available from its vector character. For questions of structure in solids, X-rays are chosen because their wavelengths are comparable to the distances characteristic of atom-atom spacings in solids. For questions of electronic structure, the characteristic energy for bandwidths and for interband distances is in the visible to ultraviolet region. In this case the common spectroscopies are photo-emission and absorption.

Absorption spectroscopy of visible or ultraviolet wavelengths arises from interband transitions and reveals some details of electronic structure, but there are drawbacks. First of all, there is no way to select from among a large number of possible initial states, each with its own momentum and energy. In other words, for crystalline solids, initial states are averaged through the Brillouin zone. Most importantly, absorption spectra must reflect a joint density of states where the initial states themselves show a great degree of structure so that separating the effects of initial and final states is difficult.

At higher photon energies (≥ 20 eV), one can begin to probe deeply-bound core states¹ which has two advantages. The energy widths of core levels are small (< 1 eV through the first row of the

transition series)² so that in a core level spectrum the final state energy being probed is well-defined. Also, since the initial state has a well-defined angular momentum, the final states that are measured will come only from that portion of the density of states projected into the angular momenta allowed by optical dipole selection rules. This effect was exploited recently by Müller et.al.³ However, some complications must ordinarily be taken into account because of relaxation effects as will be discussed later.

As a tool for structural studies, X-ray diffraction has done enormous service for many years. Here, a plane wave of X-ray radiation strikes a sample. If, as in crystals, there are ordered arrays of planes of spacing d_{hkl} , then there will be an intense beam of diffracted radiation when $n = 2d_{hkl} \sin \theta$ where θ is the angle with respect to the scattering plane. While the resulting set of diffraction intensities can be used to infer an atomic structure, the loss of the phase information results in ambiguities. This is the well-known "phase problem" of X-ray diffraction.⁴ Also, X-ray diffraction basically involves scattering from electron density and does not discriminate among the different atomic sites, and this ambiguity further complicates a structural determination.

A method that is complementary and sometimes superior is core-level spectroscopy in the extended region of the absorption spectrum. Otherwise known as EXAFS, it is also the result of a wave interference effect. The result of core-level absorption is an outgoing electron wave which encounters concentric shells of neighbors at distance R_i . A certain amount of wave amplitude will be backscattered from a

given shell and return to the central site. If the return wave is in phase with the outgoing wave, the result is enhanced absorption, while if they are out of phase, the result is decreased absorption. It is usually correct to exclude the possibility of more than one scattering event occurring, thus a simple relation⁵ is obtained in terms of the electron energy, atomic scattering factors, and factors for thermal effects and electron attenuation. Two important advantages of EXAFS are that (1) the spectrum is specific to the neighborhood of an atom from whose core we are exciting an electron, and (2) a material does not need to have long-range order.

For some problems, absorption measurements are inconvenient since they actually detect the light which failed to excite the solid and was transmitted. However, any technique that directly measures the final state resulting from photon absorption has inherently higher sensitivity. For photon energies greater than the work function, the absorbed photon can excite electrons to unbound states above the vacuum level, and with a suitable electron detector the state resulting from photon absorption can be probed. The resulting sensitivity makes photoemission attractive for a wide range of studies.

It is convenient to distinguish two types of photoemission: bulk and surface. Since the photon momentum in the region of interest is small compared to Brillouin zone dimensions, the direct interband or momentum conserving theory is usually a good approximation for bulk absorption. In this case, if the final-state momentum is measured, and the proper corrections are made for the effects of electron refraction at the surface, then a detailed picture of the dispersion

relations $E(k)$ in the initial bands can be drawn if final states are well-known or vice versa. In fact, angle-resolved photoemission (ARP) has demonstrated this capability on numerous occasions in the recent literature.⁶⁻⁹

The above theory assumes that the surface effects are negligible. This is not the case for several reasons. The wavefunctions for the bulk must be modified by the abrupt termination of the solid and there are corresponding changes in the charge density and transition matrix elements affecting absorption and photoemission intensity. Such enhancements of charge density and photoemission intensity are referred to as resonances, especially when they can be associated with genuine surface states at nearby values of electron momentum.

Surface states arise as single particle solutions of Schrodinger's equation for a solid whose translation symmetry is broken in one direction by the solid-vacuum interface. For the ideal case of a plane termination of the solid, momentum parallel to the surface, $k_{\parallel}$, is a conserved quantity. These states can exist at some energy and $k_{\parallel}$ for which no itinerant states exist for any value of momentum in the perpendicular direction. They have charge density mainly in the first few layers of the solid and decay both outward and into the solid.

While below the vacuum level bulk resonant states and surface states are observed, the conditions for their existence above the vacuum level are rather restrictive. They can exist for low energies, but for $E \geq \hbar^2 k_{\parallel}^2 / 2m$, surface states are degenerate with free electron states (Fig. 1). They must become resonances with high amplitude

in the surface layer and decay into the bulk, but persist in the vacuum at decreased amplitude. In a similar manner, erstwhile bulk resonances must also persist into the vacuum. Such surface resonances and their dispersion relations $E(k_{\parallel})$ have been measured by electron reflection¹⁰ from Ni(100). In photoemission, the surface resonances should be observed during excitation into a final state band gap. If the initial states were somewhat broad, then a peak in the energy distribution curve would appear whose kinetic energy was independent of photon energy. Such a phenomenon has not yet been reported.

The above discussion is all within the single-particle framework. The importance of collision processes is considerable since the generally short mean free path for electrons is the cause of the celebrated surface sensitivity of photoemission. The effect of electron attenuation is included by introducing an imaginary component to the electron wavevector to effectively damp the electron wave. The results are that the translational symmetry breaking at the surface becomes more important as the damping increases and that the surface acts as a source/sink of momentum. Even in the case of "bulk" emission, the momentum conservation requirements in $k_{\parallel}$ become relaxed, producing a surface projected (or "one-dimensional") density of states, $N(E, k_{\parallel})$. A number of monographs are available to amplify most of these points.^{11,12,13}

The purpose of this thesis is to demonstrate the application of the above principles toward the analysis of morphology and electronic structure in a variety of materials. Chapter 2 contains a discussion

of the relevant instrumentation, especially those devices and techniques that were put to use for the first time in the experiments described here. Chapter 3 describes EXAFS measurements of titanium metal, while Chapter 4 contains a structural analysis in three graphite materials and in the piezoelectric, pyroelectric polymer polyvinylidene fluoride (PVF_2). Chapter 5 describes the first attempt to use photoyield spectroscopy for EXAFS structural analysis at an oxidized aluminum surface.

The application for absorption spectroscopy for electronic structure analysis (ASESA) is considered in Chapters 6 and 7 for the cases of transition metals and graphite, respectively. Photoemission is applied as a tool for measuring the dipole layer formation and band discontinuities in heterojunction systems in Chapter 8. Also in Chapter 8, angle-resolved photoemission is exploited in for the measurement of energies and dispersion of $k_{\parallel}$ of states precursive to the formation of interface states. Total momentum is found to be well conserved for photoemission from $\text{Ag}(111)$ in Chapter 10 so that the band dispersions can be mapped, although added complications are noted and discussed.

The general plan of the thesis is in three parts. Part I contains the preliminary remarks of Chapters 1 and 2. Part II is a discussion of structural analysis in the low-photon energy regimes encompassed by Chapters 3 through 5. The measurement of electronic structure via absorption and photoemission in the photon energy range 20-1000 eV is the concern of Part III, Chapters 6 through 9.

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FIGURE CAPTION

1. Schematic of the regions of $k_{\parallel}$ for which plane wave states exist.

In the shaded region of E and $k_{\parallel}$ there is an (itinerant) vacuum state for some $k_{\perp}$, so that a true surface state cannot exist.

Below the shaded region, surface states can exist if states itinerant in the bulk are absent. The zero of energy is the vacuum level.

Fig. 1.

XBL 797 - 2297

CHAPTER 2. EXPERIMENTAL METHODS AND INSTRUMENTATION

The last chapter gave a general discussion of which types of measurements were made, and this chapter contains a more detailed discussion of what is actually measured and the apparatus with which it is done. The instrumentation used for photoemission has been abundantly described previously¹ and will be sketched only briefly here. On the other hand, new instrumentation was developed in order to make the absorption measurements in this photon energy range feasible and will receive greater attention.

Because of the extremely short absorption lengths for photons in the 12-600Å wavelength range because of the even shorter mean-free paths for low energy (~100 eV) electrons, and because of the vacuum requirements of the synchrotron light source, all experiments had to be carried out under ultra-high vacuum (UHV) conditions. This generally involved the use of stainless-steel vacuum chambers, titanium sublimation and triode ion pumps. Ultimate operating pressure (2×10^{-10} torr or lower) are only obtained after heating the chamber at ~200°C for a period of twenty four hours or more.

A. Photoemission Measurements and Instrumentation

The simplest photoemission experiment is made by measuring the current leaving the sample for a given photon energy. However, much more information is obtained by analyzing the outgoing electrons according to their energy, and considerable improvement in sensitivity is available by introducing an electron multiplier (with gains of 10^6) at the collector.

Typical analyzers are electrostatic condensers that cause the electrons emitted from the sample to follow curved trajectories. The particular trajectory that is followed is determined by the kinetic energy of the electron as measured from the macroscopic potential of the analyzer. By interposing an exit slit at some point after the analyzing plates, energy analysis is achieved. The macroscopic potential of an electron in the analyzer can differ from the potential of an electron at rest "at infinity" (the "vacuum level") so that there is generally an offset in the kinetic energy of an electron as it would be measured from the vacuum level. These differences in potential arise from the spectrometer being attached to different materials having different chemical potentials which forces a transfer of electrons from one material to another and a corresponding change in electrostatic potential. This is termed the "contact potential" and it will also be found between the analyzer and a sample being studied. As a result, there will be a small electric field between the sample and the analyzer. It is obvious from the schematic depiction of the measurement setup in Fig. 1 that the binding energy E_B of a given level with respect to the Fermi level is²

$$E_B = h\nu - E'_{kin} - \phi_{sp} \quad (1)$$

where the photon energy $h\nu$ is known and the kinetic energy in the analyzer, E'_{kin} , is measured. A separate measurement of the

spectrometer work function, ϕ_{sp} , is ordinarily not made since the energy of the Fermi level $E'_{F,kin}$ is usually obtained in the course of the measurement so

$$E_B = E'_{F,kin} - E'_{kin} \quad (2)$$

The main analyzers in use today are spherical-sector condensers, cylindrical-sector condensers, plane mirror analyzers and cylindrical mirror analyzers (CMA). The photoemission measurements reported here were performed with a modified PHI 15-255G cylindrical mirror analyzer with a coaxial electron gun. Any electron injected into the analyzer follows a trajectory given essentially by two capacitors. The angle of injection is 42.3° , (Fig. 2) which yields double focussing.³ Since the analyzer has cylindrical symmetry about an axis defined by the focal point and exit aperture, a wide range of azimuths are accepted by the CMA and a high luminosity is obtained. However, for the experiments reported here, a mask at the CMA entrance is employed to gain angle-resolving capability at the expense of luminosity.

B. Absorption Measurements

A detector system for absorption measurements in the soft x-ray region using high-flux synchrotron radiation should satisfy the following requirements:

- (1) High count rate capability.
- (2) Low dark current.
- (3) Short response time.
- (4) Ultra high vacuum compatibility.

(5) Large and monotonic quantum efficiency over energy range of interest.

(6) Suppression of higher order radiation.

A system which satisfies the above requirements is shown in Fig. 4. The incident radiation struck on a photocathode which can be interchanged in situ. The emitted electrons were collected by a channel electron multiplier (CEM). A Galileo high current CEM No. 4730 was used which can be operated at electron gains between 10^2 and 10^6 and exhibits a linear response up to output (anode) currents of 10^{-5} A. A well insulated adjustable battery box provided the anode voltage V_3 and an effective ground for the picoammeter input. The output of a high speed picoammeter was fed into a Datel VFL-10K voltage to frequency converter which is linear to 0.005%. A multichannel analyzer was used for data storage.

The system shown in Fig. 4 is designed for a photon flux of $10^7 - 10^{13}$ photons/sec. For illustration purposes, assume a flux of 10^{10} photons/sec. Typical quantum efficiencies in the soft x-ray range (4keV) lie around 10% which yields a cathode current of $\sim 10^{-10}$ A. Operating the CEM at a gain of 10^4 produces an anode current of $\sim 10^{-6}$ A. Thus, by adjusting the gain in the range $10^2 - 10^6$ photon fluxes in the $10^7 - 10^{13}$ photons/sec range can be detected with output currents in the $10^{-5} - 10^{-7}$ A range. The dark current of the detector system is determined by the battery box and was found to be 1×10^{-11} A. The response time was limited by the 30 millisecond rise time of the picoammeter. Typical CEM voltages during operation are

$$V_1 \approx 100 \text{ V}, +1\text{kV} < V_2 < +3\text{kV} \text{ and } V_3 = (V_2 + 100)\text{V}.$$

The quantum efficiency (QE) of a detector system is one of the most important parameters. For absorption experiments extending over a certain energy range (typically 500 eV for EXAFS) it is advantageous if not essential that the QE is large and a smoothly varying function. Furthermore, if the detector has a lower QE outside the energy range of interest it automatically discriminates against higher order radiation or stray light. As discussed below these are important features of the detector system shown in Fig. 3.

As discussed in detail by Gudat⁴, the QE of a material at an incidence angle θ from the surface is given by:

$$\text{QE} = f(\hbar\omega) g(\phi) (1-R(\theta)) \mu(\hbar\omega) L/\sin\theta_r \quad (3)$$

Here $f(\hbar\omega)$ is a smoothly varying function with photon energy (roughly proportional to $\hbar\omega$), $g(\phi)$ is a material-dependent function which increases with decreasing work function ϕ , $R(\theta)$ is the angle-dependent reflectivity, μ the absorption coefficient,⁵ L the effective electron escape depth,⁶ and θ_r the angle of the refracted x-ray beam⁷ from the surface. Eq. (1) holds for $\theta > \theta_T$, the angle of total reflection.

Equation (1) tells us which photocathode to choose for a given experiment. In order to obtain a large yield a material should be chosen with a small work function, a large absorption coefficient at the energy of interest and a long effective electron escape depth.⁸

The radiation should be incident at grazing angles slightly larger than the angle of total reflection. Besides the absolute magnitude the energy dependence of the QE is important as discussed above. According to Eq. (3) the energy dependence is basically determined by that of the absorption coefficient. By carefully selecting the cathode materials according to their absorption coefficients it is thus possible to suppress unwanted radiation. For example, in the energy range 750 - 2250 eV CsI should be an excellent cathode material to use. Its absorption coefficient is large⁵ and monotonically⁹ decreasing to higher energy such that higher orders are suppressed. At 750 eV the second order is suppressed by a factor 5, and at 2000 eV by a factor of 6. Table I lists some suitable cathode materials in the range 40 - 4000 eV.

The absorption experiments were carried out using the experimental arrangement depicted schematically in Fig. 4. In order to minimize the effect of variations of the incident photon flux the sample holder could be oscillated up and down to place either the sample or a blank sample holder of equal size into the beam (see Fig. 4). The oscillating motion of the sample holder was coupled into vacuum by means of a stainless steel bellows. A cam outside the vacuum was used to convert the rotary motion supplied by a microprocessor-driven stepper-motor into the required linear oscillation. The raw sample and blank spectra were thus recorded, and the optical density ($\ln I_0/I$) was calculated as a run progressed. The sample holder assembly consisting

of the individual sample holders could be vertically translated as a whole allowing six different samples to be investigated. A picture of the resulting apparatus is given in Fig. 5.

C. Beam Flux Monitors

In practice, the use of the oscillating sample holder to monitor the incident light intensity, I_0 , is satisfactory, yielding fluctuations in the signal level of the order 10^{-3} for 10 seconds counting. However, short term beam fluctuations can still damage a spectrum with "glitches" because the counting for I and I_0 are always done during separate, though nearby, periods. One alternative is to position a partially absorbing surface before the sample to serve as a photocathode to a separate electron detector similar to Fig. 4. Such a monitor has been constructed using high transmission (50-90%) Au grids as the partially absorbing element.

Precautions must be made against yield fluctuations in the case that the beam travels across the grid elements. The synchrotron radiation beam has a roughly rectangular profile with its edges in a horizontal/vertical orientation, and if the grids had a similar orientation, serious fluctuations could occur as one full wire can enter or leave beam upon a small excursion. This problem is minimized simply by keeping the grids at a 45° inclination to the vertical. The resulting setup easily yields near-maximum current (10^{-7} A) while eclipsing only a fraction of the beam. Stability of the monitor is very good but careful studies have not yet been made against a full plate photocathode as to this question and the question of linearity of output between a dual (I and I_0) system.

