



Angle-resolved photoemission study of the antimony:arsenic interface using synchrotron radiation

by James Russell Myron

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

Montana State University

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Abstract:

The electronic properties of the overlayer-semiconductor interface system GaAs(110)+Sb(0),p(1x1) where 0 = 1/2-2 ML, are studied with synchrotron radiation-based polarization -dependent angle-resolved ultra-violet photoemission spectroscopy (PARUPS).

Two core level effects are reported, Sb-4d core binding energy shifts and the Sb-4d threshold effect. The binding energy shifts of the Sb-4d core are analyzed with curve fitting procedures and indicate the existence of two inequivalent Sb bonding sites, one on Ga and the other on As. The antimony core threshold effect is observed in angle-resolved constant final energy spectroscopy (ARCFS), photoemission yield spectroscopy, and electron energy loss spectroscopy data at energies of 32.5 and 33.75 eV. This is an Auger decay mechanism (non-excitonic) which involves the Sb-4d core and an empty Sb-derived surface state S7'. The energy of S7' is inferred to be 1.18 eV above the valence band maximum (VBM).

Valence band measurements were performed with normal emission EDC and ARCFS spectra. Transitions before and after Sb evaporation were mapped onto the theoretical energy bands. A phenomenon, the characteristic amplitude effect, is reported wherein bulk band transition amplitudes are changed by the ordered monolayer. The effect is independent of light polarization, but depends on the initial states. Evidence for non-uniform band shifting is seen in EDC spectra for $h\nu = 60$ eV where the surface contribution to photoemission is more dominant. In the ARCFS study, a new GaAs+Sb interface state S4' 3 eV below the VBM, is identified for Γ -MP and Γ -MP. The Sb-derived surface state S5 near the VBM is observed. A GaAs surface state M2, detected at the M-point, is located 1.8 eV below the VBM. Bulk band state B3 has initial state in valence band 2 and shows the same characteristic amplitude effect which was studied at normal emission.

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USING SYNCHROTRON RADIATION**

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**A thesis submitted in partial fulfillment
of the requirements for the degree**

**of
Doctor of Philosophy
in
Physics**

**MONTANA STATE UNIVERSITY
Bozeman, Montana**

June 1988

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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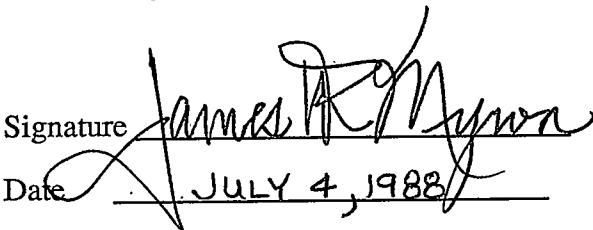
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JULY 4, 1988

This thesis is dedicated in memory of my father, Russell "Babe" Gordon Myron. His encouragement and interest in my education was a positive force from grade school through graduate school. While I was growing up, Babe would often take on all the farm chores, in order to permit me to work on my lessons. As a successful Montana farmer, his perseverance and aspiration to excellence in his endeavors were a trademark. I strived for these ideals throughout the long process of measurement, analysis, and study. My only regret is that he is not here for the thesis completion. But somehow, I feel, he knows its done.

VITA

James Russell Myron was born in Sidney, Montana on November 21, 1952, the son of Russell Gordon and Doris Bodil Myron. He has an older brother, Gordon, and two sisters, Patricia and Cheryl.

Jim attended elementary school at a two-room rural school in the small farming community of Crane, Montana. Later he graduated as Valedictorian of the Class of 1971 from nearby Sidney Senior High School. Summers and weekends were spent helping on the family farm near Crane in the Lower Yellowstone Valley throughout high school and undergraduate school years. He started college at Montana State University in September 1971. A Bachelor of Science degree in physics was obtained in June of 1976 and a B.S. degree in mathematics was received the following year. 1975 was spent touring Europe. After starting graduate school at M.S.U. in January, 1978, he joined Dr. G.J. Lapeyre's photoemission research group. A Master of Science degree was obtained in physics in June of 1980.

The summers of 1981 and 1982 were spent working on special geophysical projects for Amoco Production Company of Houston, Texas. Also in 1982, he was co-investigator on a Department of Energy Appropriate Technology Grant in Bozeman. The remaining time was devoted to thesis measurements at the Synchrotron Radiation Center near Madison, Wisconsin.

In September of 1983 he took a permanent position with Amoco in Houston and is presently involved in finding and evaluating new science and technology in the exploration of oil and gas. Data reduction, analysis, and thesis writing was done in absentia while also working for Amoco.

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ABSTRACT

The electronic properties of the overlayer-semiconductor interface system GaAs(110)+Sb(θ),p(1x1) where $\theta = 1/2$ -2 ML, are studied with synchrotron radiation-based polarization -dependent angle-resolved ultra-violet photoemission spectroscopy (PARUPS).

Two core level effects are reported, Sb-4d core binding energy shifts and the Sb-4d threshold effect. The binding energy shifts of the Sb-4d core are analyzed with curve fitting procedures and indicate the existence of two inequivalent Sb bonding sites, one on Ga and the other on As. The antimony core threshold effect is observed in angle-resolved constant final energy spectroscopy (ARCFS), photoemission yield spectroscopy, and electron energy loss spectroscopy data at energies of 32.5 and 33.75 eV. This is an Auger decay mechanism (non-excitonic) which involves the Sb-4d core and an empty Sb-derived surface state S'_1 . The energy of S'_1 is inferred to be 1.18 eV above the valence band maximum (VBM).

Valence band measurements were performed with normal emission EDC and ARCFS spectra. Transitions before and after Sb evaporation were mapped onto the theoretical energy bands. A phenomenon, the characteristic amplitude effect, is reported wherein bulk band transition amplitudes are changed by the ordered monolayer. The effect is independent of light polarization, but depends on the initial states. Evidence for non-uniform band shifting is seen in EDC spectra for $h\nu = 60$ eV where the surface contribution to photoemission is more dominant. In the ARCFS study, a new GaAs+Sb interface state S_4 , 3 eV below the VBM, is identified for $A_{\perp MP}$ and $A_{\parallel MP}$. The Sb-derived surface state S_5 near the VBM is observed. A GaAs surface state M_2 , detected at the $\bar{M}$ -point, is located 1.8 eV below the VBM. Bulk band state B_3 has initial state in valence band 2 and shows the same characteristic amplitude effect which was studied at normal emission.

CHAPTER 1

STATEMENT OF THE PROBLEM

In its most general form, the thesis problem was to understand better the properties of ordered overlayer-semiconductor interfaces by investigation of a specific model system. This model system should possess the ideal interface properties of junction abruptness, chemical stability, and structural order.

It would be necessary to prepare this interface reliably and measure its electronic properties *in situ*, with polarization-dependent angle-resolved ultra-violet photoemission spectroscopy (PARUPS) using synchrotron radiation. Of principal importance would be identification of overlayer-induced interface states. Characterization of these states would allow an experimental check on existing theoretical calculations. However, general exploration of any interface associated phenomena would be valuable in furthering our understanding of these interfaces, including core electron and bulk electron behavior.

In order to study the model interface system adequately, completion of the design and construction of a new photoemission experimental system with advanced PARUPS capabilities would be necessary.

CHAPTER 2

INTRODUCTION

"During the last thirty-five years much experimental evidence has been brought to bear upon the phenomenon that a large current will pass in one direction and small current, if any at all, in the opposite direction, through contacts of certain dissimilar solids." (Hartsough 1914).

This quotation refers to the rectification effect, which lay at the heart of the theory of metal-semiconductor (MS) interfaces. The MS interface was the principal focus of this thesis. Several MS theories have been proposed over the years (Schottky 1939, Bardeen 1947, and Brillson 1982), however today no single theory correctly predicts the complete behavior of even simple interfaces.

Even though interface related work has been done for over one hundred years, the study and characterization of solid state interface systems is currently a rapidly growing field of surface science. The basic research community has investigated the surface and bulk properties of clean crystalline materials for the last several years and they are generally regarded as understood (Weaver 1986). We are now in a good position to take the next logical step; examination of the bonding region between dissimilar materials - the interface. For basic science, it affords the opportunity to extend many ideas, including chemisorption on semiconductors, semi-classical junction models, and band bending theories (Dalven 1980). For applied science and microelectronics, the importance cannot be overstated. Within this decade, the characteristic gate size of electronic

integrated circuits will move into the submicron regime and as the surface to volume ratio of gates becomes larger, interface effects will play a significant role in device performance (Harris 1984).

For compound semiconductors, the chemical and electrical behavior at MS interfaces is very complex (Brillson, 1982) and often occurs over large microscopic distances (tens of angstroms) as opposed to an abrupt interface. The metal atoms can interact strongly with the clean semiconductor to produce two chemically distinct regions with varying properties. First, the reaction region is where new metal-cation or metal-anion bonds are formed. And second, the interdiffusion region is caused by either an outdiffusion of semiconductor atoms through the metal (*e.g.*, InAs(110)+Au) or metallic indiffusion (*e.g.*, GaAs(110)+Au) towards the semiconductor.

According to Brillson, it is the chemical reactivity of the metal with the semiconductor which governs, through interdiffusion, the interface thickness. Empirically, the stronger the metal-anion bonding, the more abrupt will be the interface.

Finding a good model system without the complications noted above was desirable in order to study the fundamental interactions occurring at the interface. The interface system chosen was the cleaved (110)-face of gallium arsenide GaAs, with overlayers (1/2-2 ML) of antimony Sb, deposited at room temperature. This system, GaAs(110)+Sb,p(1x1), was a good model system for the following reasons:

- (1) GaAs(110) is a well understood and technologically important material. (Blakemore 1987, Ferry 1985).
- (2) Sb grows as an ordered, epitaxial overlayer at room temperature on cleaved GaAs(110) (Skeath 1982 p.13).

- (3) GaAs(110)+Sb forms an abrupt interface with little diffusion of Sb into the bulk or Ga/As out to the surface region, which is not the case for many other metal-GaAs systems (Lin *et al.* 1987)
- (4) The surface unit net is preserved in size and mirror symmetry when going from GaAs, *as-cleaved* to the overlayer system.
- (5) The antimony on the surface is in a single crystal phase and resists oxidation compared to GaAs, *as-cleaved*, since the new surface has no unsatisfied bonds.
- (6) Multiple layers of antimony will thermally desorb for temperatures between 250° C and 350° C (Carelli and Kahn 1982).
- (8) Important theoretical calculations of the electronic structure have been performed by Bertoni *et al.* (1983) and Mailhoit *et al.* (1985).

CHAPTER 3

THEORY OF PHOTOEMISSION

Several surface analytical measurement techniques were used in the course of investigations of GaAs(110)+Sb. Figure 1 schematically defines these various techniques and indicates the general characteristics of each.

At the top is Ultra-violet Photoemission Spectroscopy (UPS), which is a subclass of Photoemission Spectroscopy (PES) where the incident particle is a photon ($h\nu = 10$ to 100 eV). It is a highly surface sensitive method with an investigation depth of 5 to 18 Å (1 - 3 ML). By conservation of energy, the photoelectron ejected from the sample has a energy equal to the photon energy reduced by the binding energy E_b of the electron when it was in a bound state and by the work function ϕ of the sample.

The second technique in Figure 1 is Electron Loss Spectroscopy (ELS) which uses a low kinetic energy incident electron (50 - 100 eV) as the incident particle and measures the energy of the emitted electrons. These spectra have an elastic peak, composed of the electrons which undergo elastic Coulomb scattering, and a wide variety of energy loss features due to plasmons (collective charge excitations), Auger transitions, and other inelastic processes. We employed ELS first as a nondestructive technique to quantify the thickness of the antimony overlayers which were evaporated onto the GaAs crystal. Latter, ELS was found to reveal new effects which could be related to the formation of the overlayer. These new effects which were revealed in the ELS data will be discussed in the section on the antimony core threshold studies (Chapter 6).

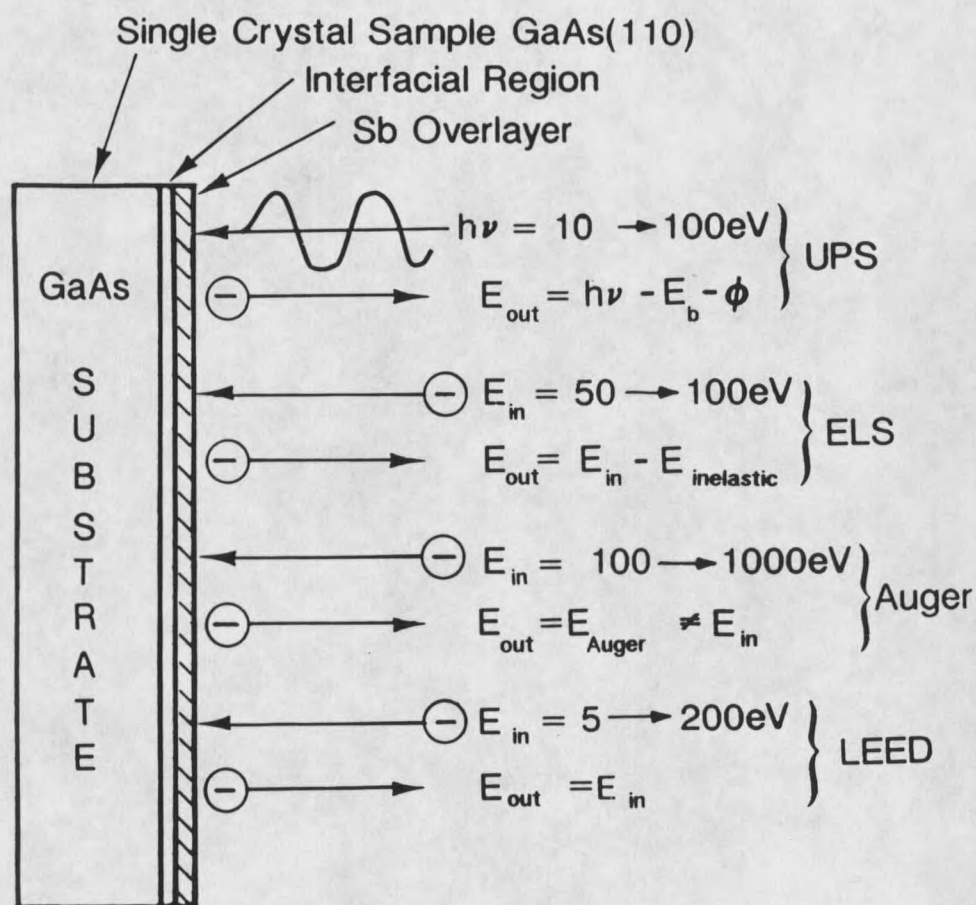


Figure 1. Surface analytical spectroscopies used in this work. The output particle of each technique is an electron of kinetic energy E_{out} . The input "probe" particle is either a photon of energy $h\nu$ (UPS) or an electron of energy E_{in} .