Table I. Cathode Materials for $40\text{eV} < h\nu < 4000\text{eV}$

Energy Range (eV)	Cathode Material	Reference
40 - 80	Au	1,2
70 - 160	CsI	1,2,6
80 - 340	LiF	1,2,6
100 - 260	Al ₂ O ₃	3,4
170 - 500	ZnS	5
250 - 1100	Au	6
300 - 1400	KCl	6
750 - 2250	CsI	7
1310	MgF	8
1850	SiO ₂	9
2300	Au	7
2600	PbO	7

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9. Note that the main jumps occur at K, L_{III} and M_V absorption edges.

Fig. 1.

(a) Top view

(b) Axial view

Fig. 2.

XBL 797-10736

Fig. 3.

XSL782-240

Fig. 4.

XBB797 9820

Fig. 5.

CHAPTER 3. X-RAY ABSORPTION FINE STRUCTURE ABOVE THE Ti L-EDGE

Recent applications of extended x-ray absorption fine structure (EXAFS) spectroscopy to a wide variety of structural problems have proved it a technique capable of providing unique structural information. The availability of an intense, highly-collimated, variable-energy x-ray photon source at the Stanford Synchrotron Radiation Laboratory (SSRL) has played a major role in the recent revival of interest in EXAFS. Until now, however, EXAFS studies by absorption have been largely restricted to photon energies above 3-4 keV: thus to elements with $Z > 20$. Because this excludes the (chemically most interesting) first- and second-row elements, it is important to extend the EXAFS method to lower energies. It is toward this end that a study on the $L_{II,III}$ edge of metallic titanium foil was undertaken. To my knowledge, this is the first instance in which EXAFS has been observed by photon absorption and analyzed in detail in this energy range.

Absorption measurements in the soft x-ray region between the carbon K-edge (~280 eV) and about 1500 eV pose several problems, and only very few absorption investigations have been reported for this energy range.¹⁻⁶ The main experimental difficulties arise from contamination of the optical elements (mirrors and grating) resulting in low photon fluxes and a high scattered light background.⁴ Another factor which is particularly important for EXAFS studies is the close proximity of absorption edges (carbon at 284 eV, nitrogen at

399 eV, and oxygen at 532 eV) in the soft x-ray range. The short x-ray absorption lengths⁷ in this region furthermore necessitate thin film ($\sim 2000\text{\AA}$) samples.

In contrast to absorption from K-edges, there are actually three L excitations, which can leave a $2s_{1/2}$, $2p_{1/2}$, or $2p_{3/2}$ hole. There are usually labeled the L_I , L_{II} , and L_{III} -edges, respectively. This multiplicity can cause serious interference unless one of the following three criteria is satisfied:

- 1) the spin-orbit splitting is small compared to the period of the EXAFS oscillations;
- 2) the energy separation between edges is larger than the energy range needed to interpret EXAFS (several hundred eV); or
- 3) the successive edges are too weak to interfere.

For high Z elements ($Z > 50$)⁸ the second criterion is fulfilled, and L-edge spectra for the high Z elements Au,⁹ Pt,¹⁰ W and Ta¹¹ have been reported and analyzed. Assuming a value of 10 eV for a typical EXAFS oscillation period the first criterion can be satisfied for $Z \leq 25$ (Mn).⁸ Measurements on such low-Z-element L-edges have been performed mainly by the DESY group.¹² Unfortunately these experiments only extend to about 100 eV about the $L_{II,III}$ -edge and are, therefore, not well suited for an analysis of the EXAFS structure.¹³ Titanium ($Z = 22$) is an intermediate Z element with a L_{III} - L_{II} spin-orbit splitting of 6 eV and a L_{III} - L_I separation of 109 eV.⁸ While the spin-orbit splitting appears small enough not to disturb the EXAFS oscillations, the L_I edge is a priori more problematical. From the systematics of L-edge jump ratios⁷ and

L-edge jump is expected to be less than 20% of the L_{III} jump. We will show below that the L_I jump in Ti is indeed a weak, broad structure which can be removed by a suitable background subtraction procedure.

A. Experimental

The experiments were performed on the 4^o port of Beam Line I at SSRL. The grazing incidence "grasshopper" monochromator has been described elsewhere.¹⁴ Before the present measurements were made, new optical elements were installed to minimize the carbon build-up on the optical surfaces, which occurs on exposure to high fluxes of synchrotron radiation.¹⁵ Measurements of the monochromator transmission indicated the presence of monochromatic radiation up to at least 1400 eV. At the time of these measurements the bandpass of the monochromator was ~ 0.2 , corresponding to ~ 3 eV resolution of the Ti L-edge (455 eV).

The titanium foils are prepared by evaporation. First a thin layer of KCl or NaCl is vacuum evaporated onto a glass plate. Titanium metal is then vacuum evaporated with a electron beam furnace onto the salt film. The titanium film is scored to size and freed from the substrate by dipping the plate into distilled water at an angle of about 30^o to the surface. Finally, the foils, which float off due to surface tension, may be picked up as free foils on suitable frames.

B. Results and Discussion

The experimental transmission intensity through a free-standing 75 $\mu\text{g}(\text{cm})^{-2}$ thick Ti metal foil is shown in Fig. 1. The spectrum was collected in one hour using a Au cathode detector. We have plotted $x = \ln(I_0/I)$, where I_0 is the incident and I the transmitted intensity, as a function of photon energy in the range 435-800 eV. Above the threshold peak, pronounced fine structure oscillations are apparent which extend beyond the 800 eV cutoff of the present measurements. No obvious sharp structure is observed at the expected L_I threshold indicated by an arrow in Fig. 1. A more detailed discussion of the near-edge structure and of the L_I threshold is reserved for Part III. While the L_I contribution to the absorption served to complicate the background associated with the Ti EXAFS, it was nonetheless satisfactorily accounted for by fitting the absorption tail to a (low-order) polynomial spline function.

It is worth noting at this point that background subtraction in an EXAFS spectrum must be done carefully, and there appears to be no completely rigorous, unique way to do it. We were very hesitant at first to make a background correction and particularly to correct for the L_I -edge, for fear of biasing the results of our analysis. It turned out, however, that the main features in the results were insensitive to the details of this correction provided that a "stiff", or low-order polynomial, spline function was used. The final choice of background could be made by demanding that the spurious low frequency signal be minimized. This insensitivity is aided by the relatively low 2s photoelectric cross section.

The spectra well above the absorption edge, together with the smooth background for the $L_{II,III}$ -edge, plus the L_I edge structure, can be seen in Fig. 2 as the top and middle curves, respectively. In addition to the sharp initial peak and the gradual decrease in absorption strength, fine structure oscillations are apparent. These oscillations are peculiar to molecular and condensed phase systems and are not observed in atomic absorption. For atomic absorption the core electron is photoexcited to an outgoing spherical wave

$$\chi_o(\vec{r}) = \sum_{\ell m} A_{\ell m} h_{\ell}^{(1)}(kr) Y_{\ell m}(\Omega) \quad (1)$$

where each component has amplitude $A_{\ell m}$ and h and $Y_{\ell m}$ are the standard hankel and spherical harmonic functions. The effect of the surrounding atoms is to modify the final state by scattering the outgoing electron wave. This is a familiar problem in the field of solid state physics and many methods have been developed for calculating accurate wave functions for solids. However, these methods have not been tested for energies up to 1000 eV above the Fermi level, so this direct applicability is unknown. In addition, a consideration of the infinite lattice is almost certainly unnecessary. Present EXAFS studies do not show evidence of backscattering contributing to the absorption signal from any further than about 5Å distant. The rapid damping is presumably due to the effects of electron attenuation and thermal disorder. For this reason, a cluster-type theory is considered to be sufficient, and one can calculate the change in the absorption coefficient.^{16,17}

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0} =$$

$$\sum_{j_1 m_{o_1} L_1 L'} -4\pi \langle L_0 | \hat{\vec{E}} \cdot \hat{\vec{r}} | L' \rangle Y_{L'}^* (-R_j) Y_{L'}(R_j) \langle L | \hat{\vec{E}} \cdot \hat{\vec{r}} | L_0 \rangle \left(\sum_{m_{o_1} L} |\langle L_0 | \hat{\vec{E}} \cdot \hat{\vec{r}} | L \rangle|^2 \right)^{-1}$$

$$\times \sin(2kR_j + \phi(k)) e^{-2R_j/\Lambda(k)} |f(\pi) \frac{e^{-2\sigma^2 k^2}}{kR_j^2}|$$

where μ is the total absorption coefficient and μ_0 is the atomic portion. The electron wavevector is given by

$$k = 0.5123 (\hbar\omega - E_0 + E_i)^{1/2} \text{ \AA}^{-1}, \quad (2)$$

with energies expressed in eV, where E_0 is the onset of absorption and the inner potential E_i sets the zero of electron kinetic energy. We choose $E_i = 8$ eV here so that $k = 0$ coincides with the bottom of the valence band as determined by photoemission.¹⁸ The excitation is taken to be from a core level of angular momentum $L_0 = (\ell_0 m_0)$, and in the final state one can visualize an outgoing wave L scattered with amplitude $|f(\pi)|$ to an incoming wave L' . The sum over scattering sites j is usually organized into shells J of N_j atoms in each. The harmonic term contains ϕ , which is the total energy-dependent phase shift that an electron experiences upon returning to the central site after backscattering. Thermal oscillations from the equilibrium lattice positions are described by

σ , and λ is the mean electron attenuation length.

Upon specializing to sc, bcc, fcc, or hcp lattices, the result becomes

$$\chi(k) = \frac{(-1)^{l_0}}{k} \sum_{L,J} \frac{N_J}{R_J^2} M_{J,L} |f(\pi)| \sin(2kR_J + \phi) \exp(-2\sigma_J^2 k^2 - 2R_J/\lambda)$$

$$M_{J,L} = \sum_{j \in J} \frac{4\pi}{N_J} |\langle L_0 | \hat{\epsilon} \cdot \vec{r} | L \rangle|^2 |Y_L(\hat{R}_j)|^2 / \left(\sum_{m_0, L} |\langle L_0 | \hat{\epsilon} \cdot \vec{r} | L \rangle|^2 \right) \quad (2)$$

where the parity of the Y_L and the dipole selection rules have been used.

The EXAFS signal, $\chi(E)$, is shown in Fig. 2 (lower curve), and the modulus of the Fourier transform of $k^2 \chi(k)$ is given in Fig. 4. Some of the details of the EXAFS data treatment is given in App. I. In real space the spectrum shows a sharp and symmetric peak at $R = 2.672 \text{ \AA}$, followed by much smaller peaks at approximately 3.9 and 4.8 $\text{\AA}$. These secondary peaks were not easily separated from the background, however. The primary peak is readily assigned to the first shell of neighbors in the titanium hcp lattice. Because titanium departs from the ideal hcp structure ($c/a = 1.588$), the first shell is actually composed of a close doublet (unresolved in our data); six atoms lie in the hcp plane at $R_j = 2.95$ and six out-of-plane neighbors lie at $R_j = 2.90$ (Table I). Because the spectrum is clearly dominated by the first shell, the essential phase shift information can be obtained from a fit of the spectrum to this shell.

We estimated from the Debye formula¹⁹ $(\sigma^2)^{1/2} = 0.0534$. Using a fit to the universal curve²⁰ for the electron mean-free path,

$$\lambda(y) = 43.19 - 22.745y - 5.8044y^2 + 3.6208y^3 \quad (3)$$

where y is the $\log_{10}$ of the electron kinetic energy, measured from the Fermi level, and the functional form adopted by Teo, et al.²¹ for the amplitude function,

$$f(k) = \frac{a}{1+(b(k-c))^2}, \quad (4)$$

we found $a = 0.866\text{\AA}$; $b = 0.696\text{\AA}$; $c = 5.701\text{\AA}^{-1}$; and $\phi = 12.843 - 0.484k$. In expanding $\langle k \rangle$ in powers of k , it was adequate to keep only the linear term. Keeping a quadratic term yielded only a negligible improvement in the fit to the data.

Because of the finite energy cutoff of the EXAFS data, the (Fourier transform) radial distribution function for the first shell contained significant sidebands which interfered with the signal arising from next-neighbor, etc., shells. To extract information about more distant shells, a technique of successive filtering²² was employed. Using the single empirical spatial frequency of 2.672, a fit of the same form as Eq. (1) was made to $\langle k \rangle$ to obtain a spectrum of the fundamental $\chi_1(k)$, the EXAFS signal due only to the nearest neighbors. This was then removed from the spectrum and the filtered signal $\chi' = \chi - \chi_1$ was Fourier-transformed (Fig. 4). The result shows two strong peaks at 3.90 $\text{\AA}$ and 4.80 $\text{\AA}$. These peaks were found to

be quite insensitive to the choice of cut-off point in the spectrum: a good indication that they are meaningful. A phase shift of $\alpha/z = .24$, the same amount required to bring the nearest neighbor Fourier transform peak into registry with the known Ti lattice spacings, will place the two peaks at 4.14Å and 5.04Å. The former corresponds to the second neighbor shell to within 0.01 , and the latter lies close to the doublet (5.08Å, 5.11Å) which constitutes the fourth shell. The third shell consists of only two atoms (Table I), and is expected to yield a signal much weaker than that arising from the first, second, and fourth shells, and probably not strong enough to be distinguishable from the background noise. The strength of the second and fourth shells, while low, is comparable to the intensity seen in the K-edge EXAFS measurements.²³

While the apparent constancy of the phase shift α/z implies that the same type of scattering occurs for all the observed shells, the exact partial-wave character of this scattering remains to be established. For L-edge EXAFS in polycrystalline materials the scattering occurs predominantly via sand d-partial wave states, because the electronic dipole selection rules $\ell \rightarrow \ell \pm 1$ should be nearly exact for excitations from core levels in the solid. It is instructive to compare our derived phase shifts to theoretical values. The total EXAFS phase shift,

$$\phi_{\ell\ell'} = \delta'_{\ell} + \delta'_{\ell'} + \theta, \quad \ell = 0, 2$$

has components δ'_l and δ''_l , associated with the central absorber, arising respectively from the outgoing and backscattered photoelectron waves. The component δ'_l is due to backscattering from neighboring atoms. Only the terms ϕ_{00} and ϕ_{22} will be considered in this analysis, because angle-averaging will eliminate any contributions from ϕ_{02} and ϕ_{20} . Such contributions would otherwise be allowed because the c/a ratio of 1.588 in titanium leads to a nonzero term of $Y_{2,0}$ symmetry in the crystal-field potential. The above relation thus reduces to

$$\phi_{ll} = 2\delta'_l + \theta, \quad l = 0, 2.$$

While ϕ has been calculated previously,²⁴ neither δ'_0 nor δ'_2 was available over the necessary energy range, so theoretical estimates were obtained from a fixed-core Hartree-Fock routine developed earlier by Williams and Shirley.²⁵ The phase shifts were calculated for an isolated Ti^+ atom, retaining unrelated atomic wave functions.²⁶ The theoretical phase shifts are shown in Fig. 5 together with our empirical phase shifts. The results show the empirical phase shift in very good registry with the curve for ϕ_{22} . This would argue for the scattering to occur almost entirely in the $l = 2$ channel, which is also supported by the narrow peakwidths (after accounting for the experimental window) observed in the Fourier transform. Any substantial admixture of s-character would lead to a broader line in the Fourier transform than shown in Fig. 2, or to a splitting into two lines as reported in the L-edge structure of heavy

elements.⁹ We note incidentally that a reinterpretation of those results in terms of structure in the amplitude function $f(\pi)$ has been proposed.²⁷

To put our result in proper perspective, we have also plotted in Fig. 5 ϕ_{11} (calculated in the same manner as ϕ_{00} and ϕ_{22}) and one empirical p-wave EXAFS phase shift from the data of Lytle.²⁸ The theoretical ϕ_{11} is found to be very nearly the mean of ϕ_{22} and ϕ_{00} , in agreement with physical intuition, and the three phase shifts ϕ_1 are in good agreement with previous low energy calculations.²⁹ The discrepancy of nearly $\pi/2$ between the calculated and empirical K-edge phase shift³⁰ indicates that the excellent agreement between ϕ_L and ϕ_{22} is in part coincidental and it serves as a measure of the quality of the state-of-the-art of theoretical phase shift calculation. Guided by these calculations, a model of scattering for which the d-wave contribution is in excess of 80% appears reasonable.

Previous studies have almost exclusively been on K-edge absorption which must have only one final state channel ($l=1$). The work of Lytle et. al.³¹ discouraged making EXAFS measurements from $L_{II,III}$ core levels. Their analysis of Au data seemed to indicate a spectrum with considerable interference from s-wave scattering. However, that analysis did not account for the existence of structure in the back-scattering amplitude function,²⁷ so that structural analysis should be feasible for Au with proper treatment of the data. The results of this analysis are clearly encouraging for EXAFS in the low photon energy range, in general, and for structural analysis from L-edge

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EXAFS in particular. Also, when more reliable theoretical phase shifts become available, it should be feasible to use EXAFS spectra to study the partial wave character of the continuum final states in some detail.

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Table I. Parameters for neighbor shells of atoms in titanium.

Neighbor	Occupancy of Shell	Quality Factor ^a	Distance (Å)	Experimental Distance(Å) ^b
1a	6		2.90	
		12.21		2.91
b	6		2.95	
2	6	3.06	4.13	4.14
3	2	0.79	4.68	—
4a	12		5.08	
		6.05		5.04
b	6		5.11	

^a $N_{\text{shell}}(R_1/R_{\text{shell}})^2$; $R_1 = 2.95\text{\AA}$

^b Given by (observed spatial frequency) + 0.24Å.

FIGURE CAPTIONS

Figure 1. Ti L-edge absorption spectrum. The arrow indicates the L_I transition.

Figure 2. Top curve: Ti L-edge extended fine structure. Middle curve: Background function including a broad L_I absorption feature. Bottom curve: The EXAFS oscillations following subtraction of the background function.

Figure 3. Magnitude of the Fourier transform of $k^2\chi(k)$ (arbitrary units).

Figure 4. Magnitude of the Fourier transform of the once-subtracted EXAFS signal $k^2\chi'$. The peaks at 3.90 and 4.80 are interpreted as real, and are quite insensitive to details of data handling. All the peaks at smaller R values are clearly artifacts because they are closer than the nearest neighbor distance. The peaks marked with arrows are at R values which are sums of two of the three distances 2.67Å, 3.90Å, and 4.80Å, and thus suspect as sum peaks.

Figure 5. The calculated wavevector dependent phase shifts ϕ_{00} , ϕ_{11} , ϕ_{22} (dashed curves) and the empirical phase shifts ϕ_K and ϕ_L (solid curves). The curves are all truncated at $3.0\text{\AA}^{-1}$, and grow more meaningful from left to right.

Fig. 1.

XBL 785-779

Fig. 2.

L 785-884

Fig. 3.

XBL 784-770A

Fig. 4.

XBL 784-769

Fig. 5.

XBL 786-9175A

CHAPTER 4. EXAFS FROM GRAPHITE AND THE POLYMER POLYVINYLIDENE FLUORIDE (PVF₂)

One of the major reasons for interest in extending EXAFS studies below the normal 3kV-25kV range is the prospect of applying the technique to the important elements carbon, nitrogen, oxygen and fluorine. For these elements the only core levels are found below 1000 eV and only recently have absorption measurements been made on C^{1,2}, and F². In addition, C,³ N,⁴ and O^{4,5} have been studied by the related technique of electron energy loss spectroscopy.

In this chapter, I discuss the first absorption measurements taken above the carbon K-edge in a series of graphite samples, and of the polymer polyvinylidene fluoride.

The present results show the feasibility of these measurements and their capability for yielding information that is difficult or impossible to obtain elsewhere. However, there are problems. For many materials the proximity of the low Z absorptior edge will cause difficulties. A short data range automatically decreases the real-space resolution, which goes inversely as the square root of the energy range. Since the neighborhoods of inequivalent atoms in many compounds, alloys etc., may differ only slightly in the distance of its neighbors, this problem will pose a real limitation on the complexity of the systems that can be studied.

A. Experimental

The experiments were performed on the 4⁰ port⁶ of Beam Line I at the Stanford Synchrotron Radiation Laboratory (SSRL). Before the measurements were made, new optical elements were installed to

minimize carbon buildup on the optical surfaces of the grazing incidence "grasshopper" monochromator⁶ which occurs on exposure to high fluxes of synchrotron radiation.⁷ These included a new 600 lines/mm grating blazed to 220 eV. At the time of these measurements the bandpass of the monochromator was $\sim 0.2\text{\AA}$, and measurements of the monochromator transmission indicated the presence of monochromatic radiation up to at least 1400 eV.

B. Monochromator, Polycrystalline and Microcrystalline Graphite

The absorption spectra were taken for three graphitic samples: evaporated carbon foils⁸ with a thickness approximately 50 mg/cm^2 ($2500\text{\AA}$), evaporated carbon foils that were subsequently annealed in vacuum for three minutes at 1100°C , and a thin sample cleaved from a crystal of stress-annealed monochromator graphite.⁹ The three samples differ in crystallite size and orientation. The evaporated foils generally have a crystallite size of $\sim 10\text{-}15\text{\AA}$ and no discernible orientation.¹⁰ For the purposes of our discussion, they will be referred to as microcrystalline. The foils that were subsequently annealed have a crystallite size of $2500\text{\AA}$ as determined by transmission electron microscopy and are known to show preferential ordering with the c-axis becoming normal to the surface plane.¹¹ These samples will be referred to as polycrystalline. The monochromator graphite is a well-ordered mosaic of crystallites, with the basal planes parallel to the surface plane. While the $\vec{a}$ and $\vec{b}$ in-plane crystal axes do not maintain their rotational orientation about the $\vec{c}$ direction throughout the sample, monochromator graphite is otherwise quite similar to crystal graphite.¹²

Spectra near the carbon K-edge are displayed in Fig. 2, and energies of characteristic features A-I are set out in Table I. Features in the polycrystalline and monochromator graphite spectra show a one-to-one correspondence, the edge jump ratio is much smaller in the monochromator graphite case, and absorption above the edge shows nearly zero overall slope. This results from nonuniformities in the thickness of the monochromator graphite, which we were unable to eliminate for a sample of the required dimensions (~5mm diameter). There are also differences between the microcrystalline sample and the other two. For this sample all the features are weakened or broadened, as might be expected in a highly disordered system. I will proceed first to an analysis of the polycrystalline sample.

In Fig. 1, Peak D occurs at $E_F + 40$ eV, on the threshold of the conventional extended x-ray absorption (EXAFS) regime, and might ordinarily be included in the EXAFS analysis. In fact, Peak D probably arises at least in part from simple structural effects, as evidenced by the continued presence of this feature in a weakened form in the ELS results for which the geometry forbids transitions to σ bands. However, as will be seen in Chapter 7, there is a density of states peak at $E_F + 40$ in both calculated and experimental results. Of course, the presence of band structure effects do not preclude obtaining structural information if they are properly accounted for. However, if the final-state energy is high enough (at least above Peak C), detailed band structure effects become less important and the single scattering theory generally holds,^{13,14,15} in which it is sufficient to treat the solid as a collection of atomic potentials.

In general, a radial distribution function can be deduced from the EXAFS data if the effects of phase shifts due to the atomic potentials are compensated. Figures 2 and 3 give plots of the radial distribution function

$$R(r) = |F(r)| = \int dr \frac{e^{-i\phi(k)}}{A(k)} k \chi(k) \quad (1)$$

for polycrystalline and monochromator graphite. The back-scattering amplitude¹⁶ and the phase shift¹⁷ are taken from calculated values. As in the work of Lee and Beni,¹⁵ the inner potential E_i coincide. The best results were obtained in polycrystalline graphite with E_i set 24 eV above the absorption threshold and 19 eV in monochromator graphite. Both curves show residual amplitude near $r = 0$. This is an artifact arising from the limited data range, causing the degree of noncancellation between positive and negative excursions to become serious. The problem is aggravated by the short bond length in graphite.

Table II gives the distances of the different shells in the graphite lattice, together with the number of atoms in each shell. The quality factor $Q = N_j/R_j^2$ serves as a rough measure of the expected weight of a given shell; Q neglects polarization effects, which can be important for oriented samples.¹⁸

The results for $R(r)$ in polycrystalline graphite show a main peak at $1.41 \pm 0.04\text{\AA}$ and three smaller peaks of similar strength above the main peak at 2.54, 3.84, and 4.90\AA. The first peak corresponds quite well to the first nearest neighbor (NN) distance in graphite. The

second is clearly a weighted mean of the second and third NN in the basal plane. At higher distances, the neighbors on the first "neighbor plane" (NPNN) to the basal plane containing the central atom begin to occur in addition to the in-plane nearest neighbors (IPNN). The third peak is expected to be a mean of the fourth through ninth NN, which form a fairly separate grouping of two IPNN and four NPNN. The (unknown) weighting between these two classes of neighbors is dependent upon the degree of crystalline orientation, although the polarization effect between the in-plane and nearest-plane neighbors will be less significant for distances greater than $\sim 4.7\text{\AA}$. The final peak may contain components from as far as the thirteenth NN.

The radial distribution function for monochromator graphite is shown in Figure 2. In this case, a somewhat shorter data set was obtained, which resulted in poorer resolution. Nonetheless, the first NN peak ($1.39 \pm 0.06\text{\AA}$) is obvious and there is a second peak at $3.36\text{\AA}$ which may result from a combination of the second through the ninth NN. In fact, the peak occurs at a value intermediate between a mean weighted simply by the factor q_i in Table II and one neglecting the NPNN altogether. However, the deep minimum between the first and second peaks gives clear evidence of interference of the higher neighbors with the broadened peak from the first NN, which makes further interpretation difficult.

In the microcrystalline spectrum, Fig. 1, two effects appear. All features are considerably lower in amplitude and from the disappearance of peaks E and H together with the removal of the minima between

F and G, it is clear that the higher spatial frequencies are no longer present. In fact, a plot of the remaining maxima and minima in the remaining features clearly suggest that the first MN is virtually the only remaining component.

C. EXAFS From the Fluorine K-Edge in Polyvinylidene Fluoride

The PVF₂ used was obtained from the Pennwalt Corporation as a commercial powdered resin (brand name Kynar). No further purification of the resin was attempted. Thin films were grown by dipping clean glass microscope slides into a 2% (by weight) solution of PVF₂ in reagent-grade tetrahydrofuran. After drying, each film was floated off its slide by dipping it into a water bath. Films so produced were then dried to a constant weight and measured to determine their areas. A small (7mm x 5mm) sample was then cut from each film and mounted on a sample holder. The films were transparent, pin-hole-free, and self-supporting. The above sample-preparation technique is expected to yield semicrystalline PVF₂ films composed primarily of α -phase² (or phase II)^{19,20} crystallites, which have a reported density of 1.93 gm/cm³. Thus, the 97 $\mu\text{gm}/\text{cm}^2$ film used in this study was $\sim 5000\text{\AA}$ thick.

The PVF₂ absorption spectrum in the energy range 780-1000 eV is shown in Fig. 4 along with the absorption curve above the fluorine K-edge predicted using atomic absorption cross-sections.¹⁹ The spectrum is remarkably similar in general appearance to the fluorine K-edge spectra of the fluorinated methanes obtained by La Villa.²¹ Approximating the cross-section of fluorine at the maximum absorption as 0.95 Mb (half the maximum cross-sections for CH₂F₂ yields an

optical density value of $\mu x = 2.0$ for the peak height in Fig. 4a. The observed value of 1.45 for the optical density is in good agreement with this prediction from gas phase results.

The main feature of interest in this spectrum is the modulation above the fluorine K-edge, which is shown in an expanded plot in Fig. 4b. In principle, such EXAFS oscillations could yield accurate inter-atomic distances in the polymer chain. These distances are extremely important in determining the space group of a crystal and the unit-cell dimensions, then finding the best cell and chain structures that are compatible with the X-ray data, using tabulated collections of bond lengths.²² Clearly, a superior structure may be determined if one knows the actual bond lengths of the material studied.

Figure 5 shows a plot of the radial distribution function from Eq. 1. Factors have been included to compensate for the backscattering amplitude¹⁶ and the phase shift.¹⁷ It has already been noted that the work of Lee and Beni¹⁵ suggests that the inner potential, E_i , should be adjusted until the peaks in $R(r)$ and $\text{Im } F(r)$ coincide. We note that this rule is valid only if the separation between neighbor shell distances sufficiently exceeds the peak half-width (which results from the finite data range). In fact, a calculation shows that for an experimental data window extending from k_1 to k_2 , the radial distribution function from a doublet of close neighbor shells at distances r_1 and r_2 will result in an unresolved peak if $r_2 - r_1 \approx \pi(k_2 - k_1)$. As we describe below, the rule of Lee

and Beni breaks down in our PVF_2 measurements for all shells beyond the first. Accordingly, we chose $E_1 = 5$ eV, to bring the first peak in $R(r)$ into line with the corresponding peak in $\text{Im } F(r)$.

The first peak corresponds to the F-C bond distance, which was assumed in previous X-ray work²⁰ to be 1.34 Å. The value found in the present work is 1.38 ± 0.02 Å. This value was obtained using as the fluorine-to-carbon back-scattered-phase function¹⁷

$$\phi = -6.050 - 1.0882k + 0.0323k^2 \quad (3)$$

where k is given in units of $\text{\AA}^{-1}$. The second peak at 2.45 ± 0.08 Å consists of contributions from several further neighbor shells. The model of Hasegawa et al.²⁰ yields nine higher neighbor shells in the polymer chain at distances below 3 Å (at greater distances there will also be interchain neighbors). Because the overall amplitude dependence of the EXAFS signal¹⁵ goes roughly as

$$Q_i = N_i / R_i^2,$$

certain deductions can be made about the nearby structure by comparing a mean of the secondary and tertiary neighbors (see Table III) weighted by Q_i to the observed peak position. There may be a decrease in the long-range order for a significant fraction of the PVF_2 sample beyond the secondary shell. In the tertiary shell this could occur through a decrease in the effective Debye Waller factor, $e^{-2\sigma_k^2}$, an increase in $\sigma_{\text{tertiary}}^2$, or by the existence of

disorder in the dihedral angle between tertiary neighbors. The expected results of such disorder would be to "wash out" the high end of the secondary-tertiary distribution, thereby shifting the peak to lower values compared to the "ideal" mean, which was computed₂₃ to be 2.42Å. That this is not at all the case implies that strong ordering exists in PVF₂ through the tertiary neighbor shell. All of the remaining peaks are much weaker and too dependent in their positions upon the details of the background subtraction to make a reliable interpretation.

The presence of disorder in PVF₂ is quite evident in comparing its X-ray diffraction patterns to those of any well-ordered crystal. However, there is clear evidence in the present measurements that the estimate of the thermal disorder ($\sigma^2 = 5\text{\AA}^2$ by Hasegawa et al.)²⁰ is much too great. In fact, a fit of the data with the modified distances in Table I yields a least-squares fit for $\sigma^2 \approx 0.07\text{\AA}^2$. A more accurate value could be obtained with a more accurate structure.

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Table I. Comparison of carbon K-edge absorption to ELS and SEE measurements and to the calculated density of states.

Feature	Absorption (eV)	ELS (eV)	SEE ^a (eV)	Calcd DOS (eV)
A	285.	285.		2.0
B	293	293.	9.5	9.9
C	302.	304.	19.2	18.3
D	325.	325.	40.7	42.0
E	344.			
F	362.	356.		
G	381.	380.		
H	403.	400.		
I	423.	422.		

^a The SEE results and the calculated density of states should be compared by adding the threshold energy (285 eV).

Table II. Parameters for neighbor shells of atoms in graphite

Neighbor	Occupancy of N_j	Quality ^a factor Q	Distance $R_j(\text{\AA})$
1	3	3.0	1.421
2	6	2.0	2.461
3	3	0.75	2.842
4	1	0.18	3.354
5	9	1.37	3.642
6	6	0.86	3.750
7	6	0.70	4.160
8	6	0.5	4.263
9	9	0.94	4.396
10	6	0.5	4.922
11	18	1.43	5.038
12	6	0.46	5.123
13	6	0.41	5.424
14	3	0.19	5.684

$$^a N_{\text{shell}} (R_1 / R_{\text{shell}})^2; R_1 = 1.421 \text{\AA}$$

Table III. PVF₂ Neighbor Frequencies from the Model of Hasegawa,
et al.

Neighbors	Bond Connection	Distance A	Number, N _i per F absorber ^b	Quality Factor ^c
F to C	direct	1.34(1.38)	1	1.00
F to F	secondary ^d	2.10(2.16)	1	0.41
F to C	secondary	2.24(2.27)	0.5	0.18
F to C	secondary	2.35(2.38)	0.5	0.16
F to C	secondary	2.36(2.39)	0.5	0.16
F to C	secondary	2.39(2.42)	0.5	0.16
F to F	tertiary ^e	2.70(2.70)	0.5	0.13
F to C	tertiary	2.76(2.77)	0.5	0.066
F to C	tertiary	2.85(2.87)	0.5	0.064
F to C	tertiary	2.95(2.99)	0.5	0.057

^a) Parenthetical values are the values that result from assuming an increase of the F-C bond length from 1.34 to 1.38 .

^b) There are two inequivalent F absorber sites.

^c) Quality factor $Q_i = N_i (1.38/R_i)^2$.

^d) That is, two bonds "distant" from each other.

^e) Three bonds "distant" from each other.

FIGURE CAPTIONS

- Figure 1. Absorption spectra for graphite in the (top) monochromator, (middle) polycrystalline, and (bottom) microcrystalline forms.
- Figure 2. The radial distribution function from the polycrystalline graphite EXAFS data.
- Figure 3. The radial distribution function from the monochromatic graphite EXAFS data.
- Figure 4. (a) Absorption spectrum of PVF_2 above the F K-edge. The dashed line is the calculated atomic absorption curve. (b) The residual EXAFS spectrum after the subtraction of a smooth background.
- Figure 5. Fourier transform of the EXAFS data after inclusion of a compensating factor for the phase shift. The second peak is due to a number of higher-neighbor shells (see Table I).

Fig. 1.