Auger Electron Spectroscopy (AES) was the third technique used. The basis for AES is a nonradiative transition where a vacancy (caused by ionization by an incident particle) in an inner shell of an atom is filled via the two-electron Auger process. Here an electron fills the vacancy and releases a characteristic amount of energy to a correlated electron (the Auger electron). Subsequently, this Auger electron is ejected from the sample with a unique energy E_{Auger} related to the binding energies of the atomic orbitals involved in the process. The Auger transition energy is rather like a unique chemical "fingerprint". At low kinetic energies (100 eV) the technique is very surface sensitive, since a low-energy Auger electron can escape only from the first few sample layers. Although AES has quantitative capabilities (Carlson 1975, Feldman and Mayer 1986), it was only used in this work when the overlayer sample could be sacrificed, since Zurcher (1982) had reported electron beam damage in GaAs(110)+Ge samples.

The last technique, Low Energy Electron Diffraction (LEED), was used routinely to characterize the sample surface before and after overlayer growth and to orient the symmetry axis of the crystal. LEED relies on elastic scattering and diffraction of slow electrons (50-200 eV) to determine the surface net and therefore the surface order. Of all these techniques, UPS was the principal method employed in this research work and will be the subject of the remainder of this chapter.

The Photoemission Process

Photoemission has a rich heritage in the physics community. The photoelectric effect was discovered by Hertz in 1887 (Weidner *et al.* 1968). An explanation of the effect, which postulated the quantization of light, was proposed by Einstein in 1905. Later, Millikan, through careful experimentation, verified Einstein's theory of the

photon, and constructed one of the first photoemission systems (Trigg 1975). Today the effect is exploited as a powerful spectroscopic technique for studying the quantum properties of solids. Spicer (1982) gives an interesting account of the role photoemission has played in the development of surface science.

A closely related research field to PES is the optical properties of solids (Wooten 1972) where the optical reflectance of a sample is measured as a function of the photon energy $h\nu$ of the incident light. The optical spectra manifest excitation processes within the material, but photoemission is more specific since it examines the electrons which have escaped from the sample as a result of irradiation by monochromatic light. Therefore PES, unlike optical reflectivity, gives the final state energy of the excitation as well as the excitation energy, which is of importance in understanding the electronic and optical properties of solid materials.

Experimental Aspects

Consider an arrangement as shown in Figure 2. Light (photons) impinges on the surface in a direction (θ_i, ϕ_i) , with energy $h\nu$ and polarization given by the vector potential $\vec{A}$. The photoelectron ejected into the vacuum travels in a direction (θ_p, ϕ_p) with a kinetic energy E_k and momentum $\vec{p}$ towards the detector.

The detector acts as a directional kinetic energy bandpass filter. The energy passband is termed the detector's energy window. By scanning the energy window and keeping a fixed direction, a histogram of the number of photoelectrons at each kinetic energy value, called an Angle-Resolved Energy Distribution Curve (AREDC) results. A hypothetical EDC is shown in Figure 2, and is composed of several parts:

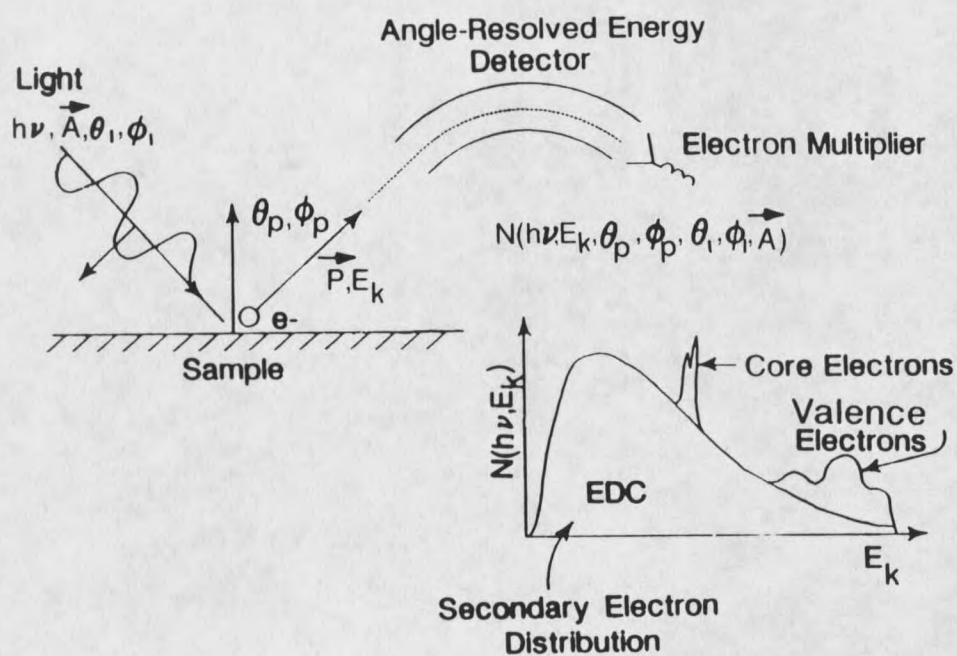


Figure 2. Generalized concept of photoelectron spectroscopy. Shining light onto the sample produces photoemitted electrons which are energy analyzed by the angle-resolving detector, resulting in an EDC.

- (1) The secondary electron distribution (SED) is a broad background curve with a long decaying tail resulting from inelastic scattering of the photoelectrons within the sample (Caroli 1973). Generally, this background is subtracted from the EDC in preliminary processing. These electrons are amongst the slowest-velocity electrons in the EDC and, because of their rather featureless nature, they are not of interest to us here.
- (2) The core electron peaks are rather sharp features which result from electrons excited from deep core states. These core states are the tightly bound inner electronic shells of the atom. The studies presented in Chapter 6 pertain to interface related effects manifested in the core states.
- (3) The valence electron features manifest the electronic bonding or band structure of the material and directly reveal the behavior of the solid; in this case, the interface system. These states are very sensitive to the many acquisition parameters of the experiment. When the detector is moved to a new analysis angle, the valence features will generally change and in the case of GaAs, the changes will often be dramatic, since the band structure is complex. Chapter 7 will cover several experiments which were designed to study these features.

Photoemission spectroscopy is inherently very rich in information. The purpose of much of the effort in a photoemission experiment is to define and measure the many parameters. The photocurrent J is a function of at least ten parameters, most of them related to the source and detector configuration:

$$J = J(h\nu, \theta_A, \phi_A, \theta_I, \phi_I; E_k, \theta_P, \phi_P, S; X) \quad (1)$$

where

the source parameters are:

photon energy: $h\nu$.

polar angle of the light's vector potential, $\vec{A} : \theta_A$.

azimuthal angle of the light's vector potential, $\vec{A} : \phi_A$.

polar angle of the light's propagation direction: θ_I .

azimuthal angle of the light's propagation direction: ϕ_I .

the detector parameters are:

kinetic energy of the photoelectrons: E_k .

polar angle of the photoelectron's momentum vector, $\vec{p} : \theta_p$.

azimuthal angle of the photoelectron's momentum vector, $\vec{p} : \phi_p$.

Lastly, the sample parameters are:

The photoelectron's spin polarization s , which we will ignore, and a manifold of sample characteristics which complicate the method. They have been lumped under the X factor. These include the type of material, crystal face, sample preparation, and surface cleanliness. Careful experimental technique is of paramount importance here in order to characterize the system.

Experimentally, we fix all the acquisition parameters (source and detector), usually adjusting only the photon energy $h\nu$ and scanning the kinetic energy E_k . This is the angle-resolved energy distribution curve (AREDC) mode of photoemission, resulting in a curve like shown in Figure 2. With this AREDC data (angle-resolved and energy-analyzed photocurrent), we try to determine the properties of the material. Using theoretical

models of photoemission as a basis (*e.g.* the three-step model) coupled possibly with theoretical calculations of the electronic structure of the system, we relate the data back to properties and excitation mechanisms of the material. In particular, our goal is to understand better the nature of the Ga-Sb and As-Sb bonding and how it relates to properties of the GaAs+Sb interfacial region.

Up to now we have only talked about the empirical aspects of photoemission, namely, measuring the kinetic energy and momentum of photoemitted electron after light has irradiated a material. A conceptual and theoretical understanding of the physical processes occurring within the sample, which result in our observations, is important in order to infer the properties of the material from the rather complex photoemission data. Two of the most popular models proposed for describing these processes are the microscopic one-step model (Feibelman and Eastman 1974) and the semiphenomenological three-step model (Spicer 1958). The one-step model is an elegant quantum mechanical approach, insofar as it treats photoemission as single wave function phenomena. The semi-classical three-step model works well for low excitation energies and is quite intuitive. The simpler three-step model has several shortcomings (*e.g.* surface effects) which the one-step model does not have. However, both models have importance in understanding the current research and will be used.

Three-step Model of Photoemission

The independent steps in the three-step model are (1) photoabsorption by a bound electron, (2) transport of that electron to the surface, and (3) its escape into the vacuum. Consequently, the photocurrent in Equation 1 factors into three parts:

$$J(E_f, h\nu) = P(E_f, h\nu)T(E_f, h\nu)D(E_f, h\nu) \quad (2)$$

where P , T , and D are the photoabsorption, transport, and escape factors, respectively. The final energy of the photoelectron is E_f .

Figure 3 puts the three-step model in context with the notions of the solid/vacuum interface, the VB and CB density-of-states, and the three acquisition modes of photoemission. It shows a hypothetical semiconductor, analogous to GaAs, with a shallow valence band density-of-states B (*e.g.*, VBs 2,3,4 in GaAs), a deeper VB feature called C (*e.g.*, VB 1 in GaAs), and a sharp core state called D (Ga-3d). The conduction band has a abrupt edge at the conduction band minimum and various conduction band structures. Of these, feature A will be of interest here. We have taken the Fermi level to be at mid-gap as it would be for an intrinsic semiconductor. The vertical direction represents energy, whereas the horizontal takes on many connotations depending on the curve in question. To the left of the solid/vacuum interface are the processes which occur inside the solid. Those to the right, like the measurement processes, happen in the vacuum.

The photoabsorption process (step 1 in Figure 3) can occur inside the semiconductor anywhere from 60 to 300 Å below the surface (Pankove 1971), because of the relatively long photon attenuation length in the solid. An electron in an initial valence band state of energy E_i absorbs a photon of energy $h\nu$ and jumps into a final conduction band state of energy E_f . Applying this reasoning to all electrons in the B structure, produces a distribution of excited conduction band electrons called B which is identical to the valence band structure B , provided the conduction band density-of-states are not changing. The same argument applies to features C and D , however these features are not drawn in Figure 3 for clarity of presentation.

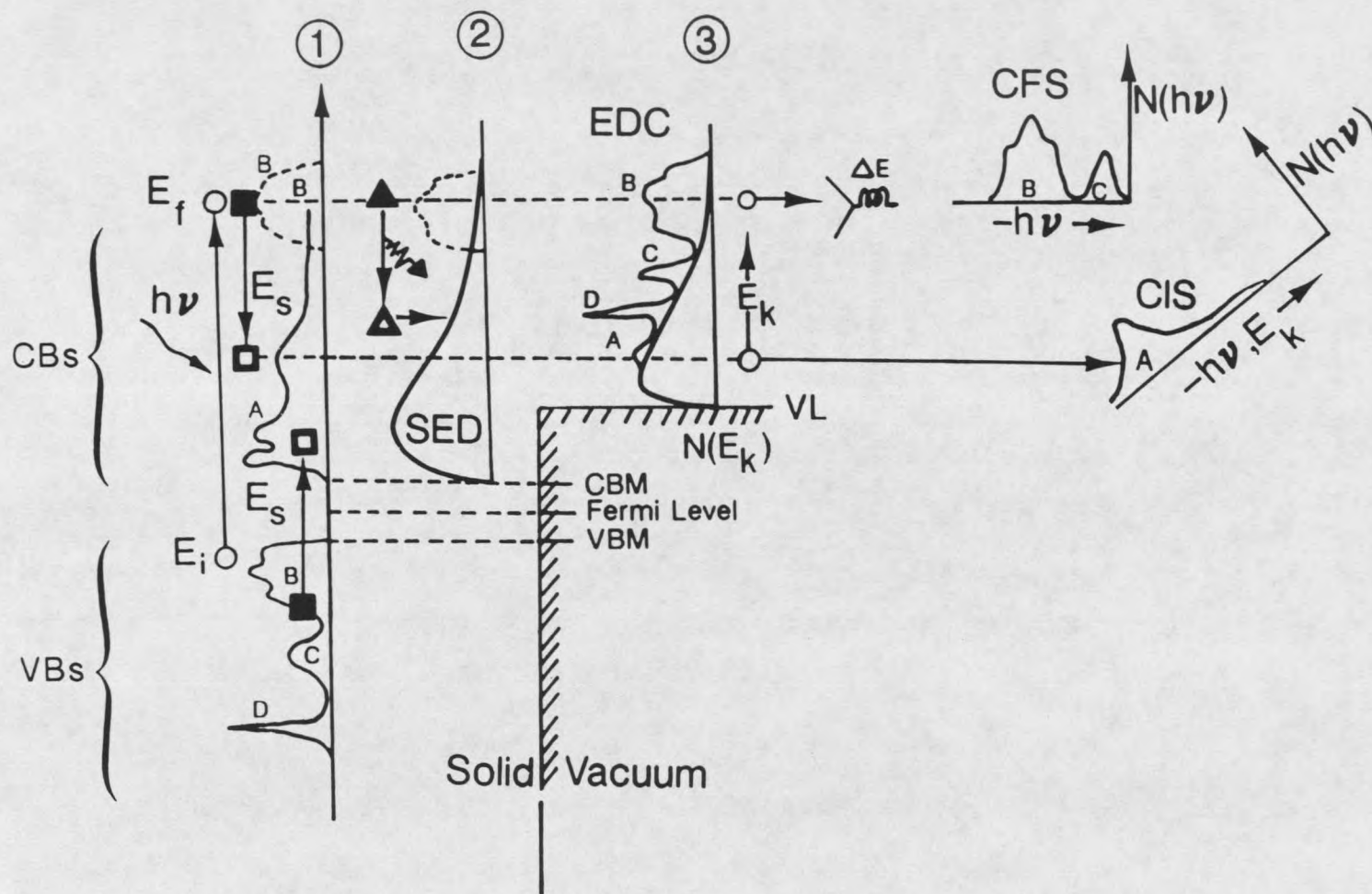


Figure 3. The three-step model of photoemission. Also shown is the relationship between the three-step model and the EDC, CFS, and CIS modes of measurement.