XBL 798-10804

FIG. 2.

Fig. 3.

XBL 793-877

Fig. 4.

XBL 792-8481

Fig. 5.

XBL792-446

CHAPTER 5. SURFACE EXAFS IN THE SOFT-X-RAY REGION: STUDY OF AN OXIDIZED Al SURFACE

The interaction of oxygen containing molecules with solid surfaces is one of the most important problems in catalysis and surface science. From previous studies of bromine chemisorbed on graphite¹ it is clear that the extended x-ray absorption fine structure (EXAFS) above the adsorbate K or L absorption edge can provide unique information on the adsorbate-substrate system. However, EXAFS studies of the most important adsorbates carbon and oxygen have been impeded in the past due to the lack of monochromatic photon radiation in the 250 1000 eV range. Furthermore, the study of these elements and adsorbates is complicated by the back ground introduced by the substrate. The purpose of this chapter is to demonstrate that such measurements are feasible using monochromatized synchrotron radiation as the excitation source and electron yield spectroscopy as the detection technique.

The difficulties in surface EXAFS measurements that are introduced the background signal originating from the bulk are especially important for the low - Z adsorbates C and O since their atomic cross sections in the range of interest (300 - 1000 eV) is of the same order of magnitude as that of the atoms constituting the substrate.² Thus, opposite to the previously studied system Br₂ on graphite¹ where the atomic cross section ratio of adsorbate and substrate atoms above the bromine edge is 10^{-3} , measurements on low-Z-adsorbates cannot be carried out in the conventional transmission mode. Even with the thinnest pinhole free substrate films available, the signal

to background ratio will not exceed $\sim 10^{-2}$. Fluorescence detection of the EXAFS above low-Z K-edges can be excluded because fluorescence yields are extremely small ($\sim 10^{-3}$).³ One is left with one of the various electron yield detection techniques. Recently, monitoring the intensity of the adsorbate Auger line corresponding to the core excitation of interest has been discussed as a possible way to carry out surface EXAFS experiments.⁴ However, for C and O as adsorbates this technique cannot be applied since the measured Auger electron signal is strongly modulated by the core electrons photoemitted from the substrate. With increasing photon energy above the adsorbate K-edge, substrate core lines of binding energy in the 10 500 eV range and their inelastic tails will be successively swept through the energy window of the KVV Auger transition. The resulting intensity modulations are usually much stronger than the EXAFS wiggles due to the adsorbate and it appears impossible to subtract them out reliably.

The method of partial-yield spectroscopy⁵ sets the electron energy to be analyzed (E_{kin}) in the inelastic tail of the spectrum (typically $1\text{ eV} \leq E_{kin} \leq 10\text{ eV}$), and avoids the above problem as long as the substrate does not have an absorption edge in the energy range of interest ($\sim 300 - 1000\text{ eV}$). For C and O this criterion is fulfilled for many important substances. At high photon energies partial-yield spectroscopy which collects electrons a few eV above the vacuum level gives results equivalent to total yield spectroscopy which has been shown to image the absorption coefficient.^{6,7} The advantage of electron yield spectroscopy over conventional absorption spectroscopy

lies in its surface sensitivity.⁷ The surface sensitivity is due to the short electron mean free path (L). Even for electrons a few eV above the vacuum level (i.e., about 5 - 10 eV above the Fermi level) L usually does not exceed $\sim 30\text{\AA}$.^{7,8} Thus, yield spectroscopy is comparable to a transmission measurement using a less than $30\text{\AA}$ thick substrate film.

A. Experimental

The partial yield spectra reported here were recorded with a cylindrical mirror analyzer (CMA). The measurements were carried out in the "constant-final-state" mode with the energy window of the CMA set at $E_{\text{kin}} \approx 2$ eV. Operating the detector at a pass energy of $E_{\text{pl}} = 50$ eV (i.e., a resolution of $E = 0.8$ eV) yielded 3×10^4 counts/sec just above the oxygen K edge. The p-polarized light was incident on the sample at a grazing angle of about 10° .

B. Results

The partial yield spectrum of an untreated Al sample⁹ which is known to be covered with a "natural" $\sim 30\text{\AA}$ thick¹⁰ oxide layer is shown in Fig. 2 in the energy range $500 \text{ eV} \leq h\nu \leq 800 \text{ eV}$. The spectrum was recorded in about 20 minutes. A sharp increase in count rate is observed around 530 eV, corresponding to the oxygen K-edge. Above the edge, the signal oscillates and 3 maxima and 4 minima can clearly be distinguished. That these oscillations do not arise from modulations of the incident photon flux was carefully checked by measuring the photoyield of samples which do not have any absorption edges in the energy range of interest.² As expected for low Z-elements, the absorption falls off fairly rapidly above the edge. It appears that

the EXAFS oscillations extend to $\hbar\omega > 800$ eV but unfortunately this energy range was not covered due to experimental difficulties at the time of the measurements. The specific surface sensitivity of the present yield measurements is demonstrated by the fact that we were unable to observe the oxygen K edge by studying a 1500 Å Al film in transmission.¹¹

C. The Transformation to Real Space

Fig. 3a shows the EXAFS $\chi(k)k$ where $\chi(k) = (\gamma - \gamma_0)/\gamma_0$, as a function of the photoelectron wavevector k . The background function γ_0 which was subtracted from the yield γ , was taken to be a spline polynomial and the "zero" of the EXAFS energy scale was taken to be at the inflection point of the edge. The Fourier transform of the data in Fig. 3a yields the neighbor-shell separations from the O atoms provided that the k -dependent phase shift function $\phi(k)$ is known. Since the present investigation is to our knowledge the first EXAFS measurements above the O K-edge, $\phi(k)$ is not known experimentally. We have, therefore, used the parameterization scheme for the phase shifts and backscattering amplitudes $A(k)$ by Lee et al.¹² and Fourier transformed the function¹³

$$F(k) = \chi(k)k e^{-i\phi(k)} / A(k) \quad (1)$$

in the range $2.2\text{\AA}^{-1} \leq k \leq 8.0\text{\AA}^{-1}$. The absolute value $|F(r)|$ of the Fourier transform is shown in Fig. 3b. the function exhibits three main peaks A, B and C which are relatively insensitive to the cutoff values of $F(k)$. Raising the lower cutoff to $2.9\text{\AA}^{-1}$ or lowering the

upper cutoff to $7.0\text{\AA}^{-1}$ (see Figure 3a) causes a maximum shift of peak A by $-0.06\text{\AA}$, of peak B by $+0.05\text{\AA}$ and of peak C by $+0.11\text{\AA}$. The peaks in Fig. 3b fall at $1.93\text{\AA}$, $2.70\text{\AA}$, and $3.36\text{\AA}$ respectively, when $\phi(k)$ and $A(k)$ are calculated for an Al backscatter. For an oxygen backscatterer $|F(r)|$ looks almost identical and peaks A, B and C fall at $1.92\text{\AA}$, $2.67\text{\AA}$ and $3.33\text{\AA}$. The peak position of peak A compares well with the average O-Al nearest neighbor distance of $1.915\text{\AA}$ in bulk crystalline Al_2O_3 where each O atom is surrounded by four Al atoms, two at $1.86\text{\AA}$ and two at $1.97\text{\AA}$.¹⁴ The positions of peaks B and C also agree with neighbor-shell separations from the oxygen atoms in Al_2O_3 . The second nearest neighbor shell consists of oxygen atoms at a mean distance of $2.72\text{\AA}$ and the third nearest neighbor shell is formed by Al atoms at a mean distance of $3.52\text{\AA}$. In the light of the uncertainty associated with the calculated phase shifts (especially at low k values) the discrepancies of $0.15\text{\AA}$ for the first, $0.05\text{\AA}$ for the second, and $0.16\text{\AA}$ for the third shell are remarkably small. Our findings are consistent with previous soft x-ray emission¹⁵ and absorption^{7,15} measurements which yielded identical spectra for oxidized Al surfaces and bulk crystalline Al_2O_3 samples. The data do not reveal the bond length difference of $0.11\text{\AA}$ between the central O atom and the inequivalent Al nearest neighbor atoms expected for crystalline Al_2O_3 . This is not surprising since it is known that the optimal resolution ΔR for which two scattering shells are clearly separated in the Fourier transform of the EXAFS signal is $0.3\text{--}0.4$.¹⁶

The accuracy of the present data is limited by the relatively short EXAFS range, by the decreasing energy resolution of the monochromator (from ~ 4 eV at 500 eV to ~ 10 eV at 800 eV) and by the lack of experimental phase shift information. However, our results clearly demonstrate the feasibility and potential of surface EXAFS measurements on low-Z-adsorbates. As such, it establishes surface EXAFS through partial yield spectroscopy as a technique which may have many applications in catalysis and surface science. Surface EXAFS experiments have certain advantages over LEED investigations because of their higher sensitivity to bonding distances, the simplicity of their analysis, their possible applications to disordered overlayers, and because of the considerably lower probability of radiation damage.

It would be desirable to measure gas-phase EXAFS spectra of carbon and oxygen containing molecules¹⁷ in order to obtain more reliable phase shift information. Also, present technique of studying surface EXAFS can also be improved. By carefully choosing the kinetic energy and emission geometry of the measured electrons the surface sensitivity can be increased.^{5,7} The angle of light incidence⁷ and the orientation of the electric field vector with respect to the sample¹⁸ are other parameters which should be optimized for a given system. It should then be possible to measure adsorbate coverages of a monolayer or less or look at atoms in the outermost layer of a solid. Finally, the development of improved monochromators (throughput, resolution) in the soft x-ray region¹⁹ will greatly benefit measurements of the present kind.

D. Summary to Part II

In summary, Part I has shown that the soft-x-ray regime can serve as a valuable tool for structural analysis. In addition to being the only energy range capable of probing the low-Z elements Be through Ne, it can yield useful information from higher edges, such as the $L_{II,III}$ edge of P through Cu. Most importantly, the elements C, N, O and F can be studied. Measurement of the extent of long-range order in polymers and presumably amorphons or disordered systems seems possible. Finally, a first experiment testing the feasibility of measuring surface EXAFS using photoyield promises to make structural analysis available for adsorbate systems, and especially those species critical to the investigation of corrosion and catalysis.

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FIGURE CAPTIONS

Figure 1. Partial electron yield spectrum of an untreated Al sample in the energy range 500-800 eV. Maxima and minima of the EXAFS structure above the O K-edge are indicated by arrows.

Figure 2. a) The EXAFS signal $\chi(k)k$ as a function of electron wavevector k .
b) Absolute value of the Fourier transform of the function $F(k)$ defined in equation (1).

Fig. 1.

XBL 782-7317

Fig. 2.

XBL 782-7318

CHAPTER 6. NEAR-EDGE ABSORPTION IN TI AND NEAR-EDGE PHOTOYIELD IN FE AND CU

As was pointed out in the introduction, soft x-ray absorption spectroscopy may obtain information of the empty density of states which would be difficult to obtain without the advent of synchrotron radiation facilities. The absorption coefficient from an n, ℓ core level is

$$\mu(\omega) = \frac{4\pi^2 e^2}{h c} P \sum_{\vec{k}, b} |\langle n\ell | \hat{\epsilon} \cdot \vec{r} | \vec{k}, b \rangle|^2 \delta(\hbar\omega - E_{\vec{k}b} + E_{n\ell})$$

where the final state is a band-like state of momentum $\vec{k}$ and band index b . The particle density is P . If the final state were actually an eigenstate of angular momentum ℓ' , then of course dipole selection rules would require $\ell' = \ell \pm 1$. In a sense, the vector $\langle n\ell | \vec{r}$ can be thought of as projecting out the $\ell \pm 1$ components of the final state. In particular, for the case $\ell=0$, can be compared to the average

$$N_1(\omega) = \sum_{\vec{k}, b} \sum_{m_1} |\langle n\ell, m_1 | \vec{r} | \vec{k}, b \rangle_{MT}|^2 \delta(\hbar\omega - E_{\vec{k}b} + E_{\ell m_1})$$

where the average is taken over the muffin-tin (MT) radius. This corresponds to the symmetry-projected density of states appropriate to excitation from an s-core. In fact, the quantity $\mu(\omega)/N_1(\omega)$ has been calculated by Müller et al.¹ for the case of Pd and it was shown to be a smooth and monotonic function. It is the intent of this and the succeeding chapter to show some of the capabilities of core-level spectroscopy for measuring a symmetry-projected empty density of

states and some of the complications that can arise to prevent a simple interpretation of the data. The following discussion deals successively with the $L_{II,III}$ threshold structure, gives a comparison to unpublished data from Fe and Cu L-edges obtained from photoyield, and then considers the Ti L_I edge.

A. The Ti, Fe, and Cu 2p Core

The absorption coefficient for Ti is displayed in Fig. 1 of Chapter 3. The absorption coefficient exhibits a pronounced peak just above the threshold, which at closer inspection is split into a doublet. The inflection point of the edge falls at 454 ± 1 eV while the two peaks lie at 457 ± 1 eV and 461 ± 1 eV. The splitting of the initial peak is readily attributed to spin-orbit splitting in the $2p_{3/2}-2p_{1/2}$ hole states. Two observations support this interpretation. First, the splitting of $\sim 4 \pm 1$ eV agrees fairly well with the value of 6.1 ± 0.1 eV obtained from photoemission data.² Second, existing band-structure calculations give no indication of such a large splitting in the conduction-band density of states above the Fermi energy. The observed splitting, while not very well resolved, was reproducible and convincing. We note that this fair agreement of the observed energy splitting with the photoemission values is all that can be expected in such a comparison, because hole states near absorption edges are strongly perturbed by the conduction electrons. Thus, we believe that interaction with the conduction band distorts, but does not create, the splitting of the initial peak.

There has been considerable discussion recently of the "white line" structure which is observed for many materials near threshold. This term is derived from X-ray literature, in which a strong absorption immediately above an X-ray edge appeared as a white line in the photographic emulsion used as a detector. It has been studied in detail by Stern and co-workers for platinum³ and the anisotropic materials TaS_2 and WSe_2 .⁴ A study by Wei and Lytle⁵ on the Ta L-edge contains a more extensive list of materials that exhibit the "white line" phenomena. Comparing the value of μ_x obtained for Ti immediately above threshold with calculated atomic cross section⁶ shows that Ti does show a "white line". Previous measurements⁷ incorrectly show a lack of enhancement due to low resolution. While much edge structure can be understood in terms of the empty density of states, the previous absence of a "white line" in Ti had to be regarded as anomalous and the enhancement present in our measurements can be readily understood in terms of a high density of empty d-derived states immediately above the Fermi level. Theoretical calculations⁸ show a sharp peak for the Ti d-bands extending 1-2 eV above the Fermi level. Further support for this model's accuracy is given in Fig. 1. These partial yield spectra of Fe and Cu were taken in the same manner as in Chapter 5. The qualitative results are in complete agreement with what one would predict from considering the d-like density of states. Iron has a high density of d-derived states at the Fermi level and for about 2 eV above,⁹ and a sharp white line is observed in the yield. The splitting of the peak is once again the L_{II}, L_{III} edges.

As is well known, in going from Fe to Cu all the d-bands become filled. No "white line" is expected and its absence is conspicuous in Fig. 1b. Other factors certainly contribute to the occurrence of the "white line" since the DOS argument will not account for some cases such as the white line at the K edge in Ca¹⁰. However, it seems that a good model for the L-edges of the 3d metals must have the empty d-derived DOS as the main component. No attempt was made to further analyze the fine structure in the spectra since the monochromator bandwidth for the grating used becomes quite poor (~10 eV) for these high photon frequencies.

There is one other feature worth noting the Cu spectra. Instead of a sharp jump at the L_{II,III}-edge, followed by a steady decrease in yield (or absorption coefficient) there is a slow rise to a maximal value found about 70 eV above the L₃ edge. It is quite similar to the results from other L absorption studies on the low Z materials such as Be, Mg and Al¹¹, and shares the same explanation. On the basis of atomic calculations, Fano and Cooper¹² show that the dipole matrix element in terms of the radial wavefunctions R

$$M_{\ell \pm 1} \propto \int_0^R R_{n\ell}(r) r^3 R_{\ell \pm 1}(r) dr$$

will be depressed for small final state energies, ϵ , and that the effect is exaggerated for higher final angular momenta ℓ' . This is a result of the centrifugal barrier, $V_c \propto \ell(\ell+1)/r^2$, which the final state wave function must overcome to penetrate to the core region and have any significant overlap with the initial state wave function. By

way of illustration, an even more severe example is shown in Figure 2. This unpublished data shows the first measurement of the absorption coefficient at the Ag 3d threshold. In this case, the absorption is almost completely depressed for 30 eV from the threshold as determined by photoemission.

B. The Ti L_{III} -edge

Starting 109 eV above the L_{III} edge an additional absorption, associated with a $2s_{1/2}$ core hole (the L_I edge), is expected. While no sharp onset is observed, there is a broad increase in the total absorption for a range of 30 eV (see Fig. 2, Chapter 3). This is consistent with observations on the L edges of the light metals Na, Mg, and Al.¹¹ In comparison, the data of Lytle¹³ from the Ti K-edge shows a jump at threshold that is completed in only 2 eV. This observation eliminates final state effects, especially in the empty density of states, as a cause of the 2p broadening. It has been suggested by DesLattes¹⁵ that the cause is a lifetime effect. In fact, the hole-lifetime is determined by the combination of fluorescence and Auger decay lifetimes. For the case of low Z elements ($Z \leq 25$) the contribution of fluorescent decay is negligible.¹⁶ The main component, then, to the lifetime will be the rate of Auger decay and there is a good reason to expect a faster rate for the 2s level in comparison to 1s or 2p. The 2s level can decay by superallowed Coster-Kronig¹⁷ transitions which occur when all participating orbitals have the same principal quantum number (e.g., $L_1 L_2 L_3$ decay) and which have a much higher rate. In fact, one can compare photoemission half-widths of the 2s and 2p levels. The Al K_{α} excited

spectra¹⁸ show FWHM of 6.4 eV and 1.7 eV respectively and after including an instrumental resolution of 0.6 eV this would yield a ratio of 5.5 for the intrinsic lifetimes. The shorter 2s lifetime is not sufficient to account for the difference from the 2p absorption alone, but the differences in the projections in the density of state is expected to account for the remainder. At the same time the short 2s lifetime should account for the discrepancy between the 1s and 2s absorption spectra.

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FIGURE CAPTIONS

Figure 1. Partial yield spectrum for Fe (a) and Cu (b). The final state energy is approximately 2 eV.

Figure 2. Absorption spectrum of an $\sim 500\text{\AA}$ thick Ag film evaporated onto a polypropylene support.

Fig. 1.

XBL 798-2502

Fig. 2.

XBL 798-2503

CHAPTER 7. NEAR-EDGE ABSORPTION STRUCTURE IN GRAPHITE AND POLYVINYLIDENE FLUORIDE

In the previous chapter the capabilities of core level spectroscopy for investigation of electronic structure were discussed. It confirmed that a simple model of the symmetry projected density of states (SPDOS) was good as a first approximation in spite of previous measurements to the contrary in Ti. Nonetheless, it was necessary to accept two complications to the naive SPDOS model; centrifugal forces are important near the core so that matrix element effects can introduce strong modifications in the spectral intensity, and large variations in the hole lifetime must be anticipated.

In this chapter, the idea of using core-level spectroscopy for SPDOS will receive further discussion. In the case of graphite, calculations^{1,2} of the final states have been computed to much higher energies than in Ti so that a more extended comparison can be made. In addition, since the monochromator graphite sample is well-oriented instead of polycrystalline (even the annealed "polycrystalline" sample is oriented to some degree) and the probing light source is polarized, selection rules can also be exploited. In this case, the spectral features will also reflect a parity-projection in addition to angular-momentum projection, and this effect can be used to further aid the data analysis. One additional complication crops up for both graphite and the succeeding discussion of PVF₂. Many body effects such as relaxation³ definitely become important to the spectral features, especially near threshold. In the case of the polymer, an estimate is made of the size of the effect. To the

author's knowledge, the soft X-ray polymer work reported here constitutes the first experiments of this kind. However, the increasing use of specialty polymers in the photographic and electronic industries has stimulated recent interest in their electronic properties.⁴ Among the most common experimental techniques employed to study polymer valence and conduction bands are X-ray and ultraviolet photoemission (XPS and UPS) and ultraviolet absorption (UVA) spectroscopies. These techniques yield complementary data, by probing both the occupied and vacant electronic states of a material for comparison with theoretical models. In addition to valence-band studies, XPS provides chemical-state information about each atomic species in a compound via chemical shifts in core-level binding energies. The experiment of section B is intended to provide information complementary to the above techniques.

A. Near Edge Absorption Structure in Graphite

Graphite is the thermodynamically stable form of C at STP, with diamond being the unstable form. Figure 1a shows the graphite lattice. The lattice translation vectors $\vec{a}$ and $\vec{b}$ lie in the basal plane, while the vector $\vec{c}$ represents translation perpendicular to the plane. The Brillouin zone is a right hexagonal prism, shown in Fig. 1b with the symmetry points labeled. The calculated final state band structure as reported by Willis, Fitton and Painter² is reproduced in Fig. 2. The calculation is a variational LCAO method using 52 Slater-type orbitals as trial functions and is based on a full 3-dimensional lattice model instead of a single-layer lattice.

The absorption immediately above the edge is shown in Fig. 3. A peak appears at 285 eV in the polycrystalline and microcrystalline samples, and a sharp edge rises to a second peak at 293 eV in the polycrystalline case. For the monochromator sample the first peak is replaced by a low plateau and the sharp edge is rounded at the top, yielding no distinct peak. The intensity of the low-energy peak decreases in the order

$$(\text{microcrystalline foil}) > (\text{polycrystalline foil}) \\ > (\text{monochromator graphite}).$$

We attribute this to a polarization effect arising from the crystalline anisotropy of graphite. The band structure^{1,2} of graphite is quasi-two-dimensional because of the weakness of the interactions between planes, and most dispersive effects occur in the basal-plane directions.

The first states above the Fermi level have the character of bonds arising from p_z orbitals directed out of the plane. This band starts near E_F where the density of states has a shallow minimum. It has a rather flat saddle point about 2 eV above E_F and at the zone face Q (see Fig. 4). Because the band structure is quasi-two-dimensional, the saddle point should contribute a near-logarithmic Van Hove singularity to the density of states. We therefore assign the peak at 285 eV to transitions to that critical point of ϵ_0 at Q (labeled Q_{2g}^- in Ref. 1) and the second peak at 283 eV to the peak in the density of states calculated to lie at 8.5 eV in Ref. 2. The latter is mainly sp^2 in character and due to the bands labeled σ_1 and σ_2 at Q (Q_{1g}^+ in Ref. 1). From the band symmetries,

transitions from the $1s$ core level to the σ bands are forbidden for the light polarization vector $\vec{E}$ parallel to c , and transitions to the π bands are forbidden for $\vec{E} \perp c$. Our results are explained by noting that, as the c -axis of the crystallites becomes progressively more aligned with the foil surface plane, the $1s \rightarrow \pi$ transition becomes forbidden.

The separation of the first and second peaks (8 eV) is 1-3 eV larger than is calculated.² This effect can be explained by comparison with the XPS measurements of the carbon $1s$ binding energy.⁵ Because the measured binding energy is 284.7 eV, the saddle point at Q would not be expected below 287 eV in a simple one-electron picture. Relaxation effects arising from the attraction of the low-energy electron to the core hole must account for the 2 eV shift of the π -peak. A rigid shift of the density of states above the Fermi level would place the absorption onset at approximately 283 eV and indicate the formation of bound excitonic states in graphite, although a complete distortion of the density of states is possible. The very recent high-resolution ELS results of Mele and Ritsko⁶ indicate that such a distortion is probably correct--the observed onset in their data is no more than 0.2 eV below the carbon $1s$ binding energy and a model calculation gives a good fit to the distortion in the density of states at the π -peak.

For Peak B and all those at higher energies, our results can also be compared to the secondary electron emission (SEE) spectra reported by Willis, Fitton, and Painter² (see Table I). In addition, one

feature (peak D) has been observed in a photoemission study.⁷ Peak B in Fig. 2, at 293 eV, corresponds well to a feature reported in the SEE measurements at 9 eV above the Fermi level (i.e., at 29 eV) as well as to the peak at 292 eV in the ELS spectrum. Peak C has no analogue in the ELS spectrum, but it does correspond to a feature at 19.2 eV in the SEE results and a peak in the calculated density of states due mainly to critical points in the σ bands at Q. All three results show that there is a broad peak at 41 eV above E_F where the theoretical calculation predicts a broad peak due mainly to σ bands.

On the whole, the agreement with available experimental data is quite good. There is more structure in the secondary electron emission and still more in the calculated DOS. Two factors should be noted though; the resolution of the monochromator was relatively poor, and the reported SEE results are twice-differentiated to better resolved the weak structure. In the future, it should be easy to obtain data with higher resolution and with a signal/noise ratio suitable for multiple differentiation.

B. Absorption Near the C K-Edge in PVF₂

To explore the electronic structure of polymers most effectively, both multitechnique analysis and theoretical understanding of the materials studied are required. This section presents results of soft-X-ray-absorption (XUVA) spectroscopy on a thin-film polymer; the particular material studied was a ca. 5000 Å thick sample of polyvinylidene fluoride (PVF₂), an industrially important polymer⁶ (chemical formula $(CH_2CF_2)_n$). The results underscore several weaknesses of the above-mentioned spectroscopic techniques as applied

to the study of polymers, and show that information obtained from XUVA data on the electronic and morphological properties of PVF₂ is indeed complementary to that obtained from electron spectroscopies and UVA.

To be a viable technique for the study of any material, XUVA must provide clear advantages over the techniques listed in the introduction and/or yield complementary data; in principle, XUVA fulfills both of these conditions. The most troublesome difficulty with photoemission experiments of insulating materials is sample charging caused by the ejected photocurrent. This loss of electronic charge may be compensated by various means, but the difficulty remains of reproducibly referencing the binding energies of the spectral features. Attempts to avoid such complications involve referencing the peak positions to the Fermi level of a standard such as gold or carbon in electrical contact with the sample. This procedure implicitly assumes that the Fermi level of the reference is somehow related to a property of the polymer, which (as discussed below) is generally not the case. The study of valence bands by XPS is complicated by their low cross-sections for photoemission at higher (>1 keV) photon energies; in the time required to collect a valence band (VB) spectrum the sample may suffer sufficient radiation damage to affect its electronic structure. In UPS the photoelectron inelastic mean free paths are extremely short, rendering the observed spectra unduly sensitive to surface contamination and surface-localized effects,⁴ as well as to structure in the conduction bands.⁸

Among the disadvantages of UVA are the facts that the photon energies are generally not high enough to probe the entire VB, that observed spectra are complicated convolutions of the occupied and vacant densities of states, and that the absorption lengths are extremely short, necessitating very thin film ($<500\text{\AA}$) or solvated samples.⁹ Thus, if one is primarily interested in the bulk electronic properties of a polymer, UVA is practically eliminated from consideration. There is still the possibility of performing X-ray fluorescence¹⁰ or electron loss¹¹ experiments. However, both of these techniques require bombarding the sample with electrons at rather high power density in order to collect a spectrum, which may produce severe radiation damage of a solid polymer. As was discussed in the introduction, many of these problems are avoided in core level spectroscopy. These results of PVF₂, together with the EXAFS discussion of Chapter 4 illustrates the entire range of information to be gained from soft x-ray absorption studies of polymers. This may help workers interested in the chemistry and physics of polymers to evaluate XUVA as a viable spectroscopic tool. It also demonstrates the requirements that XUVA research places on the development of synchrotron radiation facilities.

Figure 4 shows an uncorrected XUVA spectrum of PVF₂ collected over the energy range 270-450 eV. The important features in this spectrum are the sharp peak at the onset of absorption and the structure in the spectrum near 343 eV, which is due to attenuation of second-order light by fluorine K-edge absorption. Second-order light was found to comprise ca. 3.5% and 2.5% of the total radiation

intensity at 300 and 400 eV, respectively, as measured through a Ti filter by a ZnS photocathode detector. Thus, even using a filter to attenuate radiation above 455 eV (the Ti $L_{2,3}$ edge) and a detector with a decreasing photoyield with energy (and thus less sensitive to the higher-order harmonics), the carbon K-edge region absorption spectrum suffers from higher-order interference. We did not attempt to Fourier-transform the carbon K-edge data because the expected EXAFS structure would have roughly the same intensity as the fluorine K-edge second-order interference.

The absorption spectrum in Fig. 4 is comprised of a large, broad peak which joins smoothly to the carbon K-edge continuum structure. The amplitude of the peak structure is actually suppressed due to the second-harmonic interference; allowing a correction for this effect yields an "adjusted" optical density of 5.5 for the peak maximum. Also plotted in Fig. 1 is the "theoretical" optical density of $97 \mu\text{g}/\text{cm}^2$ film of PVF_2 , computed from the atomic absorption cross-sections of C and F compiled by Veigela.¹² The agreement between this prediction and the measured values is excellent below the C K-edge (where the ratio of second-harmonic radiation to primary is very small) and at the higher photon energies shown, which lends credence to the ability of the present measurements to obtain accurate quantitative determinations. However, comparison of the peak height in the present measurements to a similar peak preceding the C K-edge in the reported absorption spectra of gaseous fluorinated methanes¹³ would yield an optical density of 68.1 (for a "carbon atom cross-section of 14 Mb) for our PVF_2 sample, over an order of magnitude higher than the

corrected value of 5.5 stated above. The discrepancy is attributed to an error in the cross-section determination of the fluoro-methanes because the cross-section reported in Ref. 12 both above and below the C-edge are much higher than predicted by Veigele.¹²

A more detailed plot of the absorption onset region is given in Fig. 5. This spectrum shows that the large peak preceding the absorption edge is actually a doublet, with the components falling at 288.6 and 292.5 eV. The 3.9 eV separation between these two peaks corresponds quite well to the energy difference between the main peaks observed for gaseous CH_4 and CH_2F_2 at 288 and 292 eV, respectively. Thus, they most likely arise due to excitations from the 1s level to the (localized) lowest-lying molecular orbitals of the correct symmetry for the two chemically inequivalent carbon species in PVF_2 . The observed peaks may be the initial and most intense members of a molecular Rydberg series (as expected from atomic theory),¹⁴ leading up to the polymer's ionization potential. Further structure is apparently obscured by the superposition of the two series of discrete lines and the finite resolution of the experiment.

The carbon K-edge absorption data may also be compared to XPS studies of PVF_2 .^{15,16} The splitting observed in the discrete absorption doublet agrees fairly well with the chemical shift of 4.5 eV observed between the C(1s) signals in the XPS spectrum.^{15,16} This is consistent with the expectation that the discrete doublet is due to excitations from the two chemically inequivalent carbons in

PVF₂ to the lowest unoccupied molecular states. However, the splittings obtained in photoemission and in absorption should not necessarily be equal. Studies by Duke et al.¹⁷ have shown that electronic transitions in polymers and molecular solids are more highly localized than normal band theory allows. Thus, the allowed final states for electronic transitions originating on chemically inequivalent sites may not fall at the same energy, because constituents such as fluorine can cause chemical shifts in the energies of the local "conduction" states, just as they do in the core levels (although these shifts should be smaller than core-level shifts due to the spatially more diffuse nature of the levels involved). Indeed, the absorption doublet structure is split by 0.6 eV less than the chemical shift of the C(1s) photoemission peaks. The explanation for this significant difference may be phrased in several different manners, but the essential feature is that the final states in an absorption experiment are also subject to chemical shifts that are observable due to their highly localized nature.

Another interesting comparison with the XPS data lies in the absolute numbers presented for the photoemission C(1s) binding energies. Clark et al.¹⁵ reported values of 286.1 ± 0.1 and 290.6 ± 0.1 eV for the 1s binding energies of the chemically inequivalent carbon in PVF₂, referenced to a binding energy of 83.8 eV relative to the Fermi energy for the Au 4f_{7/2} line. The absolute energy calibration of the PVF₂ spectra were achieved by using the C(1s) signal from the background vacuum contaminants as a standard. Pireaux et al.¹⁶ have determined binding energies of 286.4 ± 0.1 and

290.9 $\pm$ 0.1 eV by referencing the PVF₂ spectra to the C(1s) line of polyethylene, which had previously been determined to be 284.6 eV¹⁸ with respect to the gold Fermi level for a gold 4f_{7/2} binding energy of 83.8 eV. Both of the above determinations were therefore supposedly given with respect to the Fermi level of Au. However, comparison of photoemission data to absorption results is complicated by attempts to reference the XPS results to a Fermi level, even if charging effects have been properly handled. This important and general problem is discussed below.

Referencing XPS spectra of a wide-band-gap molecular solid of polymer with respect to the Fermi level of a metal in electrical contact with the insulating sample does not yield binding energies that are intrinsic properties of the unperturbed sample. Rather, these binding energies are specific to the particular insulator/metal interface. Contact charge exchange experiments^{19,20} have shown that the Fermi level of a metal at polymer-metal interface may fall anywhere within the band gap, above the "conduction band" minimum, or even below the valence-band maximum of the unperturbed polymer. Upon electrical contact with a polymer surface, the Fermi level of a metal does not equilibrate with the "Fermi level:" of the insulator. The ionic states formed by the initial charge transfer between polymer and metal do not delocalize throughout the polymer sample. Thus, a charged layer builds up at the polymer surface until the electrostatic potential due to the charged surface is effectively equal in magnitude and opposite in sign to the chemical potential difference between the polymer and metal.

Thus, XPS binding energies of solid insulators in which ionic states are highly localized can vary with the metal standard used as a reference. A more meaningful reference for XPS spectra of insulators in the VB maximum energy, as determined by the onset of photoemission from the VB of the sample. From reference 16 this value lies at 5.8 ± 0.1 eV binding energy relative to the gold Fermi energy. The binding energies of the C(1s) signals with respect to the VB maximum are thus 280.6 ± 0.2 and 285.1 ± 0.2 eV.