In a more theoretical manner, the photoabsorption factor P is derived from time-dependent perturbation theory. The effect of the photon field is represented by a time-dependent Hamiltonian $H'(t)$, which is weak compared to system's time-independent Hamiltonian H_0 . Therefore, the total Hamiltonian is the summation of two:

$$H = H_0 + H'(t) \quad (3)$$

We are looking for approximate solutions to the time dependent Schrödinger equation.

$$H\Psi(\vec{r},t) = (i\hbar/2\pi) \frac{\partial \Psi(\vec{r},t)}{\partial t} \quad (4)$$

We can write the wave function of H as a superposition of eigenfunctions $\psi_n(\vec{r})$ which are stationary states of H_0 with eigenvalues E_n (see Equation 6).

$$\Psi(\vec{r},t) = \sum c_n(t) \psi_n(\vec{r}) \exp(-i2\pi E_n t/\hbar) \quad (5)$$

$$H_0 \psi_n(\vec{r}) = E_n \psi_n(\vec{r}) \quad (6)$$

Here the expansion coefficients c_n are functions of time. By substituting Equation 5 into 4 and simplifying (Saxon 1968 p.209), we obtain the time evolution of the system through the c_n 's. The rate of change of these coefficients is proportional to $\langle \psi_f | H' | \psi_i \rangle$, the matrix element coupling the initial state $\psi_i(\vec{r})$ to the final state $\psi_f(\vec{r})$. The transition probability that the system will go from the unperturbed initial state ψ_i to the unperturbed final state ψ_f after the interaction is $|c_n(t)|^2$.

Now let's consider the effect of an oscillating electromagnetic field in the form of a periodic perturbation (Wooten 1972, p. 109),

$$H' = \frac{V(\vec{r})}{2} \{e^{i\omega t} + e^{-i\omega t}\} \quad (7)$$

For this, the probability of an electron going through an interband transition due to the radiation field is

$$|c_n(t)|^2 = \frac{16\pi^2 |M_{fi}|^2 \sin^2[\frac{1}{2}(\omega_{fi} - \omega)t]}{h^2 (\omega_{fi} - \omega)^2} \quad (8)$$

where ω_{fi} is the frequency difference between states ψ_i and ψ_f .

As usual, we examine the amplitude in state ψ_f as $t \rightarrow \infty$ (Wooten 1972). This gives, according to Fermi's Golden Rule, the probability per unit time W_{fi} for a transition from a discrete initial state ψ_i to a continuum of final states ψ_f as:

$$W_{fi}(E_i, E_f, h\nu) = \frac{4\pi^2}{h} |M_{fi}|^2 \delta(E_f - E_i - h\nu) \quad (9)$$

The matrix element M_{fi} in Equation 9 contains much of the physics of the expression. It is also the most difficult term to evaluate, because we would need to know the wave functions in order to do so. It is called the "dipole matrix element" of the solid and can be written as a sum of a core electron part and a valence electron part:

$$M_{fi} = M_{core} + M_{valence} \quad (10)$$

We will disregard the first matrix element term, since it deals mainly with atomic effects. However, the second matrix element term in Equation (10) contains most of the solid state physics of interest here.

$$\begin{aligned} M_{fi} &= \langle \psi_f | H_{fi} | \psi_i \rangle \\ &= \langle \psi_f | \vec{A} \cdot \vec{p} | \psi_i \rangle \end{aligned} \quad (11)$$

The excitation Hamiltonian is simply $\vec{A} \cdot \vec{p}$, if we use the Coulomb gauge (Plummer *et al.* 1982). The initial state wavefunction is ψ_i and the final state is ψ_f .

Therefore, the photocurrent in direction $\vec{R}$ due to light of energy $h\nu$ and final energy E_f (inside the solid) is given by

$$\mathcal{J}(\vec{R}, E_f, h\nu) = \frac{4\pi^2}{h} e \left\{ \frac{e}{mc} \right\}^2 \sum_i |M_{fi}|^2 \delta(E_f - E_i - h\nu) \quad (12)$$

In order to understand the technique further, we can assume that there are equal excitation probabilities between ψ_i and ψ_j so that $|M_{fi}|^2$ is constant and can be taken outside the summation over initial states, so that

$$\mathcal{J}(\vec{R}, E_f, h\nu) \propto |M_{fi}|^2 \sum_i \delta(E_f - E_i - h\nu) \quad (13)$$

$$\mathcal{J}(\vec{R}, E_f, h\nu) \propto |M_{fi}|^2 \int_S d\vec{k} \frac{\delta(\vec{k} - \vec{k}_n)}{|\nabla_k E_{fi}(k)|} \quad (14)$$

$$\mathcal{J}(\vec{R}, E_f, h\nu) \propto |M_{fi}|^2 \int_S \frac{dS}{|\nabla_k E_{fi}(k)|} \quad (15)$$

where S is a surface of constant energy E_{fi} is momentum space.

The properties of delta functions were used in going from Equation 13 to 14. Equation 15 shows that the photocurrent can be written as a matrix element times a joint density of states (Ashcroft and Mermin 1976, p.144). Physically, this means that the number of photoelectrons with a final energy E_f is proportional to the convolution of the VB-DOS and the CB-DOS at that energy. This convolution is modulated by matrix elements and added to/subtracted from by inelastic scattering and surface effects. More simply stated, the photocurrent entering the detector for a specific source/sample/detector configuration is governed by the initial density of states, where each state ψ_i will

contribute to the signal if the energy conservation conditions are satisfied. Moreover, the strength of the contribution will be determined by the square of the matrix element M_{fi} , barring any other effects.

Wooten (p.114) also provides a tie point here with macroscopic optical properties of solids by relating Equation 10 to the dielectric function ϵ . This can provide a convenient bridge between photoemission studies and optical properties of solids as we mentioned previously.

Photoelectron transport to the surface is quantified by the transport factor T of the form (Cardona and Ley 1978):

$$T = \frac{l(E_f)/\lambda_p}{1 + l(E_f)/\lambda_p} \quad (16)$$

where $l(E_f)$ is the mean free path given by the universal escape curve (Figure 4) and λ_p is the photon attenuation length. (Smith 1978, p.237)

Besides electron-electron scattering, inelastic collisions of photoexcited electrons can involve phonons, plasmons, impurities, or crystal defects. Each can make some contribution to the broad secondary electron distribution. The importance of these mechanisms depends on the nature of the sample (*e.g.*, crystalline versus non-crystalline), the purity of the material (*e.g.*, doping concentration or bulk impurity concentration) and the final state energy (Caroli 1973).

However, it frequently happens that the excited CB electron will lose some of its energy, usually through inelastic Coulomb scattering, and emerge elsewhere in the EDC. If this scattering involves another electron (square) E_e energy is exchanged. This is shown in step 1 of Figure 3. Even though the electron is promoted into the CBs, it cannot escape to be measured because it is below the vacuum level.

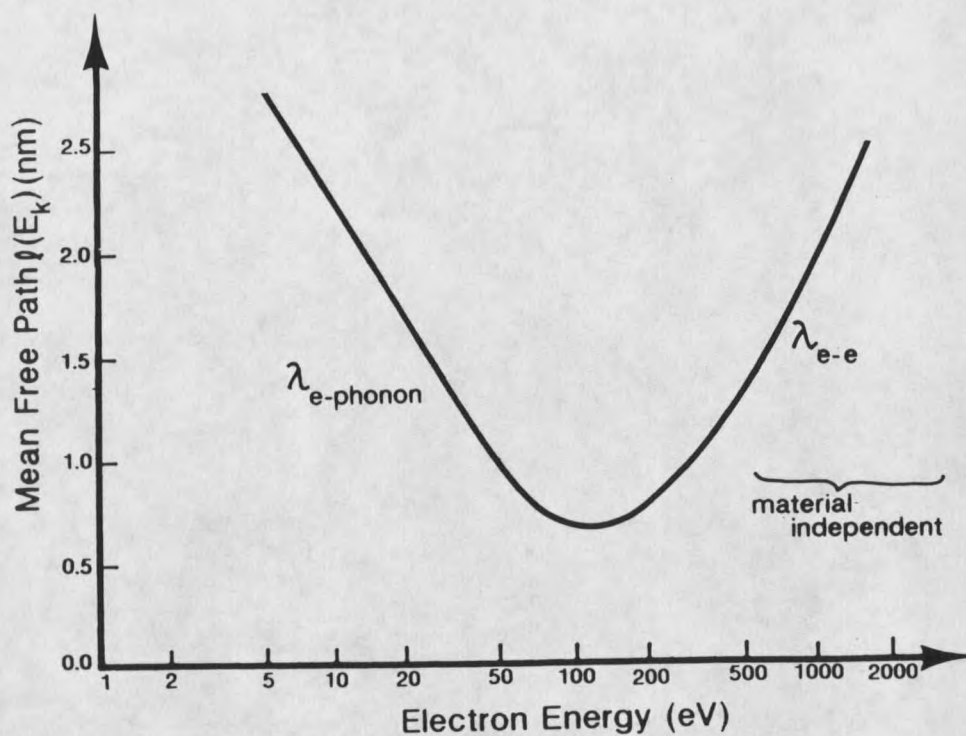


Figure 4. The universal escape curve. Maximum surface sensitivity occurs near a photoelectron kinetic energy of 50-100 eV.

As a result, the photoexcited electron (upper square) falls into a large CB-DOS and contributes to peak A' in the EDC. This phenomenon is termed a final state effect and it is not uncommon in EDCs.

Besides the electron-electron scattering which we have mentioned above, there are other possible channels for energy loss. For example, electron (triangle) interacts with a phonon on its way to the surface (step 2 in Figure 3). Ejection of these scattered electrons into the vacuum, called secondary electron emission (SEE), will account for the vast majority of electrons in the EDC.

Photoelectron escape into the vacuum is quantified by the escape factor D and is usually taken as a step function in the classical picture (Smith 1978):

$$D(E_f, h\nu) = 0, \quad \text{if } E_f(k) - E_{vac} < E_{||} \quad (17)$$

$$= 1, \quad \text{if } E_f(k) - E_{vac} > E_{||} \quad (18)$$

where $E_{||} = \hbar^2 k_{||}^2 / 8\pi^2 m$. At normal emission, $k_{||} = 0$, so that the condition for escape is $E_f(k) = E_{vac}$. In other words, the final kinetic energy of the hot electron must at least be as great as the vacuum level.

Effectively, this truncates the distribution in step 2 at the vacuum level, resulting in the EDC seen in step 3. Any electrons which have final states below the vacuum level are therefore not directly observed in the photoemission data. The curve in step 3 is measured at the detector.

Three Modes of Photoemission

Up to now we have only considered the EDC mode of operation for photoemission measurements, wherein the energy window of the analyzer is scanned while keeping the

photon energy fixed. The EDC intensity can be expressed as

$$N = N(E_f; h\nu = \text{fixed}) \quad (19)$$

If EDC measurements are repeated at closely spaced photon energies a data surface results, which is called the "photoemission surface". Figure 5 illustrates a hypothetical photoemission surface with just two features A and B. The surface is spanned by three orthogonal axes; kinetic (or final) energy E_f , photon energy $h\nu$, and intensity N .

Everything we can know about the photoemission response of the system for a given set of source/detector/sample parameters is embodied in this surface. In addition to this EDC-slice method, two other ways of constructing the emission surface are possible. These modes were termed "Constant Final energy State" (CFS) and "Constant Initial energy State" (CIS), by Lapeyre and Anderson (1975).

Slices parallel to the $h\nu$ -axis and orthogonal to the EDCs are CFS curves. This mode is allowed because of the tunable property of synchrotron radiation, *i.e.*, the energy of the light $h\nu$ from the synchrotron can be scanned. The CFS can be thought of as showing a picture of initial state emission into a fixed final energy. By synchronously scanning $h\nu$ and E_f , a CIS is acquired which is a diagonal cut through the emission surface. Conversely, the CIS shows a picture of the final states from a fixed initial energy. Either of these are more simple than the EDC, which is the convolution of the valence band density-of-states (VB-DOS) and the conduction band density-of-state (CB-DOS), called the joint density-of-states (JDOS).

Simply stated, all these modes are just different ways of cross-sectionally slicing the emission surface. However, operationally various types of phenomena are better manifested in one mode versus another. The following table summarized the functional form of each mode and their uses.

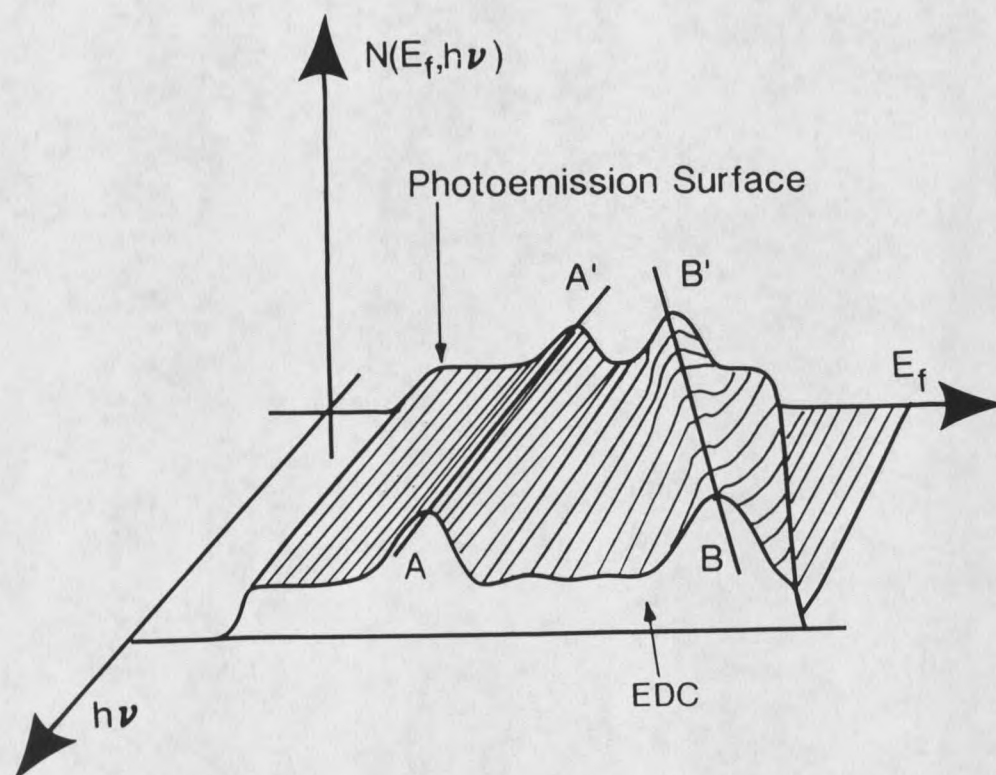


Figure 5. The photoemission surface for a hypothetical solid. Feature A-A' does not have $h\nu$ -dispersion, whereas feature B-B' does have energy dispersion.

Table 1. Three Modes of Photoemission.

Mode	Experiment Form	1-Particle Picture ¹	Uses
EDC	$N(E_f; h\nu = \text{fixed})$	$N(E_i + h\nu; h\nu = \text{fixed})$	N.E. PES ² PED ³ Core lineshape
CFS	$N(h\nu; E_f = \text{fixed})$	$N(E_f - E_i; E_f = \text{fixed})$	SS detection ⁴ Ga exciton O.N. PES ⁵
CIS	$N(h\nu; E_f - E_i = \text{fixed})$	$N(E_f - E_i; E_i = \text{fixed})$	Sample orientation Core threshold

1 $h\nu = E_f - E_i$ for 1-particle excitations only.

2 Normal emission photoelectron spectroscopy.

3 Photoelectron diffraction.

4 Surface state detection.

5 Off-normal photoelectron spectroscopy.

It is worthwhile to mention that certain mechanisms will not show up in EDC spectra, as in the case of the Ga surface exciton. Lapeyre and Anderson (1975) demonstrated there was enhanced photoemission from the vacuum level edge to the valence band maximum edge when the photon energy was scanned through the threshold for Ga-3d core to Ga empty surface state excitation. When $h\nu = 20.2$ eV, an electron is excited from the Ga-3d_{3/2} core state into the empty Ga surface state about 1 eV above the VBM. Because the excited electron and hole are bound together as a unstable exciton, direct recombination will cause its collapse. When this occurs, there is 20.2 eV of available energy to promote another electron from the maximum of the VB-DOS to the VBM of the EDC. As well, enhanced emission at the VL is seen. In fact, such excitonic effects are seen at all E_f 's for the specific $h\nu$'s across the emission surface.

In addition to the Ga exciton, which will show up numerous times in this work, this example points out the utility of CFS or CIS spectra for measuring certain phenomena. An EDC would show enhanced emission from the above effect over the entire EDC, however it would not reveal any structure, since none exists in the E_f direction.

One convenient way of analyzing an emission surface is to build the corresponding structure plot. It is nothing more than the projection of the local maximum in the emission surface onto the $(h\nu, E_f)$ plane. The ridge features (A and B) we have been studying so far map into straight lines (A'-A'' and B'-B'') in structure space. The term "structure plot" originates from the fact that the the topological "structure" of the emission surface is mapped into two-dimensional form in the structure plot.

The various spectra (CFS, CIS, and EDC), which are cross-sectional cuts through the emission surface, project into the straight lines in the structure plot. That is, the CFS and EDC structure plot lines are mutually orthogonal, while the CIS line is diagonal across the the structure plot.

The horizontal axis is the final energy and the vertical axis is the photon energy. Our two familiar features, A and B, are likewise drawn on the structure plot. And finally, the various cuts through the emission surface are shown as lines through the structure plot. These can be utilized to predict the various EDC, CFS, and CIS spectra.

The powerful nature of the structure plot is now revealed. It is a complete emission surface "map" which is tantamount to having measured all EDC, CFS, and CIS spectra with the photon and final energy window prescribed. As we will see, once the structure plot is constructed for special setup conditions, *e.g.*, normal emission, then it can be used as a guide in overlayer experiments.

One of the difficulties in doing overlayer experiments is to obtain the clean spectra as well as the overlayer spectra for comparison. We discovered a striking reproducibility amongst various independently acquired normal emission data, especially in those cases where the acquisition geometries are similar. Because of this, the normal emission structure plots contained in Chapter 7 and the Appendices at special polarization conditions may have general utility to future investigators.

When the simple density of states picture breaks down, as it does for GaAs, the emission surface will not appear as a simple "corrugated" surface like Figure 5. Instead, the direct (or vertical) transitions which occur will cause emission surface structures to appear and disappear abruptly and with large $h\nu$ -dispersion. This effect will become more apparent when we introduce the electron's momentum k into the problem, because in actuality, each EDC slice of the emission surface has a somewhat different DOS. The simple photoemission model discussed up to now ignores the electron's momentum k and this is a gross over-simplification.

Conservation of Photoelectron Momentum

Next we need to consider the subject of photoelectron momentum and the problem of determining the momentum perpendicular to the crystal surface. In the photoexcitation process, the crystal momentum is conserved:

$$\vec{k}_f + \vec{G} = \vec{k}_i + \vec{q} + \vec{Q} \quad (20)$$

By working in the reduced zone scheme (RZS), the reciprocal lattice vector $\vec{G} = 0$. The photon's momentum $h\nu/c = |\vec{q}| \sim 0$ is always negligible compared to the electron. Finally, if we consider only direct or vertical transitions, the phonon's momentum $|\vec{Q}| = 0$. Hence,

$$\vec{k}_f = \vec{k}_i \quad (21)$$

Where $\vec{k}_f$ is the final electron momentum within the solid and $\vec{k}_i$ is the initial momentum. So for each primary photoelectron which arrives at the crystal surface, its momentum has not changed appreciably from what it was in the chemical bond. The problem comes in when this electron crosses the solid-vacuum interface. This is shown in Figure 6.

When the photoelectron emerges from the solid, the perpendicular component of its momentum is not conserved,

$$p_{\perp} \neq k_{\perp} \quad (22)$$

In vacuum, the kinetic energy of the photoelectron is quadratically related to its momentum:

$$E_p = \frac{h^2 p^2}{8\pi^2 m} \quad (23)$$

If the vacuum momentum is written as a vector sum of the perpendicular and parallel components, *i.e.*, $\vec{p} = \vec{p}_{\parallel} + \vec{p}_{\perp}$, it can be shown that the parallel component is conserved within a reciprocal lattice vector $\vec{G}_{\parallel}$, for crystals which have infinitely-long, periodic surfaces:

$$\vec{p}_{\parallel} = \vec{k}_{\parallel} + \vec{G}_{\parallel} \quad (24)$$

In other words, if the surface retains the symmetry of the bulk, $\vec{k}_{\parallel}$ is a good quantum number. In the photoemission experiment, we measure the direction θ_p , and kinetic energy E_p , of the photoelectron. Knowing this, the initial energy E_i , and parallel momentum $k_{\parallel}$, can be found from formulas (25) and (26).

$$p_{\parallel} = k_{\parallel} = \sqrt{\frac{8\pi^2 m E_p}{h^2}} \sin \theta_p \quad (25)$$

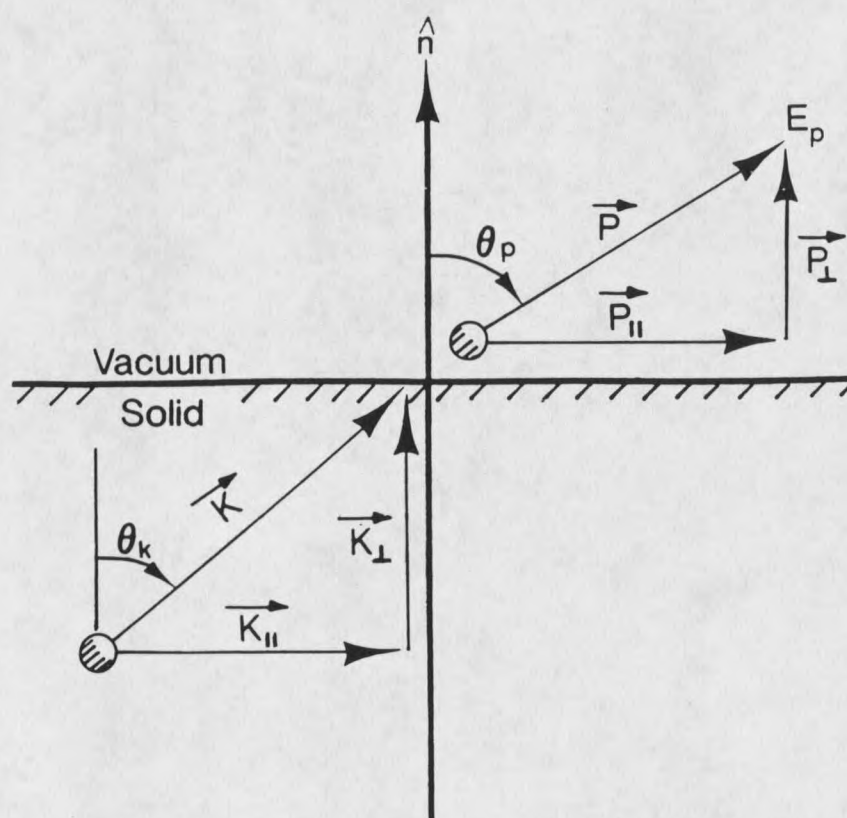


Figure 6. Electron momentum crossing the crystal/vacuum interface. The photoexcited electron has momentum $\vec{k}$ in the solid and $\vec{p}$ in the vacuum.

$$E_p = E_i + h\nu - E_{\text{threshold}} \quad (26)$$

To completely describe the electronic structure of our material, *i.e.* $E = E(\vec{k})$, we need to determine the perpendicular component of k , $k_{\perp}$ as well. As was shown in equation (22), this is problematic. Loss of symmetry perpendicular to the surface, prevents $k_{\perp}$ from being a good quantum number. Physically, the change in $k_{\perp}$ is due to ∇V near the surface or a charge density associated with ∇V .

At present, two main approaches exist to solve the problem of $k_{\perp}$ determination: (1) free electron-like final state approach and (2) the structure plot approach.

(1) Chiang *et al.* (1980) addressed the non-conservation of $k_{\perp}$ by assuming the hot photoelectron conduction state is a free-electron-like electronic state. In that case, an expression for $k_{\perp}$ can be written:

$$k_{\perp} = \frac{8\pi^2 m}{h^2} (E_i + h\nu - \phi) \cos^2 \theta_p - V_0 \quad (27)$$

However, knowledge of the inner potential V_0 is still required and is usually obtained by guessing (*e.g.*, -14.5 eV for GaAs). With this method, $k_{\parallel}$ is gotten from Equation 25 and $k_{\perp}$ from Equation 27. A limitation of this approach is the assumption of a free electron conduction band state. For $h\nu \lesssim 25$ eV, this assumption does not necessarily hold and, furthermore, the actual final state dispersion is not known.

(2) The structure plot method was pioneered by the MSU photoemission group (Williams, 1986) and will be discussed in Chapter 7. This is the approach which was taken to analyze the data in this work.

The One-step Model of Photoemission

Although the three-step model provides a great deal of insight into the photoemission process, it has several shortcomings:

- (1) The escape-factor D , ignores surface effects by treating the surface/vacuum interface classically as a simple highpass energy filter.
- (2) It does not take into account the highly excited final state in photoemission. This is because the wavefunctions ψ_i and ψ_f which are used to calculate the matrix element M_{fi} are stationary states.
- (3) By definition, it treats the photoemission process as three independent and uncoupled steps.
- (4) It ignores many-body effects (Feibelman and Eastman 1974), such as hole relaxation effects, photoelectron/hole interactions, and hole lifetime effects.
- (5) The joint density of states is used in calculating the photoabsorption factor.
- (6) It applies only in the limit of weak electron damping (*i.e.*, electrons which travel unaffected from deep in the crystal).

To correct some of these deficiencies, Feibelman and Eastman (1974) formulated the one-step model of photoemission. Even though they used only the lowest order perturbation theory which ignores many-body effects, these could be studied by including higher-order terms. They showed how this approach will yield the Fermi's Golden-Rule formula for photoemission and ultimately reduce to the three-step model in the limit of sufficiently weak electron damping. Even though the two models have these

common tie points, the physical interpretation of the models is quite different. This is the aspect which will be emphasized here and the reader is referred to the Feibelman and Eastman paper for mathematical details.