Figure 6 shows a one-electron energy diagram for photoemission and absorption in PVF_2 , referenced with respect to the VB maximum. The value of the energy gap of PVF_2 has been estimated at 14.1 eV,¹⁶ which would appear to be too large in view of Fig. 6. Duke⁴ has shown that predictions of such energy-level splittings in polymers that do not take account of relaxation effects (many-electron effects) are generally too large. However, a relatively small band gap of 7.8 eV, which would be inferred from a naive interpretation of the absorption from the C(1s) levels of PVF_2 , is almost certainly too small. Excitation of a 1s electron at threshold probably yields a localized excitonic state in which the excited molecular orbital is stabilized by the attractive force of the core hole. The one-electron picture implicit in Fig. 6 is actually inadequate for describing this system, as is often the case in solid-state problems. For example, the final levels above E_{VBM} are not states to which valence electrons can be raised. The reason is that the one-electron diagram is not an energy level diagram, but is only an approximate representation of the true energy-level structure of the system, presented

upside-down. This point was made earlier in explaining many-body excitonic effects on core-level binding energies in solids.²¹

In Figure 7 a real energy-level diagram is shown which incorporates the numerical results given above. In drawing this diagram the Fermi energy of gold is used as a reference for the photoemission data. With a diagram of this type it is easy to explain how the absorption energy $E_A = 288.6$ eV can fall several eV below the threshold for photoemission from the same core level, at 291.7 eV.

Physically, the "excitonic" binding of an excited electron to a localized 1s hole, $E_X(1s)$ is expected to be stronger than that to a more diffuse hole in the valence band, $E_X(VB)$. This is a well-known phenomenon in molecular electron spectroscopy. From energy conservation and Fig. 4 we find

$$E(\text{abs}) + E_X(1s) - E_B^F(1s) + E_B^F(VB) - E_X(VB) - E_g = 0$$

$$E_X(1s) - E_X(VB) = E_B(1s) - E_{\text{abs}} + E_g$$

$$\Delta E_X(1s) = E_g - 8.0 \text{ eV}$$

$$\text{or } E_g = 7.4 \text{ eV} .$$

Here, $\Delta E_B(1s) = E_B^F(1s) - E_B^F(VL)$ is the binding energy of the C(1s) electron referred to the valence-band "maximum"; i.e., the least-bound valence electrons, and $E_X(1s)$ is the additional excitonic binding energy of the excitonic state in the presence of a 1s hole, over that in the presence of a hole in the valence band. It is only possible to determine the excitonic binding energy difference because the VB and 1s binding energies are known only relative to a "floating" reference energy--the Fermi level of gold. To estimate the gap energy E_g we need only make a reasonable estimate of $E_X(1s)$. If the excited electrons and holes were completely delocalized, $E_X(1s)$ would be zero, and E_g would be 7.4 eV or 8.0 eV. The other extreme limit--that of a completely localized excitation, made up of an electron-hole point on the same carbon atom--is probably much closer to the truth. To estimate $E_X(1s)$ in this limit we invoke a simple localized model that has had some success in predicting excitonic energies in the past in systems ranging from metals²¹ to Auger satellite states.²² An atomic potential model is used, and atomic integrals are employed to estimate pairwise interaction energies. We consider the two separation processes

$$(\overline{VB} \text{ CB}) \rightarrow (\overline{VB}) + e^- , \quad E_X(VB)$$

$$(\overline{1s} \text{ CB}) \rightarrow (\overline{1s}) + e^- , \quad E_X(1s)$$

in which an electron is removed from the conduction band CB in the presence of either a valence-band hole or a 1s hole. The energies of

the two processes are the excitonic binding energies, $E_X(\text{VB})$ and $E_X(1s)$, respectively. The difference in these energies is approximately the difference between the coulombic interaction of the localized CB electron with a VB electron and with a $1s$ hole. In the atomic limit this difference is given to first approximation by^{21,22}

$$\Delta E_X(1s) \cong F^0(1s, \text{CB}) - F^0(\text{VB}, \text{CB}) \quad .$$

Of course the atomic-orbital composition of the CB state (and the VB state) is a priori unknown. In the extreme limit that both are assumed to be $2p$ orbitals, we have

$$E_X(1s) \cong F^0(1s, 2p) - F^0(2p, 2p) = 6.6 \text{ eV}$$

where Mann's integrals²³ have been employed to estimate a numerical value. This result is to be regarded as an extreme upper limit. The limits of E_g are therefore roughly given by

$$8 \text{ eV} \leq E_g \leq 14 \text{ eV} \quad .$$

This is a very broad range for E_g , but we note that if the position of $E_F(\text{Au})$ were known absolutely, it would be possible to deduce $E_X(1s)$ from the data, rather than only $E_X(1s)$, and thereby to gain more understanding of plausible values of E_g . The main value of this analysis is to show how absorption and XPS data can be combined into a meaningful energy-level diagram.

An estimate of the excitonic binding $E_X(1s)$ for localized states can be obtained by comparison of the absorption edge energies and core-level binding energies for C(1s) electrons in CH_2F_2 and CH_4 . Noting that carbon and hydrogen are of comparable electronegativity, the central carbons in the (C)- CH_2 -(C) and (C)- CF_2 -(C) groups in PVF_2 can be simulated by the gas-phase model compounds in $H-CH_2-H$ and $H-CF_2-H$, respectively. Because the reference level in gasphase photoemission is unambiguously the ground state, we have (cf. Fig. 4):

$$E_B(1s) = E(abs) + E_X(1s) \quad .$$

From the numerical values^{24,25}

$$E_B(C1s, CH_4) = 290.8 \text{ eV}$$

$$E_B(C1s, CH_2F_2) = 296.4 \text{ eV}$$

and, for the most intense peaks,²⁶

$$E(abs, CH_4) = 288.1 \text{ eV}$$

$$E(abs, CH_2F_2) = 292.9 \text{ eV}.$$

Thus, for these molecules,

$$E_X(1s, CH_4) = 2.7 \text{ eV}$$

$$E_X(1s, CH_2F_2) = 3.5 \text{ eV}$$

These values of E_X are about half the size of those estimated above for $E_X(1s)$. Taking these latter values to be upper limits for PVF_2 exciton energies, we would have

$$E_g(-CH_2-) \sim 8.0 \text{ eV} + 2.7 \text{ eV} = 10.7 \text{ eV}$$

$$E_g(-CF_2-) \sim 7.4 \text{ eV} + 3.5 \text{ eV} = 10.9 \text{ eV}$$

Consequently, our best estimate for E_g is 10-11 eV.

Table I. Comparison of Carbon K-edge Absorption to ELS and SEE Measurements and to the Calculated Density of States

Feature	Absorption (eV)	ELS (eV)	SEE ^a (eV)	Calcd DOS (eV)
A	285.	285.		2.0
B	293.	293.	9.5	9.9
C	302.	304.	19.2	18.3
D	325.	325.	40.7	42.0
E	344.			
F	362.	356.		
G	381.	380.		
H	403.	400.		
I	423.	422.		

^a The SEE results and the calculated density of states should be compared by adding the threshold energy (285 eV).

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FIGURE CAPTIONS

- Figure 1. The structure of graphite (a) in real space showing the crystal translation vectors and (b) the reciprocal space Brillouin zone with the labels of the symmetry points.
- Figure 2. Band scheme for graphite, after Ref. 22. The bands are labeled as to π or σ character.
- Figure 3. The near-edge absorption spectra for (a) microcrystalline, (b) polycrystalline, and (c) monochromator graphite showing to polarization effect for the first π band.
- Figure 4. Absorption spectrum for PVF_2 in the vicinity of the C K-edge. The dashed line is the calculated atomic absorption.
- Figure 5. A higher resolution scan at the C K-Edge showing the compound structure at 288.6 eV and 289.0 eV.
- Figure 6. A one-electron energy-level diagram showing the effects of absorption at the inequivalent carbon sites. Final states may or may not lie in a forbidden gap below the onset of conduction bands, because of excitonic binding.
- Figure 7. Energy-level diagram of the PVF_2 system, incorporating the data quoted in text.

(a)

(b)

Fig. 1.

Fig. 2.

XBL 797 - 2295

Fig. 3.

XBL7712-11088A

Fig. 4.

XBL 792-448

Fig. 5.

XBL 778-1687A

Fig. 6.

XBL 792-8479A

Fig. 7.

XBL 797-2035

CHAPTER 3. GaS/Ge: BAND DISCONTINUITIES THROUGH CORE-LEVEL PHOTOEMISSION AND ELECTRONIC STRUCTURE IN VALENCE-BAND ARP

The previous two chapters showed that XUV absorption spectroscopy and partial yield spectroscopy reflects the features found in the empty density of states. The final two chapters of this thesis concentrate exclusively on photoemission and its unique capabilities for probing surface/interface and bulk electronic properties of materials. The first section of this chapter makes use of core-level spectroscopy to measure variations of the dipole layer formed during the growth of a semiconductor-semiconductor interface. This is followed by a discussion of the valence band electronic structure as measured by angle-resolved photoemission (ARP).

A. Measurement of band discontinuities

During the past ten years, much effort has been devoted to understanding the physical properties of Schottky barriers and heterojunctions.¹ In both systems, the main effects originate at the interface; for example, it is well known that Schottky barrier heights, as measured by capacitance voltage (C-V) or current-voltage (I-V) characteristics, are nearly independent of the metal's work function for covalent semiconductor-metal pairs. Several theoretical models have been suggested to account for this pinning of the Fermi energy, E_f .²⁻⁴ Recent results obtained with surface-sensitive techniques such as ultraviolet photoelectron spectroscopy (UPS),^{5,6} partial yield spectroscopy,⁷ and electron energy-loss spectroscopy,⁸ however, seem to indicate that no single theory will explain the data for all Schottky barrier devices.

For semiconductor-semiconductor heterojunctions, as with Schottky barriers, the most serious problems arise from the misfit which necessarily occurs when materials of unequal lattice parameters are interfaced. The dangling bonds arising at the interface could be expected to provide electrically active states serving either as charge traps, in which case a modified band profile could result, or as recombination states which could affect the transport properties of the junction. The wide application of heterojunctions in electronics devices suggests that a better knowledge of their interface states would be useful for the "tailoring" of such devices. Nevertheless, up to now, only one surface-sensitive experiment has been reported for such heterojunctions,⁹ and that work did not establish the magnitudes of the conduction and valence band discontinuities at the interface, but only showed their orientational dependence, which is a consequence of the dipole-like potential produced by the interface.

These discontinuities may, however, be determined from angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) data. The method consists of detecting electrons which have been photoejected from the surface of one semiconductor single crystal which is covered with overlayers of a second semiconductor of various thickness. The top of the valence band, called here the valence band maximum (VBM), is marked in the photoemission by the onset of emission intensity. As the overlayer is produced, the valence band maximum will shift at the surface relative to E_f . Since the escape depth of electrons at these energies may be expected to be of the order of $10\text{\AA}$,¹⁰ the data obtained for thicknesses of such magnitude reflect the electronic

structure of the heterojunction at the surface and in its first few bulk layers. By increasing the overlayer thickness, it should be possible to observe a saturation in the substrate band bending; for overlayers of sufficient thickness (i.e., several times the inelastic mean free path), no photoemission from the substrate should be detectable, and the overlayer band bending should become observable.

The band scheme usually employed to describe a semiconductor-semiconductor heterojunction is shown in Fig. 1. In part (a), the energy levels are shown for two non-interacting (separated) materials; the characteristic parameters are the band gap (E_g), electron affinities (χ), and positions of the Fermi levels relative to the bulk valence or conduction band energies (δ). As shown in part (b), the formation of the heterojunction leaves these parameters invariant, but the charge flow across the junction, induced by the difference in chemical potential of the two materials, results in the equalization of the Fermi levels and an associated bending of the bands at the interface, given by V_D^1 and V_D^2 . The discontinuities in the valence and conduction bands, E_v and E_c , are given by

$$\Delta E_v + \Delta E_c = \Delta E_g \quad , \quad (1)$$

while the relation

$$E_f^2 - E_f^1 = V_D^1 + V_D^2 \equiv V_D \quad (2)$$

describes the band bending. The partitioning of the induced potential into V_D^1 and V_D^2 is determined by the doping of the semiconductors, with the bending being larger for the less conducting material. As is clear from the figure, a simple equation obtains for the conduction band discontinuity:

$$\Delta E_c = (\delta_1 + V_D^1) - (E_g^2 - \delta_2) + V_D^2 \quad (3)$$

Thus, a determination of V_D will also allow the calculation of E_c . This has typically been done in the past by analyzing the C-V characteristics of the heterojunction,¹ according to the relationship

$$1/C^2 \sim (V_D - V) \quad (4)$$

Such results have frequently been explained by equating the conduction band discontinuity at the interface to the difference in electron affinities,

$$\Delta E_c \cong \chi_2 - \chi_1 \quad (5)$$

but the validity of this approach has been questioned by several authors, who have proposed different theoretical models.¹¹⁻¹⁴ For the (110) interface of the GaAs/Ge heterojunction, the predictions of the self-consistent pseudopotential method of Ref. 14 and the electron affinity difference method are given in Table I, along with C-V

results.¹⁵ The variation in the C-V data seems to indicate that such measurements must be made in conjunction with microscopically sensitive techniques in order to fully characterize the interface.

B. Experimental

Briefly, electrons were photoejected by 21.2 eV (HeI) photons from an in situ cleaved n-type GaAs (110) single crystal (carrier concentration of $8 \times 10^{14} \text{ cm}^{-3}$ by Hall effect measurements) which was subsequently covered by evaporative deposition with successively thicker overlayers of Ge. The electrons were energy analyzed using a cylindrical mirror analyzer with a resolution of 0.07 eV. During the depositions the temperature of the substrate was held at the epitaxial growth temperature¹⁶ of 420°C, with a base pressure of 2×10^{-10} torr. ARP spectra were taken for various Ge coverages, ranging from a fraction of a monolayer to ca. 20 monolayers; coverages were determined by calibrating the oven with a piezoelectric thickness monitor, and one monolayer was defined as $8.85 \times 10^{14} \text{ atoms cm}^{-2}$, in conformity with previous work.⁵

C. Band discontinuity results

Selected results are shown in Fig. 2, where the spectra for clean and Ge-covered GaAs are presented for normal emission; these spectra are hereafter referred to as 0 to 6. The position of E_f was determined by measuring the photoemission edge of a tantalum strip which was in electrical contact with the GaAs.¹⁷ This strip is in contact with the spectrometer ground, and therefore, provides a stable reference level. As long as charging effects are small (as is the case here; see Ref. 18), the Fermi level of the metal and the GaAs

will be equivalent. The small peak just to the left of E_f is due to emission from the Ga 3d core level, excited by 40.8 eV (HeII) photons which are a subsidiary component of the spectrum of the discharge lamp used. The separation of this peak and E_f decreases with Ge coverage, indicating a change in the relative separation, near the interface, of E_f and the valence band. Accordingly, we have aligned the spectra 0 to 4 by keeping fixed the Ga 3d peak position; the zero of energy is set as the Fermi level for the clean GaAs sample. Spectra 5 and 6, having thick Ge overlayers, have been aligned by keeping constant the VBM, a procedure which is sufficient for our purpose of obtaining shifts in E_f . A weak 3d signal was also observed for the spectrum 5 coverage at non-normal emission, and was used to confirm the alignment.

For the Ge covered surfaces, E_f is displaced from the zero of energy as shown in Fig. 2. This displacement is summarized in Fig. 3 where we have plotted the fermi level position, relative to E_f for clean GaAs, as a function of overlayer thickness. A saturation value of the band bending is reached for very low coverages; analogous behavior was observed by Gregory and Spicer for the GaAs-Cs Schottky barrier.⁵ For such layer thicknesses, most of the photoelectrons observed are originating in the GaAs, and the saturation value thus corresponds to the maximal GaAs band bending. For the spectra incorporating thick Ge overlayers, we see a further movement of E_f towards the VBM. As the Ge layer thickness is much less than the characteristic distance for band bending (see Fig. 1), bending effects in the overlayer are negligible for such small coverages. This new

saturation value is representative of the Ge half of the heterojunction; in fact, the photoelectron escape depth is sufficiently short as to preclude, with the coverages employed in these spectra, observation of the substrate bands. From Fig. 3, we may immediately deduce that $\Delta E_v = 0.25$ eV and, with $\Delta E_g = 0.75$ eV, we obtain from Eq. (1) that $\Delta E_c = 0.50$ eV. These results, which qualitatively agree more closely with the values of Ref. 14 than with those obtained by the use of Eq. (5), seem to indicate that equating ΔE_c to the electron affinity difference is a poor approximation, and that a better knowledge of the interface physical properties should be obtained through the use of more sophisticated theoretical models which include the possibility of relaxation at the interface.

D. Interface features of the valence band photoemission

The nature of the electronic structure of metal-semiconductor and semiconductor-semiconductor interfaces, and the process by which very thin films evolve toward the limit of two bulk materials joined at an interface, are of considerable scientific and technological interest. It has only been in the last few years, however, that microscopically sensitive techniques have been utilized for studying the growth of metal films on semiconductors. Herein are reported a separate series of measurements which are intended to show the ARP may be used to more fully elucidate the detailed evolution of electronic structure in the initial stages of interface formation. In particular, we have found a number of features, some of which correspond to recent calculations of interface states.¹⁷ These features follow regular trends as successively greater amounts of Ge are deposited. In this experiment, the

sample alignment procedure was improved by using laser autocollimation from the cleaved face, and the evaporation temperature was held at 350°C. Spectra were taken as a function of θ , the polar angle from the surface normal, for azimuths corresponding to electron wavevectors along $\bar{\Gamma}\bar{X}$ ($\phi = 0^\circ$) and $\bar{\Gamma}\bar{X}'$ ($\phi = 90^\circ$) in the surface Brillouin Zone (SBZ); the geometry is summarized in Fig. 4.

A detailed analysis of GaAs photoemission has been published elsewhere,²⁰ but some brief comments are necessary as a basis for discussing the interface states. Most of the structure is associated with bulk transitions. At normal emission, all the peaks may be accounted for by the use of existing band structures^{21,22} and a direct transition model, except for the peak at ca. 13 eV. This latter feature, which is almost dispersionless with θ , was found to be cleavage-dependent, and was observed to disappear for heavy Ge coverage. It occurs in a bulk band gap for GaAs and it is, therefore, assigned as a new deeply bound surface state. No such state has been predicted for $\bar{\Gamma}\bar{X}$, although Chadi²³ has predicted a state at ca. 11.2 eV between M and X, and recent self-consistent calculations²⁴ show a surface resonance not yet split off the bulk bands at 11.5 eV.

Spectra are presented in Fig. 5 for a series of evaporations corresponding to submonolayer coverages of Ge. Here, the electrons are emitted with the parallel component of their wavevector ($k_{||}$) oriented along the $\bar{\Gamma}\bar{X}$ line in the SBZ. the primary features are labelled one through four. Several phenomena are observed upon overlayer formation. The gap between the surface state 1 at 1.1 eV

and the bulk peak 2 at 2.3 eV is seen to fill in; in addition, there is an apparent broadening of the latter feature and the peak 4 at 6.4 eV for evaporation 1 (E1). Apparent broadening in peak 2 also occurs, but has decreased by E2, as has that for peak 4 by E3.

These features are admittedly subtle. To better explicate them, we have calculated difference spectra, presented in Figs. 6 and 7, for the various evaporations relative to the clean substrate. These spectra clearly show a loss in strength for the most weakly bound states. Such behavior is frequently observed in ARP spectra of adsorbate-substrate systems, and is attributable to a transfer of intensity toward higher binding energy. In addition, several generally sharp features appear; they are summarized in Fig. 8. The features are found to fit one of two cases for the location of at least some of their associated $(E_B, k_{||})$ paired values: (1) in a region which is calculated to be forbidden to itinerant (bulk-like) states, or (2) within or at the edge of a region in which itinerant states are allowed. The first case is necessary for the formation of a truly localized state, while the second is typical for the occurrence of resonances.²⁵ In the present experiment, all features falling about 7 eV are found to persist in the region of itinerant states, regardless of whether they can be found in gaps or not. For case (1), this is shown by features C for the $\bar{\Gamma}\bar{X}$ azimuth and E, F, and G for the $\bar{\Gamma}\bar{X}'$ azimuth, all of which penetrate from a gap into the bulk-forbidden region. The features D and H are noteworthy in that they fall in the ionic gap of GaAs. The effect on the surface of the Ge deposition, in

the limit of a thick overlayer, will be to partially close the gap at $\bar{X}'$, and completely close it at $\bar{X}$. This will prevent the formation of localized states, and it is, therefore, consistent that D (and to a degree H) is strongly damped for greater depositions; in fact, feature D has disappeared by evaporation 3. All other features are persistent, and in particular the feature C agrees with the prediction of a "GeAs bond" state (B_1) by Pickett, et al.¹⁷ at 3.64 eV. The feature F can correspond to either B_1 or P_1 of the above calculations, while feature E might be a resonant precursor of B_2 or P_2 . Feature G does not correspond closely to any predicted states.

Features corresponding to the second case are peaks A and B for the $\bar{X}\bar{X}$ azimuth. The feature B is found at mid-band and is of uncertain origin. The nature of the feature A, on the other hand, strongly suggests that it too is a resonant precursor for the interface state B_2 , analogous to feature E. One can trace the center of gravity of features A and E through the successive evaporations (Fig. 6). In fact, evolution is found toward the main gap, with the trend being stronger for the E state.

These preliminary results have shown that ARP is capable of making effective measurements of the electronic structure of heterojunctions in the initial stages of interface formation. We have further found correspondence with the main features of available calculations.¹⁹ It is clearly important to extend these results to higher coverages to study any further evolution that is observable in the spectra, with the hope of following the observed features until a heterojunction has

been effectively formed. Experiments aimed at studying supermonolayers were undertaken here, but because of the less-than-desirable cleavages that were obtained, the results were inconclusive. However, they tended to confirm earlier observations and indicated that the features would still be observable at the monolayer level, but doubts were raised as to their observability at higher coverages. Nonetheless, the use of a tunable light source such as SSRL would enable one to optimize the signal level of the interface features.

Table I. Values of valence and conduction band discontinuities.

METHOD	ΔE_v	ΔE_c
ARUPS ^a	0.25	0.50
EPM ^b	0.35	0.40
C-V ^c	0.60-0.19	0.15-0.56
Eq.(5)	0.69	0.06

^aThis work.^bRef. 14.^cRef. 15.

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FIGURE CAPTIONS

- Figure 1. Band scheme (a) before and (b) after the formation of a semiconductor-semiconductor heterojunction. The ordinate is the relative energy, and the abscissa the position in real space, with $x = 0$ at the interface. See text for explanation of symbols. The figure is drawn so that GaAs would qualitatively correspond to material 1, and Ge to material 2. Note that the spatial extent of the region where the band bending occurs is of the order of a micron (See Ref. 20).
- Figure 2. Spectra at normal emission and 21.2 eV photon energy of clean (dotted) and Ge covered (solid) (110) GaAs. The magnified portion of spectrum 0 shows that Ga 3d peak due to 40.8 eV radiation. Approximate coverages are as given.
- Figure 3. Plot of the separation of the Fermi levels for clean GaAs and for Ge covered GaAs, as a function of overlayer thickness.
- Figure 4. Experimental geometry and surface Brillouin Zone for GaAs.
- Figure 5. Selected spectra for $k_{||}$ along $\bar{\Gamma}\bar{X}$ as a function of Ge coverage. Binding energies are referred to the valence band maximum at $\bar{\Gamma}$.
- Figure 6. Selected difference spectra for the $\bar{\Gamma}\bar{X}$ direction in the SBZ.
- Figure 7. Selected difference spectra for the $\bar{\Gamma}\bar{X}'$ direction in the SBZ.

Figure 8. Observed ARP features and projected surface band structure for GaAs/Ge (after Ref. 6). Cross-hatched areas are GaAs bulk-forbidden regions. Interface states are labelled with the notation of Pickett, et al., and the features in Figs. 3 and 4 are labelled as A through H. Peaks are plotted from data for all evaporations, but not all data is shown; in some cases, peak positions were identical for successive evaporations.

Figure 9. Binding energy shift for peaks A and E as a function of Ge coverage. Each point represents the mean value of the set of points common to these features for each evaporation.

Fig. 1.

XBL 785-8409

XBL 765-8411

Fig. 2.

Fig. 3.

XBL 785-8410

Fig. 4.

XBL 792-447

Fig. 5.

XBL 791-8087

Fig. 6.

XBL 791-8088

Fig. 7.

XBL 791-8094

Fig. 8.

XBL 792-8387

Fig. 9.

XBL 792-8213

CHAPTER 9 - THE VALENCE BAND STRUCTURE OF SILVER

ALONG Λ FROM ANGLE-RESOLVED PHOTOEMISSION

The last chapter gave a demonstration of the importance of surface photoemission, and attempted to evaluate the possibility of measuring not only surface effects, but also to probe the initial stages of interface formation. While this is a brand new area and deserving of further investigation, progress in bulk photoemission is advancing rapidly through angle-resolved experiments. This chapter shows that the direct transition model holds for Ag(111) and exploits this principle to obtain quantitative information about the dispersion relations of silver along Λ .

Silver occupies an interesting position among transition and noble metals because its 4d bands are relatively narrow (3 eV bandwidth), and they lie well (4 eV) below the Fermi energy. In addition, the spin-orbit coupling strength of $\xi(4d) = 0.22$ eV in the free atom is comparable to the crystal potential. In fact, early x-ray photoemission (XPS) spectra^{1,2} in silver showed a d-band density of states that somewhat resembled a spin-orbit doublet, perturbed by crystal-field splitting. Analysis^{2,3} showed that this picture was not viable, however; and later, higher-resolution XPS studies yielded additional features that require a band-structure interpretation.^{4,5}

Ultraviolet photoemission studies of silver have been carried out under a variety of conditions.⁶⁻¹⁴ The major conclusion of these studies is that angle-resolved photoemission (ARP) spectra from single crystals can be interpreted, using the direct-transition model, to yield results in good agreement with predictions based on the

theoretical dispersion relations of the valence bands of silver. Hansson and Flodstrom,¹³ in particular, gave very detailed evidence for this conclusion on the basis of their ARP studies at photon energies in the range 7.0 - 11.6 eV. These workers found nearly quantitative agreement between their experimental peak positions and predictions based on Christensen's relativistic band structure,¹⁵ coupled with the direct-transition model. Liebowitz and Shevchik¹⁴ drew similar conclusions from ARP spectra obtained using rare-gas lamps at five energies between 11.6 eV and 40.8 eV.

Encouraged by these results, as well as by our own earlier ARP studies of copper, in which the direct-transition model was found to apply for photon energies in the range 32-160 eV,¹⁶ we have carried out ARP studies of the (111) face of silver in normal emission over the energy range 6-32 eV, using synchrotron radiation. By extending the photon energy range up to 32 eV we were able to study the valence-band dispersion relation along the Λ symmetry direction to the Γ point. In particular, the d-band energies at Γ were determined for the first time. These higher photon energies also allowed us to probe the total valence bands; for photon energies $h\nu \geq 16$ eV all the valence bands were energetically accessible.

Two particularly interesting observations were made during the course of this research. A sharp resonance in the intensity of a peak arising from the Γ_7 band was observed at $h\nu = 22$ eV, enabling us to locate the energy of this band at a $\vec{k}$ point near Γ . In addition, an interesting final-state effect was observed. For $h\nu \geq 26$ eV, photo-emitted electrons are trapped in a high-energy band (or bands) with a

high density of states near Γ , which they apparently reach through scattering processes. From this state in the crystal they emerge in the normal direction at a fixed kinetic energy of 17 eV.

Experimental procedures are described in Section II. Dispersion relations along Δ are derived and presented in Section B, and the energies of the d bands at Γ are discussed. Section C is devoted to the band 4 to band 7 resonance at $\hbar\omega = 22$ eV, and the 17-eV kinetic energy feature that appears in the spectrum for $\hbar\omega > 26$ eV is discussed in Section D. A summary is given in Section E.

A. Experimental

A high-purity single crystal of silver was cut to produce a (111) surface orientation and polished to 1-micron smoothness. It was etched repeatedly in a solution of concentrated nitric acid saturated with silver nitrate to remove the damage layer. Back-reflection Laue photographs were taken to check the post-treatment crystalline orientation. They showed it to be correct to within 1° or better. Sharp diffraction features appeared in the patterns, indicating the absence of a deep damage layer. After final insertion into the ultrahigh vacuum chamber, the crystal was further cleaned in situ by repeated cycles of argon-ion bombardment and annealing at 600°K . Auger analysis showed no remaining surface contaminants: the limit of detectability was 0.03 monolayers.

The photoemission measurements were performed on the 3° branch line of Beam Line I at the Stanford Synchrotron Radiation Laboratory. The electric field vector of the highly-polarized ($\geq 97\%$) incident radiation lay in the horizontal plane defined by the Poynting vector

of the radiation and the propagation direction of the detected photoelectrons; the angle between the latter two was fixed at 145° . Only electrons emitted in a cone of 5° half-angle around the surface normal of the sample were collected. The total energy resolution (monochromator plus electron energy analyzer) was ca. 0.26 eV.

Photoemission spectra were taken normal range $h\nu = 6-32$ eV. Counting rates were excellent ($\sim 10^4 \text{ sec}^{-1}$) and a spectrum could be taken with good statistics in 5 minutes. Figure 1 shows the spectra.

B. Valence-Band Dispersion Relations

To interpret the spectra shown in Fig. 1, it is necessary to establish a theoretical model that can explain at least the principal spectral features. That the direct-transition model is adequate for similar spectra has already been well established,^{13,14,16} and we need not belabor it further here. Rather, we shall discuss briefly the qualifications that must be made before a direct-transition model interpretation can be applied, then proceed to derive band-structure information for silver along the Λ line. We note that until now it has been common practice in angle-resolved photoemission spectroscopy of metals to plot theoretical dispersion relations along symmetry lines (or elsewhere in the Brillouin Zone), superimpose experimental points, and draw conclusions about the extent of the agreement with the direct-transition model, assuming the correctness of the theoretical band structure (e.g., Refs. 13, 14, 16). Now that the model is well established, it is becoming generally worthwhile to go a step further and construct experimental dispersion relations (to the extent that this is possible), presenting results in tabular rather than only

in graphical form. Of course, this approach is fraught with obvious pitfalls (e.g., some of the Σ or even of the Λ line is inaccessible, some transitions are unresolved or unobserved, theoretical final state bands must be used to derive initial-state dispersion relations, many-body effects are neglected, etc.). Nevertheless, we shall make such an analysis below, mostly using our own spectra but also taking into account other relevant data.¹²⁻¹⁴

First let us discuss which features of the spectra arise from direct transitions. It is the nature of photoemission from solids that several mechanisms usually contribute to the spectral intensity. In the case of Ag(111) photoemission we believe that all the spectral features are at least qualitatively understood. Starting down from the Fermi energy, E_F , a surface-state peak appears at 0.13 ± 0.05 eV binding energy. This state has been well characterized previously,^{12,13} and need not be discussed further except to note that our spectra agree well with the earlier work when allowance is made for our lower angular and energy-resolution. In particular, our 7 eV and 8 eV spectra are in essential agreement with the sand p-polarized 7.8 eV spectra of Hansson and Flodstrom,¹³ when the latter are suitably weighted for our experimental geometry.

Proceeding to higher binding energy and to the higher photon-energy spectra, the first 4 eV from E_F are dominated by a low-intensity, flat plateau of spectral intensity. This is familiar as the "s-p bands" in (angle-integrated) photoemission spectra from polycrystalline samples, and of course, in the density of states.² In angle-resolved photoemission the source of this plateau is less

obvious. It cannot arise from direct transitions from the s-p bands, which lead instead to a peak in the 0-4 eV binding-energy region that moves across this region as the photo energy is varied. This peak is clearly visible in the spectra for photon energies in the $\hbar\omega = 6 - 12$ eV range. The plateau must be attributed instead to indirect transitions, especially (and perhaps exclusively) phonon-assisted transitions.

The remaining features of these spectra are the direct-transition peaks, discussed below, the 17-eV kinetic energy peak, discussed in Section C, and the inelastic tails in the electron distribution. About this tail we simply note that electrons can be scattered both in the sample and in the spectrometer, so that precise comparisons of data from different sources may show different intensities in this feature.

Peak positions derived from our spectra are shown as open circles in Fig. 2. In deriving the $(\vec{k}, E)$ coordinates of these data, we used the following procedure:

1. On the basis of the direct-transition model, the final states were found to lie in the second BZ along the (111) direction, for all the photon energies that were used. Thus, the reciprocal lattice vector $\vec{G} = (1,1,1)$ connects the initial and final crystal momenta in the equation $\vec{k}_f = \vec{k}_i + \vec{G}$.
2. From Christensen's band structure, only one final-state band along the line is available for photoemission throughout the entire lower portion of the photon energy range covered. This is the seventh band from the bottom, which has mostly $G = (1,1,1)$

character up to 16 eV, where it becomes strongly admixed and a gap develops. We ignored this gap. To derive final-state k_f values at higher energies, we extended this band using a free-electron dispersion relation.^{14,16}

3. The above procedures yielded the k_i coordinate, for projecting the crystal momentum back into the first BZ. Energy difference between initial and final states were given by the photon energies. Relative energies of valence bands were therefore determined quite accurately (to ± 0.05 eV) from relative peak positions. Careful monitoring of the analyzer voltages assured that the observed binding energies varied smoothly to within these limits as the photon energy was raised.