First, we will discuss the theoretical aspects of the one-step model of photoemission by considering the irradiation of an independent-electron solid with light. The vector potential of the radiation is

$$\vec{A}(\vec{r}, t) = \vec{A}(\vec{r}) \cos \omega t \quad (28)$$

The photocurrent j_r in the direction $\hat{R}$ of the detector (solid angle $d\Omega$) with kinetic energy E_k and bandwidth ΔE is

$$j_r(\hat{R}, E_k, h\nu) = \frac{v}{R^2} A \sum_i \delta(E_f - E_i - h\nu) |M_{fi}|^2 \quad (29)$$

where A is related to fundamental constants and v is the photoelectron velocity in vacuum. The summation in Equation 29 is over occupied initial states. The delta function insures conservation of energy in the one-electron approximation. This means that if relaxation effects, chemical shifts, and many-body effects are ignored, the final energy is the initial energy plus the photon energy. The matrix element is

$$M_{fi} = \int d^3r \psi_{vac}^* H' \psi_{xli} \quad (30)$$

where ψ_{vac} is the wavefunction measured at the detector and ψ_{xli} is an eigenstate of the crystal.

It has been pointed out that the wave function seen by the detector ψ_{vac} is an eigenstate of the vacuum (plane wave state). It was shown by Pendry (1976), that this final state is the time-reversed plane wave LEED state. That is,

$$\psi_{vac}(r, t) = \psi_{LEED}(r, -t) \quad (31)$$

and Figure 7 shows this conceptually.

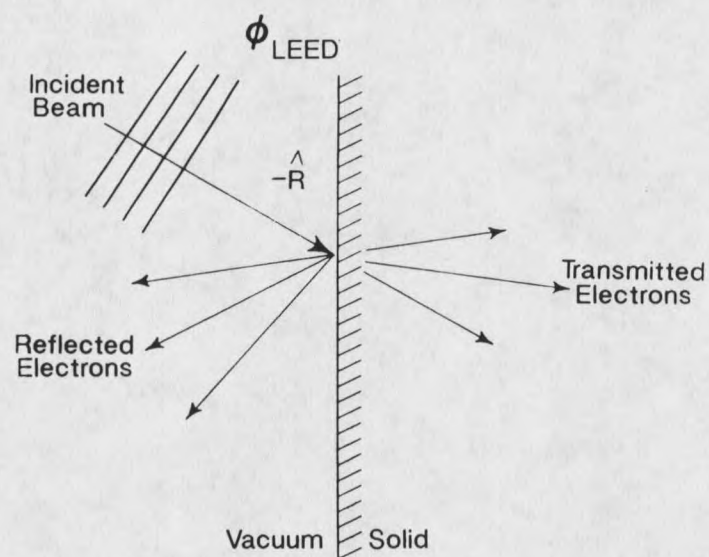
In the LEED experiment, an electron beam is shot at the surface. This is a plane wave traveling in the direction $-\hat{k}$. When it interacts with the surface, it splits into transmitted beams and reflected beams. The reflected electrons are used to conduct the LEED study. In the PES experiment, the photoelectron leaving the surface in the direction of $+\hat{k}$ is the plane wave which is the time reversal of the previous LEED beam. It is as though we are watching a movie of the LEED experiment run backwards (See Figure 8). In other words, the photoelectron which approaches the surface from the bulk as a hot electron conduction band state and escapes into the vacuum traveling towards the detector as a plane wave is the time-reversal of the LEED electron traveling towards the solid as a plane wave vacuum state and crossing the solid/vacuum interface to become a hot electron conduction band state in the solid. The surface can be thought of as a filter which is decomposing the incoming wavefunction (see Figure 8). From a practical viewpoint, this means matching boundary conditions at the solid/vacuum interface involves the same procedure in photoemission as in LEED.

Assume the target is a semi-infinite crystal with an ideal surface of two-dimensional periodicity. Then the wavefunction in Equation 30 can be expressed as functions U and V with periodicity along the crystal surface according to Bloch's Theorem (Kittel 1971, p.306).

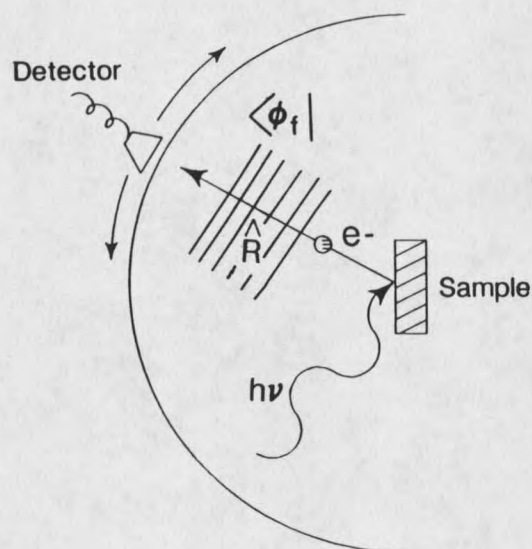
$$\psi_{vac}(\vec{r}) = \exp(i\vec{p}_{//} \cdot \vec{\rho}) U(\vec{\rho}, z) \quad (32)$$

$$\psi_{sl}(\vec{r}) = \exp(i\vec{k}_{//} \cdot \vec{\rho}) V_{\vec{k}_{//}, \vec{k}_{\perp}}(\vec{\rho}, z) \quad (33)$$

where U and V can be expressed as linear combinations of propagating and evanescent Bloch functions of z , respectively, and $\vec{\rho}$ and z are the radial and vertical space variables.

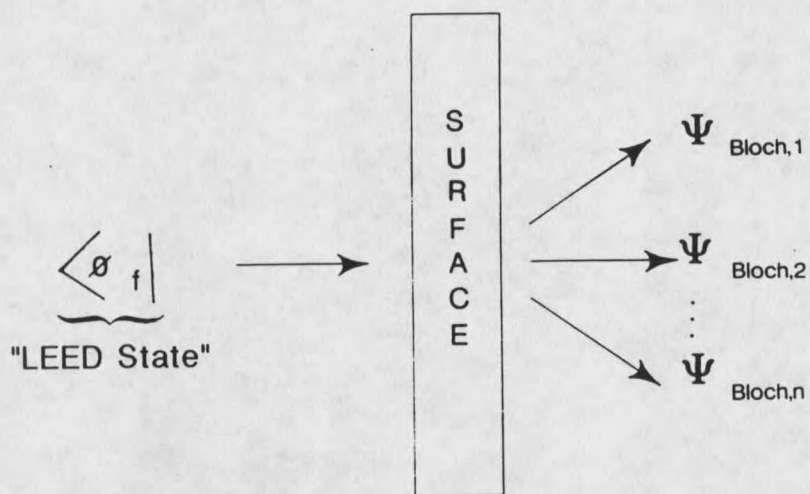


LEED Experiment

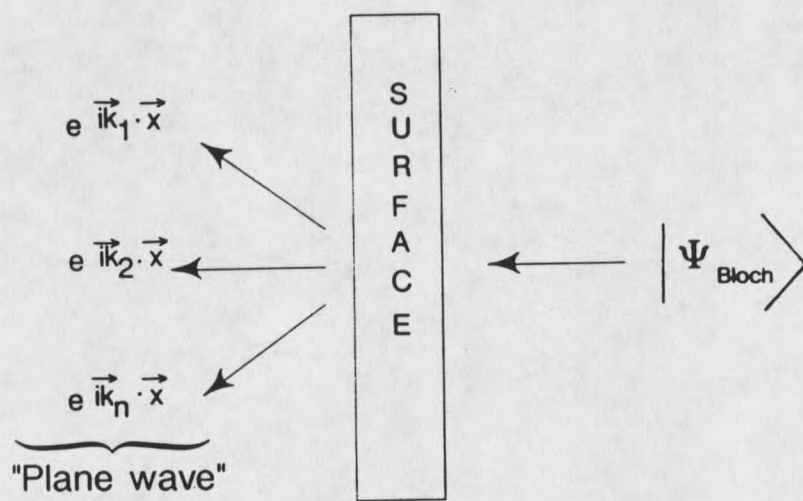


Photoemission Experiment

Figure 7. Comparison of photoemission experiment to LEED experiment. The photoelectron wavefunction measured at the detector ψ_{vac} is the time-reversal of the LEED wavefunction ψ_{LEED} from the electron gun.



LEED Experiment



Photoemission Experiment

Figure 8. Wave function decomposition in LEED versus photoemission.

In other words, U is a wave function. The perturbation Hamiltonian is

$$H' = \vec{A} \cdot \vec{p} = (-i\hbar/2\pi)A\hat{\epsilon} \cdot \nabla \quad (34)$$

where A is the magnitude of the light's screened vector potential within the crystal. It is taken to be spatially constant for $\hbar\nu < 200$ eV.

By substituting Equations 32, 33, and 34 into 30, and integrating over momentum space, we obtain

$$M_{fi}(k_{\perp}, \hat{R}, E_f - \hbar\nu) = \int dz \int_{\Omega_2} d^2\rho U^* \left(\vec{\epsilon}_{\parallel} \cdot \vec{k}_{\parallel} + \frac{1}{i} \hat{\epsilon} \cdot \nabla \right) V \quad (35)$$

Feibelman and Eastman expended considerable theoretical effort in understanding the nature of the matrix element in Equation 35 by casting the U and V into linear combinations of propagating and evanescent Bloch functions. One conclusion is that the peaks of M_{fi} show $\hbar\nu$ dispersion. Consequently, one should be able to use observed $\hbar\nu$ -dependence of EDC peaks, heights, and widths in addition to model calculations of the bands to determine energy dispersion relations of the sample. This is another way of stating the structure plot method.

Feibelman *et al.* also show that in the limit of small momentum broadening (long photoelectron escape depths or high $\hbar\nu$), the one-step model reduces exactly to the semiclassical three-step model. We are aware that in the important energy range of UPS (20 to 100 eV), the electron mean free path is short. In this case, photocurrents would need to be calculated from the one-step model matrix element since surface effects will be important.

Several photoemission regimes present themselves and can be understood within the context of the one-step model. These cases are shown in Figure 9 where we have a standard one-dimensional solid/vacuum energy band diagram (without k dependence). The solid is divided into a bulk and surface region (width d). The hypothetical material is a semiconductor with a VB/CB energy gap E_{gap} , between regions 1 and 2. Further, there is a conduction band energy gap separating CBs 2 and 4. The vertical direction is energy and the horizontal is distance, with the sample's surface/vacuum interface at zero. Three cases present themselves:

(1) The bulk photoemission regime occurs when the photon energy is low enough ($h\nu < 10$ eV), so that according to the universal escape curve (see Figure 4), the electron's mean free path will be long. This corresponds to the case of weak damping of the wave function. In this instance, the $h\nu$ -dependent structures in the EDC spectra are governed by the joint density of states. This is shown in case 2 of Figure 9. The CB state after photoabsorption is essentially an undamped Bloch state of the bulk, ψ_2 . Shown directly above ψ_2 is the corresponding time-reversed LEED state ϕ_2 with damping length λ_2 . Since the overlap integral $\langle \psi_2 | \phi_2 \rangle$ is large, excitations deep within the crystal will couple out to the vacuum and be measured at energy E_2 . However, strictly speaking, there are not three wave functions (ψ_1, ψ_2, ϕ_2), but rather one for the entire process, *i.e.*, one-step.

(2) Next we consider the surface photoemission regime. When the photon energy is in the typical UPS/SXPS regime (10 to 100 eV), we know the photoexcited electron in the solid experiences the most attenuation through scattering (see Figure 9). In case 4 of Figure 9, the CB wave function is damped out within a distance λ_4 of the photoabsorption event.

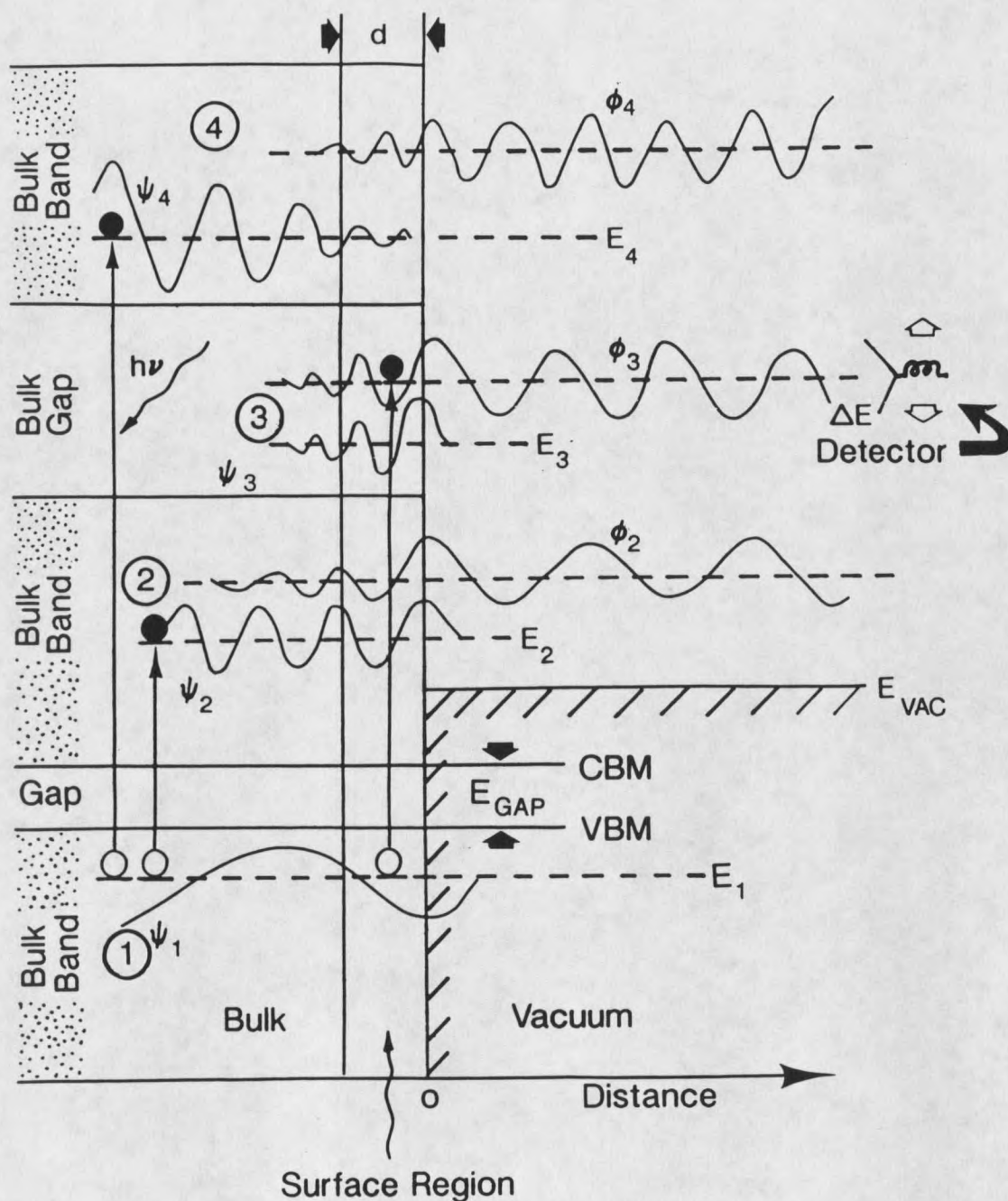


Figure 9. Bulk-like, band-gap, and surface-like photoemission. Case 2 is bulk-like effect where there is large overlap between the vacuum and Bloch wavefunctions. Case 3 shows band-gap effect involving evanescent states. Case 4 shows a bulk states which will not couple well with the vacuum state.

If $\lambda_4 \ll d$, the width of the surface region, there will be essentially zero overlap between ϕ_4 and ψ_4 . Therefore, photoemission will be very surface sensitive and few bulk excitations will be seen.

(3) Finally, there is the band gap photoemission regime. It is known from Bloch's theorem that any solution to the Schrödinger wave equation in a periodic solid must be of the following form:

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) \exp(i\vec{k} \cdot \vec{r}) \quad (36)$$

where $u_{\vec{k}}(\vec{r})$ must have the periodicity of the crystal lattice and $\vec{k}$ may be complex. Since all physically possible wave functions must be normalizable, the bulk electronic states must also obey the boundary condition that $\psi_{\vec{k}}(\vec{r} \rightarrow \infty)$ is a bounded function. Because of the plane wave factor, this means k must be a real number. However, if the normalization region is kept finite, the Schrödinger equation will allow solutions where k is an imaginary number. These are referred to as "evanescent waves" and must be surface localized. They are manifest in three different forms: (1) the decay tail of a vacuum state (ϕ_3 in Figure 9), (2) intrinsic surface states (ψ_3 in Figure 9), (3) adsorbate surface states.

In general, any wave function with complex k will be an admixture of propagating and evanescent Bloch functions. In particular, within the surface region of a crystal, there will always be a final state (e.g. ψ_3) in which to excite a given initial state ψ_1 . If the overlap integral $\langle \psi_1 | \psi_3 \rangle$ is sufficiently large, ψ_1 can contribute to the photoemission signal. This happens to electronic states which are themselves surface localized, like surface states of the clean crystal or adsorbate.

Since the bulk electronic state $\phi_{3,bulk}$ is non-existent and not shown in Figure 9, only surface related phenomena will be seen as the detector scans through region 3. This effect could produce amplitude variations in the peak and we would expect such peaks to be very surface sensitive. This is seen several times in the normal emission EDC study (see Chapter 7).

Relationship Between Experiment Parameters and Theory

A powerful aspect of ARPES is its ability to measure the electronic structure of a material at selected places in reciprocal space. Figure 10 shows the standard Face Centered Cubic (FCC) bulk Brillouin Zone (BZ) for GaAs. It is a truncated octahedron with special symmetry points: X at the center of each square face, L at the center of each hexagonal face, W located at the corners formed by two hexagons and a square, and K at the midpoint of the edge of the hexagonal faces. The Γ -point defines the center (0,0,0) of the BZ.

The conventional coordinate system inside the solid is formed by k_x , k_y , and k_z . High symmetry lines in the BZ are Σ (from $\Gamma \rightarrow K \rightarrow X$ in the next BZ), Λ ($\Gamma \rightarrow L$), and Δ ($\Gamma \rightarrow X$). Bulk band calculations are usually done along these symmetry lines.

Actually, when measuring through the crystal surface, as in photoemission, the two-dimensional projection, called the Surface Brillouin Zone (SBZ), is more germane. To obtain the SBZ for the (110) surface from the BZ, one can imagine slicing the BZ along the dotted lines as shown in Figure 10. For clarity of presentation, this SBZ has been moved away from the BZ along the dot-dashed lines. The Table 2 shows how symmetry elements in the BZ correspond to the symmetry elements in the SBZ.

An important point not revealed in the previous discussion is that the $\bar{M}$ -points in the SBZ, labeled $\bar{M}(As)$ and $\bar{M}(Ga)$, have different photoemission responses. They are photoelectrically distinct because all the doubly-occupied Ga dangling bond orbitals are oriented as shown in Figure 10 and the empty As orbitals are pointing in the opposite direction. Consequently, photoemission spectra taken at $\bar{M}(As)$ will, in general, be different from spectra taken at $\bar{M}(Ga)$.

Table 2. Symmetry elements in BZ and SBZ for GaAs(110)*.

BZ	Description	SBZ	Description
Γ	Center of zone	$\bar{\Gamma}$	Center of SBZ
K	Edge of hexagon	$\bar{\Gamma}$	Center of SBZ
W	Corner of hexagons	$\bar{M}$	Corners of SBZ
X	Center of squares	$\bar{X}$	Midpoint of SBZ sides
L	Center of hexagons	$\bar{X}'$	Midpoint of SBZ top/ bottom
Σ	$\bar{\Gamma} \rightarrow K \rightarrow X$	$\bar{\Gamma}$	Center of SBZ
Λ	$\bar{\Gamma} \rightarrow L$	$\bar{\Delta}'$	$\bar{\Gamma} \rightarrow \bar{X}'$
Δ	$\bar{\Gamma} \rightarrow X$	$\bar{\Delta}$	$\bar{\Gamma} \rightarrow \bar{X}$

*For a more comprehensive treatment of symmetry properties see Slater (1965).

The six angles which completely characterize a photoemission experiment are referenced to the SBZ (shown in Figure 11). The convention will be to use the surface normal vector $\vec{n}$ [110] as the zero for the polar angles, $\theta \equiv 0^\circ$, and the direction of the Ga dangling bond as the zero for all the azimuthal angles, $\phi \equiv 0^\circ$. Experimental determination of the Ga dangling bond direction is covered in Chapter 5.

The polar angle of the angle-resolved detector is θ_p , while its azimuthal angle is ϕ_p . Therefore, these are also the direction angles of the photoelectron momentum in vacuum. The light $h\nu$ strikes the crystal at a polar angle of θ_i and a azimuthal angle ϕ_i . Finally, the orientation of the light $\vec{A}$ has a polar angle θ_A and azimuthal angle ϕ_A . We know $\theta_i + \theta_A = 90^\circ$ and $\phi_A + \phi_i = 180^\circ$ because of the properties of light, hence not all the six angles are independent.

Since the polarization of the synchrotron radiation was fixed (*i.e.* $\vec{A} \parallel$ lab floor), different polarization conditions were obtained by rotating the sample about it's surface normal.

Figure 11 shows the SBZ looking from the (110) direction. The same special symmetry points in the previous figure are marked along with the radial distance in k-space to the point from the SBZ center. The relationship between kinetic energy, momentum, and polar angle shown in Equation 25 can be rewritten as

$$p_{||}^2 = (0.2628)E_p \sin^2 \theta_p \quad (37)$$

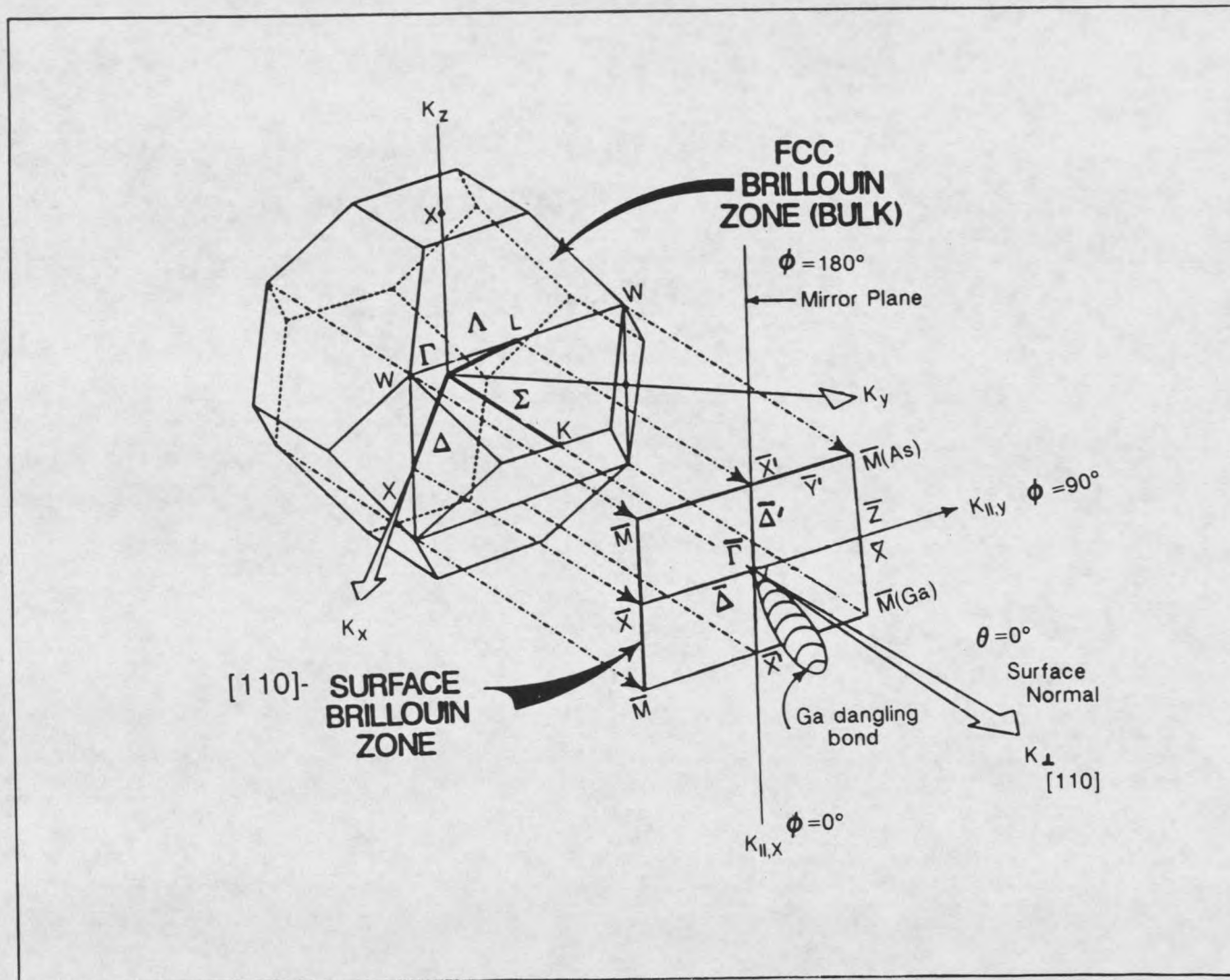


Figure 10. Surface and bulk Brillouin Zone for GaAs(110).

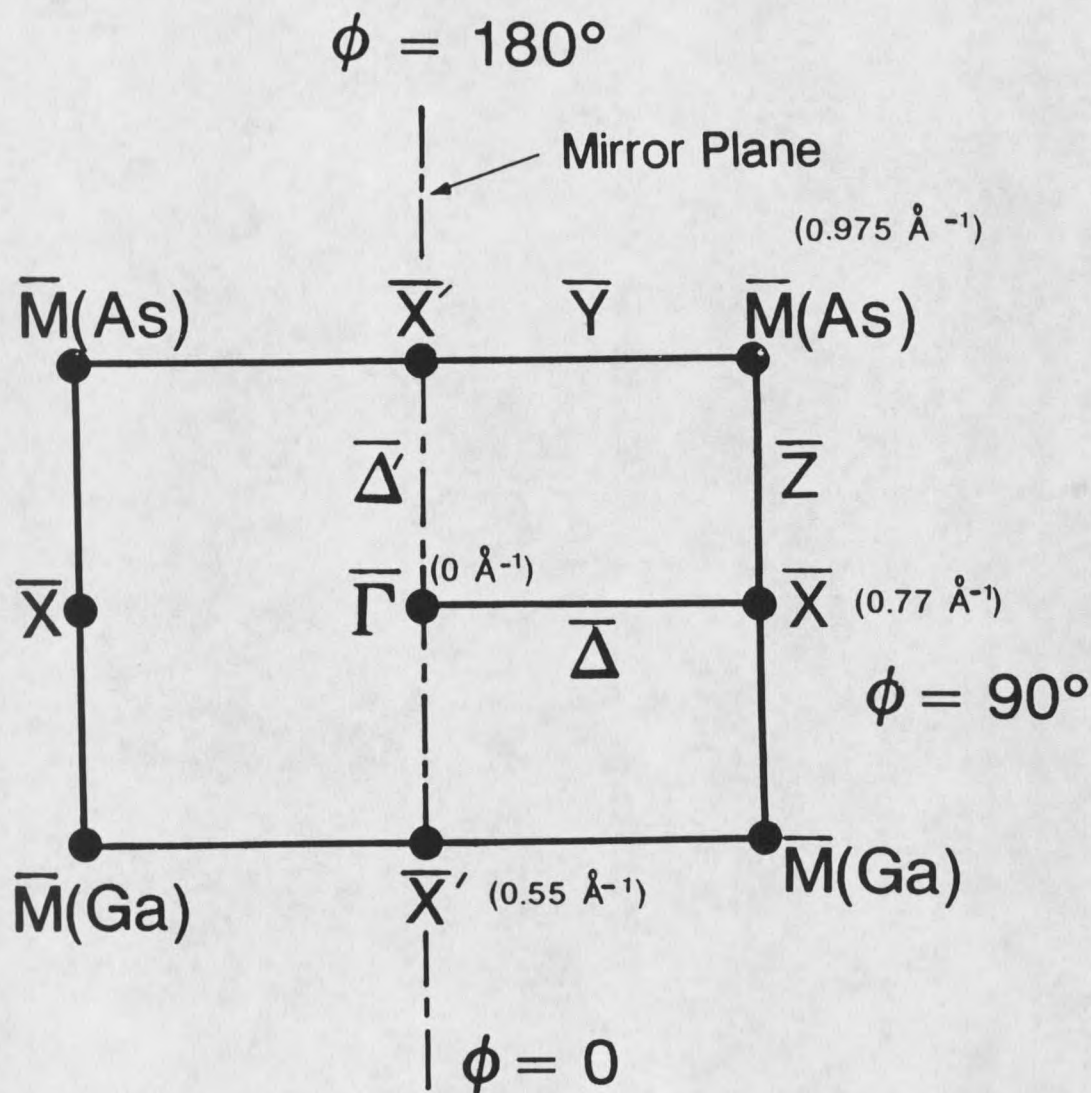


Figure 11. Surface Brillouin Zone for GaAs(110). The only surface symmetry operation for GaAs is the mirror plane (MP). The convention for azimuthal angle zero is the direction of the Ga dangling bond (downwards on page).