4. The Fermi energy was taken as the energy at half-height on the incline at the end of the "s-p band" plateau, for spectra in which this feature was clear: i.e., about two-third of our spectra. Reference voltages were used to establish the Fermi energies of the other third. In the adjusted spectra, the derived work functions showed an rms scatter of only ± 0.03 eV.

As Fig. 2 shows, our data yield smooth variations of E with k, and they show generally very good agreement with Christensen's band structure. All six bands in fact yield data points somewhere along Λ , and there are no peaks in our spectra that yield points which do not correspond to a band along Γ . The valence bands were energetically inaccessible near L. Elsewhere in the BZ, band 1 did not appear near Γ , presumably because its s-like character near Γ leads to a low photo-emission cross section. Band 3 was missing from most of our spectra.

With these exceptions, all bands yielded peaks (or definite evidence for unresolved peaks) in nearly all spectra.

In addition to our Ag(111) spectra, taken at 17 photon energies, ARP spectra are also available taken with laboratory sources at some 11 distinct energies, from three other laboratories.¹²⁻¹⁴ Peak positions derived from these other spectra on the direct transition model are shown as filled circles in Fig. 2. The relative peak positions in all the other 11 spectra were all in excellent agreement with ours, to the extent that comparisons could be made, when due account was taken of the somewhat higher resolution of Hansson and Flodstrom's data,¹³ and of the very high resolution of the spectra of Roloff and Neddermeyer.¹² However, we found that the absolute binding energies of the bands relative to E_F did not agree among the three sets of data as well as would be expected on the basis of their precision. The cause of this discrepancy may lie in the placement of the Fermi energy by the three groups, or it may arise from different methods used for locating peak binding energies. We note in this connection that the peak binding energies which we would derive from Fig. 3 of Ref. 13 are somewhat higher than those shown in their Fig. 13. At any rate, a unique explanation of the binding-energy discrepancy has eluded us. For the purpose of this paper, we have brought all the data very nicely into register by adding 0.18 eV to the binding energies given by Hansson and Flodstrom¹³ in their Fig. 13, and subtracting 0.25 eV from the binding energies of the 21.22 eV and 16.85 eV spectra of Roloff and Neddermeyer.¹² The data, thus adjusted, were re-plotted in Fig. 3. The energy bands have been

adjusted somewhat where the data warranted, to afford better agreement with experiment. With the exception of three points, all the experimental data are in satisfactory agreement with the adjusted bands; i.e., in most cases within 0.1 eV or less. The discrepancies were slightly larger for the lowest band and for the middle point from the 40.8 eV spectrum of Liebowitz, and Shevchik (at $E_B = 6$ eV, $k = 1.3$): in these two cases, the experimental uncertainties in peak position were also larger.

In adjusting the bands, the photoemission data did not extend to the L point, but fortunately the electron tunneling results of Jaklevic and Lambe¹⁷ could be used to tie down the position of the highest valence band (band 6) at $E_F - 0.3$ eV.

The three data points that showed genuine disagreement with the direct transition model all lie near 4 eV binding energy, and each is derived from a small shoulder on the low- E_B side of the main peak in the high-resolution spectra of Roloff and Neddermeyer,¹² at photon energies of 11.83 eV, 16.85 eV, and 21.22 eV, respectively. Although only in these spectra was the energy resolution high enough to resolve this weak feature, evidence for it (in the form of extra width near the foot of the main peak) can be found on careful inspection of the 11.6 eV spectrum of Ref. 13 and of our own spectra between 12 eV and 20 eV and at 30 eV photon energy. We interpret this small peak at 4 eV as arising from indirect transitions involving valence bands that rise up to ($E_F - 4$ eV) and become flat near the BZ boundary (e.g.,

near the X, K, and L points¹⁵). As in the case of the "s-p bands" plateau, such transitions could be phonon-assisted, and they would in the limiting case yield a spectrum resembling the density of states.

We have derived valence-band dispersion relations for the Λ line of silver from the adjusted bands in Fig. 3. They are set out in Table I. While the adjustment gave a visually dramatic improvement, the actual adjustment of the bands was in fact very small, rarely exceeding 0.2 eV and in most places being essentially nil. The only adjustment that is easily apparent by inspection is the distance between bands 4 and 6 where they appear to be repelling, about halfway between Γ and L. We find these bands about 0.9 eV apart at this point, while they approach one another to within about 0.6 eV in Christensen's RAPW band structure.¹⁵ With this exception, the agreement between this theoretical band structure and experiment is excellent.

C. The Γ_7 - Γ_8 Resonance at $\hbar\omega = 22$ eV

In this section and the next, there will be a brief discussion of two unexpected effects that arose during this study. Both are attributed to the structure of the conduction bands, and both may be expected to arise in other angle-resolved photoemission studies. The first is a Γ_7 - Γ_8 resonance at $\hbar\omega = 22$ eV.

Near Γ the d bands of silver are flat and fall into the Γ_8 Γ_7 Γ_8 levels, as discussed above. For photon energies of 24 eV and about the two Γ_8 peaks dominate the spectrum (Fig. 1), while the Γ_7 peak is not evident. At photon energies of $\hbar\omega = 20$ eV and below the four bands formed by splitting of the two Γ_8 bands are nearly

always resolved. The Γ_7 band, which (theoretically) remains essentially flat along Λ to the L point, is not evident in the spectra for photon energies below 20 eV or above 24 eV. At $\hbar\omega = 22$ eV, however, it yields the highest feature in the spectrum, as a third peak between the two Γ_8 -derived features. At $\hbar\omega = 21.2$ eV it also appears, better resolved¹² but less intense, in the same position. By curve-fitting, we establish this feature as present, but weak, in the spectra at $\hbar\omega = 20$ and 24 eV. Thus the Γ_7 peak intensity appears to be resonant around $\hbar\omega = 22$ eV. We attribute this behavior to the final-state band labeled 6^- in Christensen's band structure (Fig. 5), which becomes flat over a sizeable fraction (~ 0.2) of the Λ line near Γ , and lies at 22 eV above Γ_7 . The probability of photoemission along (111) appears to be resonantly enhanced by the very large joint density of states afforded by the flat initial- and final-state bands (Γ_7 and Γ_6 , respectively) at $\hbar\omega = 22$ eV. A similar effect would be expected in ARP spectra from gold along (111) in the photon energy range $\hbar\omega = 16$ -22 eV, because the conduction bands are calculated to be similar to those of silver and the valence bands are also flat near Γ .²⁷

D. The 17-eV Kinetic Energy Peak

For photon energies of $\hbar\omega = 26$ eV and above, our spectra show an additional weak feature which falls at ~ 17.5 eV kinetic energy relative to E_F , independent of photon energy. This feature is about 1 eV wide, but its low intensity and the presence of inelastic background inhibit an accurate determination of its width and shape. We attribute this feature to conduction electrons that have been excited

to higher energies, then inelastically scattered and trapped in band 7 and perhaps band 8 (see Fig. 4). These bands lie at about 17 eV about E_F , as discussed above for band 7 (Γ_6), are quite flat, and should contain a significant amount of plane-wave character with a (111) propagation direction. Thus, these bands possess all the attributes of a high probability of being occupied (and no unoccupied bands below them for electrons to scatter into) and the correct crystal momentum and energy to be observed in this experiment. Furthermore, we can think of no other mechanism leading to a constant kinetic energy peak at 17 eV.

This particular effect is unusual in angle-resolved photoemission, but the idea of structure in the inelastic tails of photoemission spectra due to conduction-band density-of-states (DOS) effects is well-known. Energetic electrons must move through the lattice in conduction-band states, and the "true" inelastic tail from the sample (as opposed to contributions from scattering on the analyzer grids) must be related to the conduction band structure. Of course, angle-averaging, coupled to the relatively featureless shape of the typical conduction-band DOS, preclude observation of significant structure in most cases. For Ag(111) the angle-resolved nature of this experiment, together with the unusual character of band 7, combine to produce a peak strong enough to be noticed accidentally.

In a broader context, this effect is simply a manifestation of angle-resolved secondary electron emission (ARSEE), which has been studied in detail by Willis and co-workers.¹⁹ In fact, our experiment differs from theirs only in the excitation mechanism, using

photoelectrons rather than high-energy electrons. If the experimental conditions were carefully adjusted, photon-stimulated ARSEE might be made to provide conduction-band information complementary to that obtained from constant initial state photoemission or from electron-induced ARSEE.

E. Summary to Part III

In Part III, it was found that the near edge absorption and partial photoyield reflect the feature found in the empty density of states. However, account must be taken of additional complications arising from atomic-like matrix element effects, large variations in the hole lifetime, and excitonic effects. Both surface and bulk-like photoemission were exploited in different materials. A deeply bound surface state on GaAs was discussed. Photoemission results were used to measure the band bending at the surface during the deposition of an epitaxial Ge overlayer, and the band discontinuities at the interface were deduced. Angle-resolved photoemission was then used to measure the energy and dispersion relations of states occurring during the formation of the interface. Finally, the direct transition model was found to hold (with some exceptions) in Ag(111), and the valence band dispersion relations were measured.

Table I. Derived Valence-Band Energies for Silver Along (in eV).^a

$k/(\frac{\pi}{4a})$	band 1	band 2	band 3	band 4	band 5	band 6
000()	(7.44)	5.92	5.92	5.48	4.78	4.78
— ^b		.02	.02	.02	.03	.03
111	7.05	5.89	5.85	5.39	4.74	4.72
—		.00	.00	.00	-.07	-.01
222	6.62	5.81	(5.30)	5.11	4.62	4.16
—		-.01	(.01)	.06	-.04	-.37
333	(6.84)	5.80	(5.45)	4.55	4.27	2.33
—		-.13	(.00)	.14	.11	-.09
444(L)	(6.94)	(5.82)	(5.53)	(4.20)	(3.96)	0.30
—		(-.17)	(.00)	(.00)	(-.01)	.14

^aBinding energies relative to E_F are given, with deviations of these numbers from those in Christensen's RAPW calculation given below. Parentheses mean that no data were available at these points.

^bBand 1 was not adjusted. The sparse data fit the RAPW curve very well.

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FIGURE CAPTIONS

Figure 1. Electron energy distributions at normal emission for Ag(111) in the range $\hbar\omega = 6$ to 32 eV. The region of predominantly sp emission near E_F is magnified for most spectra. For $\hbar\omega = 26$ to 32 eV the region containing the constant final state feature is also magnified.

Figure 2. Valence-band energies of silver along Λ , versus the k-point along Λ in the second zone that corresponds to each photoemission peak. A partial photon energy scale is indicated along the top, together with dashed curves for the conduction band (band 7) displaced down by 6 eV and by 10 eV. Christensen's band structure is plotted, together with our data (open circles) and those of Hansson and Flodstrom (filled circles from 7 eV to 11.6 eV), Roloff and Neddermeyer (filled circles at 11.83, 16.85, and 21.22 eV), and Liebowitz and Shevchik (filled circles at 26.9 and 40.8 eV).

Figure 3. Valence-band energies of silver along Λ after adjustment. The binding energies of Hansson and Flodstrom's data were increased by 0.18 eV and those of Roloff and Neddermeyer were reduced by 0.25 eV, bringing the experimental points into very good agreement. Christensen's bands were then adjusted to fit the data, with the additional constraint that band 6 lie 0.3 eV below E_F , as required by the tunnelling results of Jaklevic and Lambe. Derived energies are set out in Table I.

Figure 4. The Ag band structure along Λ as calculated in Ref. 15.

Fig. 1.

XBL 7810-11893

Fig. 2.

XBL789-2273

Fig. 3.

XBL789-2274

XBL 7810-11892

Fig. 4.

APPENDIX 1 - THE TREATMENT OF EXAFS DATA

This appendix will be a relatively informal discussion of the means for going from an extended x-ray absorption fine structure spectrum to a real-space picture of the neighborhood of a particular absorber site. The informal tone is appropriate because the field is still undergoing development and qualitative changes in the methods are likely in the future, and because some of my observations have not been either quantified or proved absolutely. What is intended here is to present some of the practical aspects of a "working" package of EXAFS analysis procedures. At present, this is embodied in a series of programs intended for batch processing. It should become obvious, though, that the analysis procedures involved are ideally suited to adaptation for interactive processing. Since the local conditions for interactive work are going from terrible to tolerable, this option should be considered.

The first step of the EXAFS treatment is the subtraction of the atomic-like smooth background from the absorption spectrum. An ab initio calculation of the background is unsatisfactory because of the possibility of systematic errors of the order of 5%.¹ The effect of a systematic error is to introduce a peak at frequencies $\leq 1.0\text{\AA}$ (depending on the data range and the shape of the function with respect to the optimum value).

In fact, the minimization of the spurious low-distance frequencies is one of the main criteria for optimization of a fit. The standard technique for an EXAFS background subtraction is to use a least-squares routine with the fitting function constrained to some

polynomial form. It should be recognized that the correct process strikes a balance between two antagonistic goals; 1) to achieve as close a fit as possible (the least-squares principle) and 2) to fit only to the smooth trend in the data while leaving the more rapid EXAFS oscillations untouched. The second goal can be termed "choosing the correct stiffness" to the fit, and it can be achieved by putting the proper constraints on the fitting function.

The simplest type of fitting is achieved by using a polynomial of degree $N-1$ (N fitting parameters) over the data range. In general, the lower the degree, the stiffer the background function obtained. Values of $N = 3$ to 5 are common. However, it is often the case that the variability of simple polynomials is too limited to make a satisfactory fit, and some type of spline routine is used for the fitting function. The spline² is a function which is subdivided into regions demarked by nodes. Within each region the function is a polynomial but the polynomials of different regions are allowed to be different. At the nodes, the polynomials and their first two derivatives are constrained to be continuous. The spline fit is a least-squares fit that is fully specified by the number of regions and the degree of the polynomial in each region.

One pragmatic matter that must be faced before any fit is made is the range of data to use. As it turns out, the results are sensitive enough that it deserves discussion. In the first place, data from less than 40 or 50 eV above the threshold often does not fit the simple EXAFS theory. To be conservative, is truncated for the background subtraction for $E \leq 20$ eV or more above threshold and

truncated further at the next stage of analysis. Also, the fitting routines have a tendency to place the first and last crossings of $\mu(E)$ about $\mu_0(E)$ inward from the data range. In particular, if it is apparent that the first cross of μ and μ_0 in the general range of interest occurs at E_0 , then the background fit should start at an energy $E_- < E_0$ for which the slope of $\mu - \mu_0$ nears zero (minimum or maximum).

These fits to the absorption data should be considered merely a numerical refinement of careful observations made by the experimenter beforehand. While some choices of the parameters are manifestly wrong, the simple fact is that there are not any objective criteria of the accuracy of the background fit that are sufficiently stringent so that the process can be run automatically. The data analyst must remain in the control loop and use an informed eye together with the amount of low frequency signal in the Fourier transformed EXAFS, and all the chemical/structural information that is known for the material in judging the goodness-of-fit.

At this point, two paths are commonly taken. The synthetic route compares the experimental data, χ , to a spectrum derived from a model structure, and then varies the structure to optimize the fit. I have used the more popular and direct Fourier transform route, using synthesis as an adjunct technique.

In this method, the modulus of a fast Fourier transform (FFT)³ is taken of the data after being compensated for phases, etc. as in Eq. 4.1. Also, one ordinarily includes an additional power of k to partially compensate for the attenuation of the spectrum. In order to

avoid spurious oscillations in the transform, it is desirable that the spectrum drop smoothly in amplitude towards the ends of the data range (a bell-shape envelope). This is commonly done by including a window function

$$W(k) = \begin{cases} 1 - \cos \omega_1(k-k_1) & k \leq k_1, \\ 1 & k_1 < k < k_2 \\ \cos \omega_2(k-k_2) & k_2 < k \end{cases}$$

Ordinarily, I have found that it is more efficacious to terminate the data at a zero-crossing, and that the proper choice of n in the k^n factor inserted in the integrand of the transform yields a satisfactory bell-shape without introducing additional functions. One further alteration is done to the data in a good EXAFS program. One must artificially simulate the effect that the physical range of k is infinite, $0 \leq k \leq \infty$, since the FFT⁴ is by nature a Fourier series instead of an integral transform. This is done by extending the actual data range by a factor of 10 - 100 by inserting the necessary number of $\chi = 0$ values to the data array.

The resulting real-space distribution function can then be interpreted directly or further treated. A number of innovations are cropping up, and filtering techniques (i.e., Chapter 3 or the method of Martens et al.⁵) in particular, are becoming more important.

Finally, mention should be made of the very important subject of the phase function. Most phase functions have been calculated and these can be used. However, it is not clear that the theoretical

results are accurate enough for careful quantitative EXAFS yet, and most often an empirical phase function is obtained from the EXAFS of model compound whose structure is already known. A phase function can be derived from the model compound by a nonlinear fit to a phase function given the structure, or the method of Ref. 5 can be used.

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$$A_{k+1} = 2 \sum_{j=0}^{n-1} x_{j+1} \cos(2\pi jk/N)$$

$$B_k = 2 \sum_{j=0}^{n-1} x_{j+1} \sin(2\pi jk/N)$$

for $k = 0, 1, \dots, N/2$

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