CHAPTER 4

PREVIOUS STUDIES

The surface science community has acquired an active interest in the interface system, GaAs(110)+Sb, stemming from a general interest beginning in the late 1970's regarding thin overlayers of column III, IV, and V elements on III-V compound semiconductors. Carelli and Kahn (1981) reported on the LEED, Auger electron spectroscopy (AES), and thermal desorption characteristics of the system. They found that for antimony (Sb) evaporated at room temperature (RT) onto GaAs(110), *as-cleaved*, "a continuous and sharp interface was formed with the substrate. For a coverage of one monolayer, LEED indicates a well ordered (1x1) structure which produces diffracted intensities very different from those measured from the clean substrate. Thermal desorption experiments show the particularly strong bonding between the first Sb monolayer and the substrate..."

Further, Carelli and Kahn reported, "Above 1 ML, Sb forms an amorphous overlayer. No overlayer-substrate interdiffusion can be observed and the AES Ga and As signals decrease according to their respective escape depth.... The structure of the interface is not modified by the heat treatment and no chemical shift is observed after the annealing cycle. A preliminary LEED analysis of the intensity profiles indicates two possible types of structures: chains of Sb atoms, extending in the (1 $\bar{1}$ 0) direction, with one Sb bond to the surface Ga or Sb dimers, with one Sb bonded to the surface Ga."

Overlayer-induced surface electronic structure can be classified into three main types (Bertoni *et al.* 1983):

- (1) Overlayer states are electronic states localized in the overlayer plane and are not involved in bonding with the substrate. These are shown schematically in Figure 12a.
- (2) Chemisorption-induced states (shown in Figure 12b) are due to bonding between the adatom orbitals and unsaturated substrate bonds.
- (3) Substrate surface states (shown in Figure 12c) are normally considered surface states of the clean surface and are modified or energy shifted by chemisorption.

Skeath (1982) was the first to look at the system with photoemission, although collaboration with Kahn *et al.* (1982) on LEED I-V measurements resulted in basically the same conclusions as above. Using XPS, Skeath studied, in some detail GaAs(110)+Sb with and without oxygen exposure. He noted the inertness of the Sb overlayer compared with bulk Sb, on the basis of chemical shifts of the Sb-4d core peak. It was only after an exposure of 1×10^7 langmuir of O_2 that a clear chemical shift in the core was seen. Finally, a limited set ARPES data was taken at three polarizations ($\phi_A = 0^\circ$ or 90° , $\phi_A = 180^\circ$ and $\phi_A = 270^\circ$), with a polar detector angle of 42.5° and photon energies $h\nu = 15, 17, 21, 23$ eV. These photon energies correspond to locations in k-space anywhere from $k_{||} = 0.6 \text{ \AA}^{-1}$ to $k_{||} = 1.5 \text{ \AA}^{-1}$, depending on the kinetic energy of the photoelectron in the EDC. Skeath pointed out that overlayer induced attenuation of the sharp GaAs(110) features was in excess of what is expected from reasonable escape depth considerations.

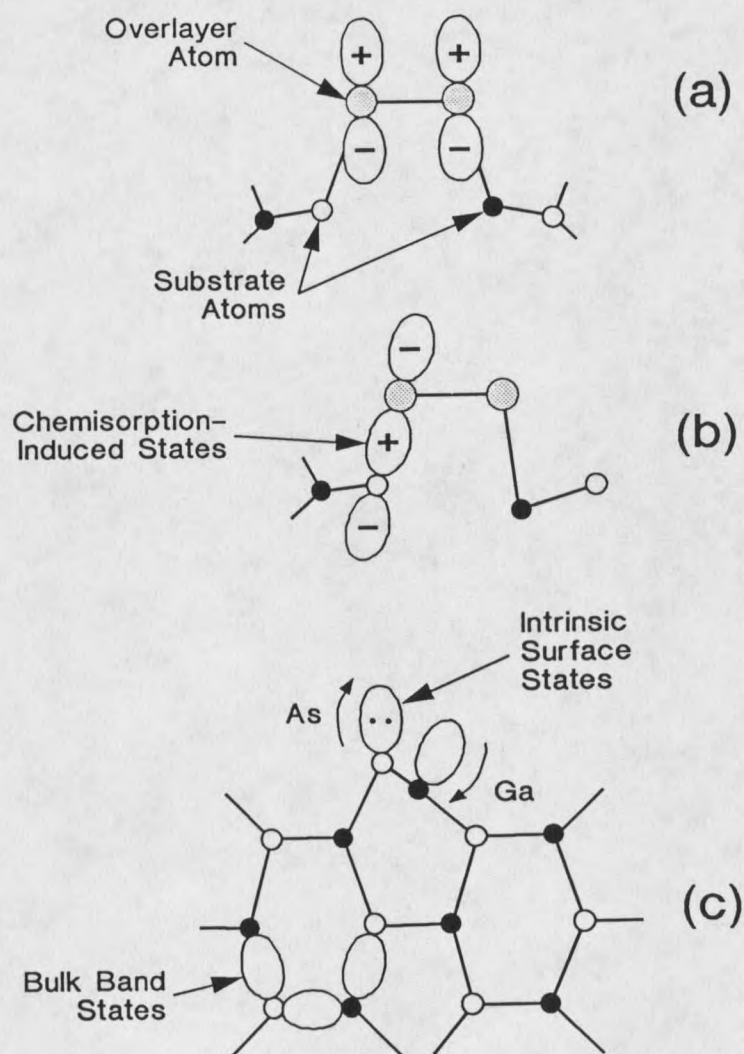


Figure 12. Overlayer-induced electronic states on III-V semiconductors. Overlayer states (a) are localized on the overlayer atom while chemisorption -induced states (b) are bonds between the overlayer atom and the substrate. Substrate surface states (c) are intrinsic to the substrate.

Skeath suggested that the features are "surface sensitive", but he did not quantify the effect further or propose what mechanism might be causing the phenomena. He also observed a strong increase in the emission near the VBM, seen in all angle-integrated data and angle-resolved data, but found no strong evidence for other new states.

The pioneering work of Kahn, Skeath, and coworkers prompted theoretical calculations. Such calculations could be done after a surface geometry model was determined. Using a dynamical LEED calculation, Duke *et al.* (1982) found a best-fit model. This surface geometry model is seen in Figure 13, where the upper panel shows a view from the side and the lower panel shows the same model from the top. Various dimensions (in angstroms) are indicated.

To a good approximation, the GaAs(110)+Sb,p(1x1) model shows that the reconstruction of the clean surface is "healed-out" by the antimony, yielding a nearly ideal bulk arrangement of atoms. That is to say, the antimony atoms are positioned in the locations of the next gallium and arsenic atoms, as if the lattice continued without termination.

Table 3. Bonding geometry of GaAs(110)+Sb.

Bonding atoms	Bond lengths	Bonding type
Sb-Sb	$2.8 \pm 0.1 \text{ \AA}$	p ² -covalent
Ga-Sb	$2.61 \pm 0.17 \text{ \AA}$	same as Ga-As bond
As-Sb	$2.70 \pm 0.17 \text{ \AA}$	purely covalent

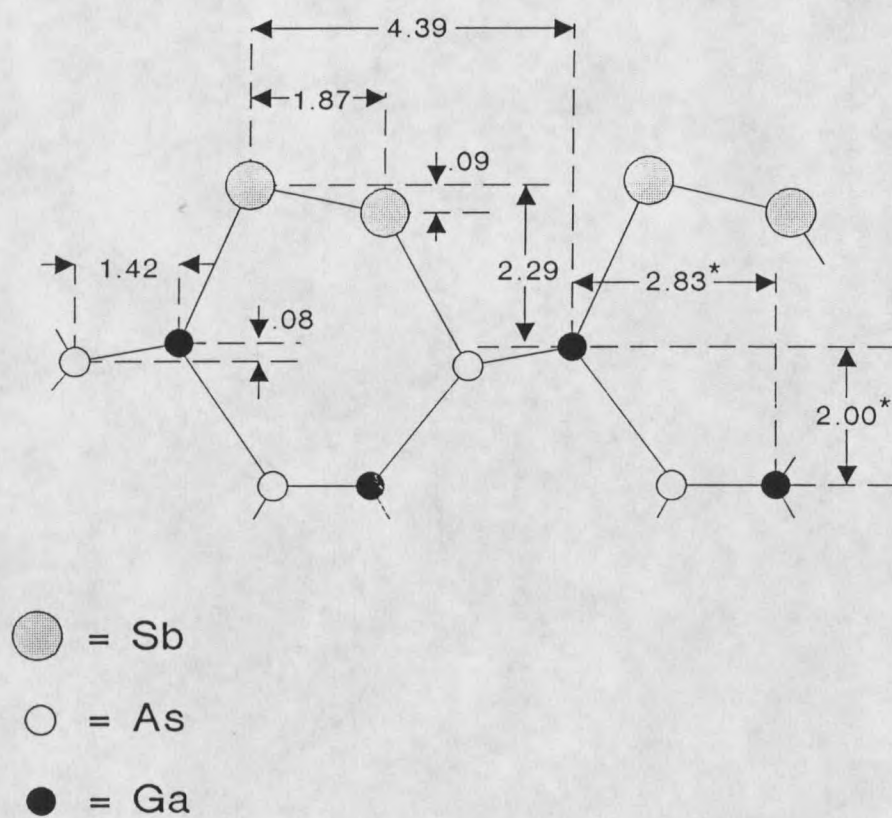
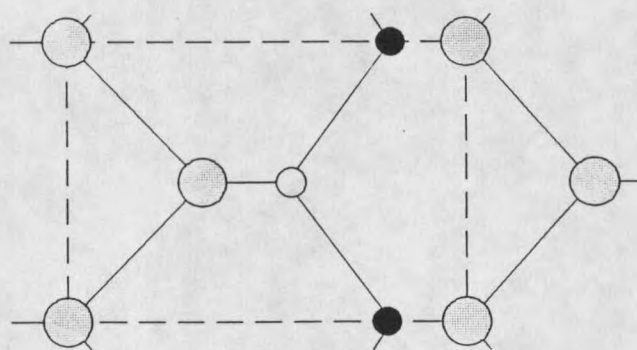


Figure 13. Atomic structure of GaAs(110)+Sb(1 ML),p(1x1). All distances are measured in angstroms (Duke *et al.* 1982).

After settling on a surface model for the system (Figure 13), Bertoni *et al.* (1983) calculated the electronic states using a self-consistent pseudopotential approach. This calculation showed that Sb is covalently bonded strongly to the substrate and that various overlayer-induced electronic states appear throughout the valence bands. The following table summarizes the states calculated by Bertoni *et al.* The first eight states (S_1 through S_8) are Sb related states, whereas the last three states (A_1 , A_2 , and C_1) are associated with the substrate atoms. The class of the state is noted in the second column of Table 4 according to the classification scheme of Bertoni *et al.* From the third column we obtain the occupancy of the various states. In particular, we note that states S_7 and S_8 are empty levels in the conduction bands. Finally, the last column provides a description of the physical significance of the orbital according to Bertoni *et al.*

Table 4. Theoretical surface states for GaAs(110)+Sb (Bertoni et al. 1983).

State	Class	Occupied	Description
S_1	Overlayer state	Filled	s-like Sb state on As atom
S_2	Overlayer state	Filled	s-like Sb state on Ga atom
S_3	Chemisorption state	Filled	Sb bonded to As sp^3 orbital
S_4	Chemisorption state	Filled	Sb bonded to Ga sp^3 orbital
S_5	Overlayer state	Filled	Lone pair on Sb atom (As)
S_6	Overlayer state	Filled	Lone pair on Sb atom (Ga)
S_7	Chemisorption state	Empty	Sb empty p orbital effect
S_8	Chemisorption state	Empty	Resonant character
A_1	Substrate state	Filled	s-like As state *
A_2	Substrate state	Filled	s-like As state *
C_1	Substrate state	Filled	s-like Ga state *

* Not present in clean GaAs(110)

A second theoretical calculation was carried out by Mailhoit *et al.* (1985) using a total-energy minimization method; the authors calculated the surface state eigenvalue spectra using scattering theory. This calculation used the Duke surface model described above as a starting point. The approach was taken in two steps: (1) eigenvalue spectrum of an isolated (p^2 -bonding) Sb-chain and (2) effect of bonding the chain to GaAs(110). The Mailhoit states will be summarized in a similar fashion to Bertoni *et al.*

Table 5. Theoretical surface states for GaAs(110)+Sb (Mailhoit et al. 1985).

State	Bonding type	Members	Occupancy	Description
S_1	Non-bonding	Sb	Occupied	s-orbital derived states
S_2	Non-bonding	Sb	Occupied	s-orbital derived states
S_3	Non-bonding	Sb-Sb	Occupied	Intra-chain bond p-states
S_4	Non-bonding	Sb-Sb	Occupied	Intra-chain bond p-states
S_5	Bonding	Sb-As	Occupied	Mixing π/sp^3 orbitals
S_6	Bonding	Sb-Ga	Occupied	Mixing π/sp^3 orbitals
S_7	Anti-bonding	Sb-As	Unocc.	Mixing π/sp^3 orbitals
S_8	Anti-bonding	Sb-Ga	Unocc.	Mixing π/sp^3 orbitals
p_x^*	Anti-bonding	Sb-Sb	Unocc.	Intrachain states
p_y^*	Anti-bonding	Sb-Sb	Unocc.	Intrachain states

Mailhoit *et al.* investigated the coupling of the p^2 -bonded Sb chain with the GaAs(110) substrate. They found that the substrate alters the chain eigenstates little for the non-bonding states S_1 , S_2 , S_3 , and S_4 . Whereas the bonding and anti-bonding states, S_5 , S_6 , S_7 , and S_8 are affected substantially by the substrate coupling.

Following my measurements in 1981-82, two additional studies have been conducted. First, Mattern-Klosson *et al.* (1986) studied Sb overlayers on *p*- and *n*-type GaAs(110) with UPS (He-I and He-II radiation), XPS (Al $K\alpha$), and ellipsometry. It was determined that Sb overlayers are semiconducting up to 20 ML, where metallic behavior takes over. This is when photoemission at the Fermi edge occurs. The authors report that a film of this thickness is polycrystalline since there is no LEED pattern and very broad, featureless UPS spectra. An unexplained result reported by Mattern-Klosson *et al.* was the different behavior of the work function on *n*- and *p*-type GaAs. It is suggested that for coverages below 1 ML, work function differences are due to changes in band bending, electron affinity of the semiconductor, and dipole moments between the overlayer and the substrate. At 1 ML of Sb, a shift of the energy levels of the Sb overlayer relative to the Fermi level might cause the decrease in the work function for *p*-type GaAs. In addition, the suggestion was made that interband transitions between states S_7/S_6 and S_7/S_8 could account for the maxima observed in the overlayer dielectric functions.

The second experimental study on GaAs(110)+Sb was conducted by Mårtensson *et al.* (1986). These measurements were done on *n*-type GaAs(110) as opposed to *p*-type GaAs in this work. They reported three Sb-induced states, S' , S'' , and S''' . In agreement with Skeath and this work, S' is actually S_7/S_6 determined by both of the theoretical calculations discussed above and is easily seen everywhere in the SBZ. Their state S'' is only observed as a weak shoulder near the $\bar{X}$ point and is interpreted to be state S_5 . The S''' state was mapped along the $\bar{X} - \bar{M} - \bar{X}'$ line. Their interpretation supports Mailhoit's results, namely that this is mainly a p_x and p_y derived state associate with the Sb-Sb bond in the overlayer.

CHAPTER 5

EXPERIMENTAL EQUIPMENT AND PROCEDURES

The five sections of this chapter discuss all of the experimental equipment, methods and techniques needed to study properly the GaAs + Sb system. The first section describes the photon source at the Synchrotron Radiation Center. The photoemission experimental system, which was built with the thesis measurements in mind, is presented in the next three sections. This discussion covers the ultra-high vacuum (UHV) main experimental chamber and attached apparatus, electron energy analyzers, and the computer acquisition system. The last section contains procedures on sample preparation.

Synchrotron Radiation Center

Numerous discussions of the research merits of synchrotron radiation have been published over the last several years (Rowe *et al.* 1974, 1977). Several of these unique and desirable properties are:

- (1) A continuous wavelength tunability over a wide spectrum, permitting a usable photon energy range from 9 to several thousand eV.
- (2) A very high light flux especially at short wavelengths.

- (3) Plane-polarization, which permits testing of symmetry characteristics and selection rules.
- (4) Stable light emission in position and intensity provide a constant optical alignment.
- (5) A highly collimated beam gives a typical spot size of 1 mm on the sample. This allows the experimenter to measure selectively from good areas of the sample surface.
- (6) UHV-compatibility is consistent with vacuum requirements for surface studies.

Electron Storage Ring - Tantalus II

The source for monochromatic photons utilized in the photoemission measurements was the Tantalus II electron storage ring operated by the University of Wisconsin's Synchrotron Radiation Center (SRC). Besides the photon source, SRC provided monochromators and support equipment for experiments. These will be discussed in the second section.

Tantalus II is a 3 meter diameter storage ring which magnetically contains a circulating electron charge at a energy of 240 MeV (See Figure 14). Although a radio-frequency cavity is used to replenish the electron's energy lost to radiation, beam lifetimes are limited to 4-5 hours, due to collisions with residual gas. A microtron (40 MeV) is used to inject beam currents on the order of 180-200 mA, making Tantalus a reasonably bright source for photoemission work. Recently, Tantalus has been superseded by a larger and more energetic source named Alladin.

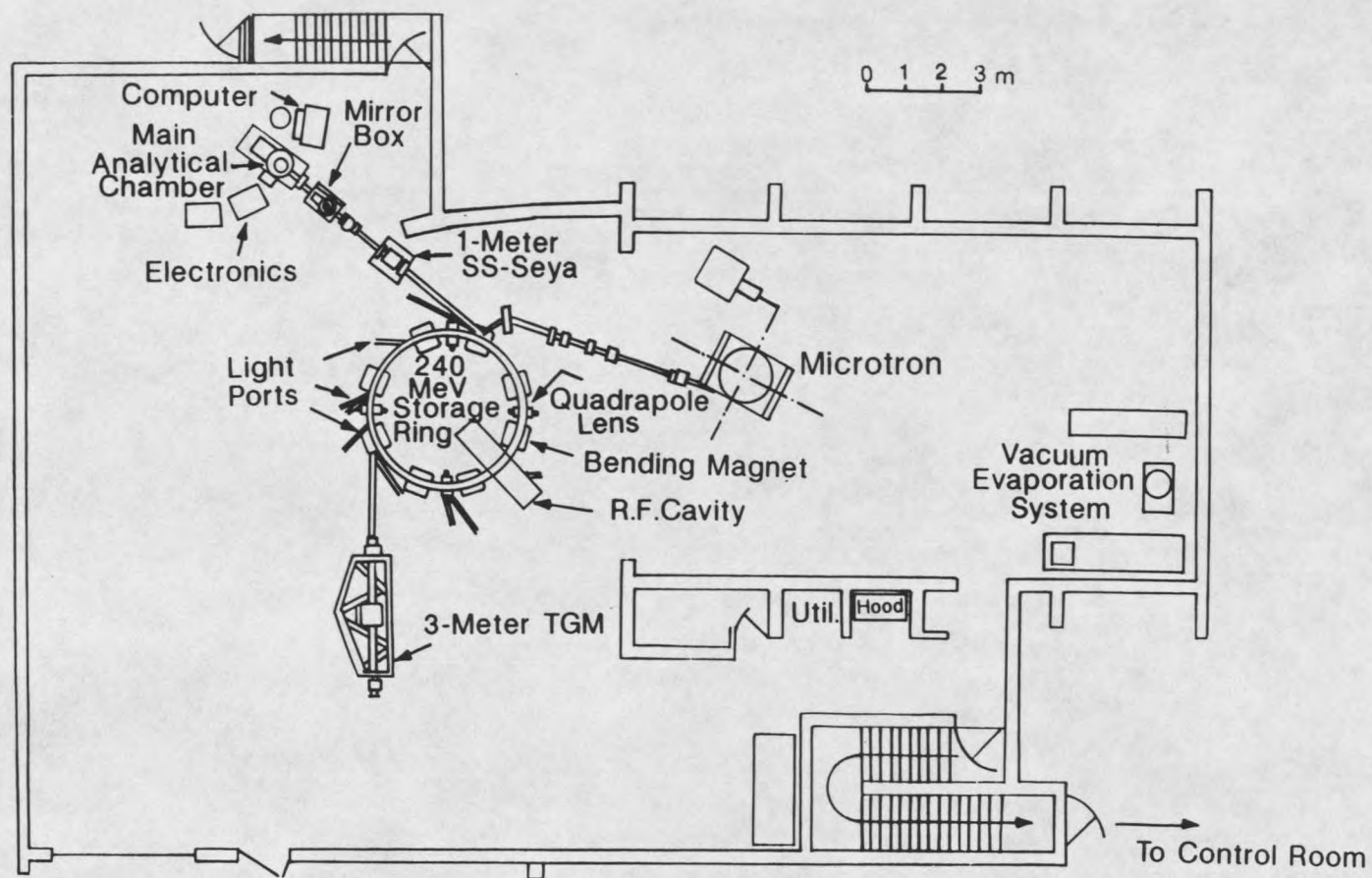


Figure 14. Experimental layout at the Synchrotron Radiation Center.

At the time of the thesis measurements, Tantalus was able to support 6-8 concurrent experiments. Figure 14 shows the two monochromators used in my thesis measurements, along with the plan view of the main experimental chamber, mirror box, and three relay racks of electronics.

Monochromators

Use of shared facilities, such as SRC for laboratory measurements is not typical in the physics community, although it is becoming more common. Factors such as scheduling availability of monochromators is important. Consequently, because different monochromators perform differently, flexible experiment strategy was a key element in successful measurements. The monochromators used in my thesis measurements are discussed below.

The stainless steel Seya-Namioka monochromator (SS-Seya) shown in Figure 15 was used extensively for valence band studies, since the usable photon range was from about 10 to 33 eV for a 600 lines/mm grating. It had a resolution of $0.2 \text{ \AA}$ with micrometer slits set at 35, making 6.3 meV at 20 eV (Pruett 1983).

If a concave grating is used in a monochromator, both focusing and dispersion can be attained with a single grating element. To have maximum resolution, the object and image points must be on the Rowland circle. The diameter of the Rowland circle is the principal radius of the spherical grating surface.

The SS-Seya was a 1-meter Rowland circle instrument designed around a vertical dispersion plane which is intended to enhance polarization of the light by virtue of the Fresnel reflection properties.

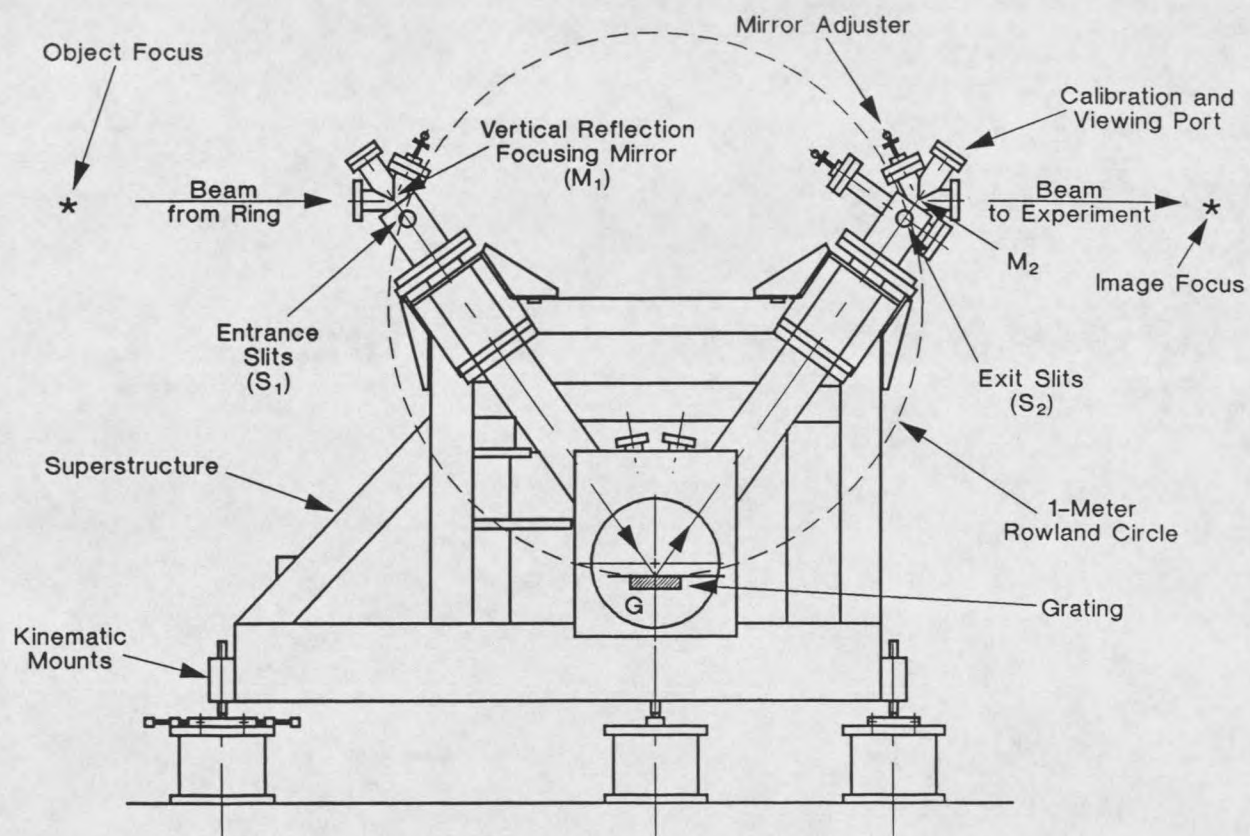


Figure 15. One meter Seya-Namioka Monochromator.

The grating is rotated by a sine-drive mechanism driven with a digital stepper motor, which allowed our acquisition computer to scan the monochromator. This capability was needed in CIS and CFS experiments which are covered in Chapter 7.

Light from Tantalus enters the SS-Seya from the left and is reflected off a vertical reflection focusing mirror of gold-coated fused silica M1. Entrance slit S1 is located on the Rowland circle. The radiation is dispersed off the grating G, through the exit slit S2, and finally reflects off the exit mirror M2 towards the target spot on the user's sample.

The toroidal grating monochromator (TGM) is a 3-meter Rowland circle device. Figure 16 shows the general concept of this device. This monochromator is equipped with two gratings. The high energy grating (HEG) is most effective from 50-130 eV and was useful for measuring core level spectra, whereas the low energy grating (LEG) covers 9-50 eV and was mostly useful for valence band measurements. It was possible to switch between the HEG and LEG *in vacuo*. The TGM has excellent optics due to its 15° grazing incidence angle and it can produce a very bright, small (< 1 mm diameter) spot at the sample location. The total scan range is from 80 to 1300 Å. The entrance and exit slits are discretely adjustable, permitting the user to optimize the flux/resolution factor for a given experiment.

Main Experimental Chamber

Prior to my thesis measurements, I participated in building a completely new experimental system. The system was first routinely used in December 1980, although various modifications and upgrades occurred over the next twelve months.

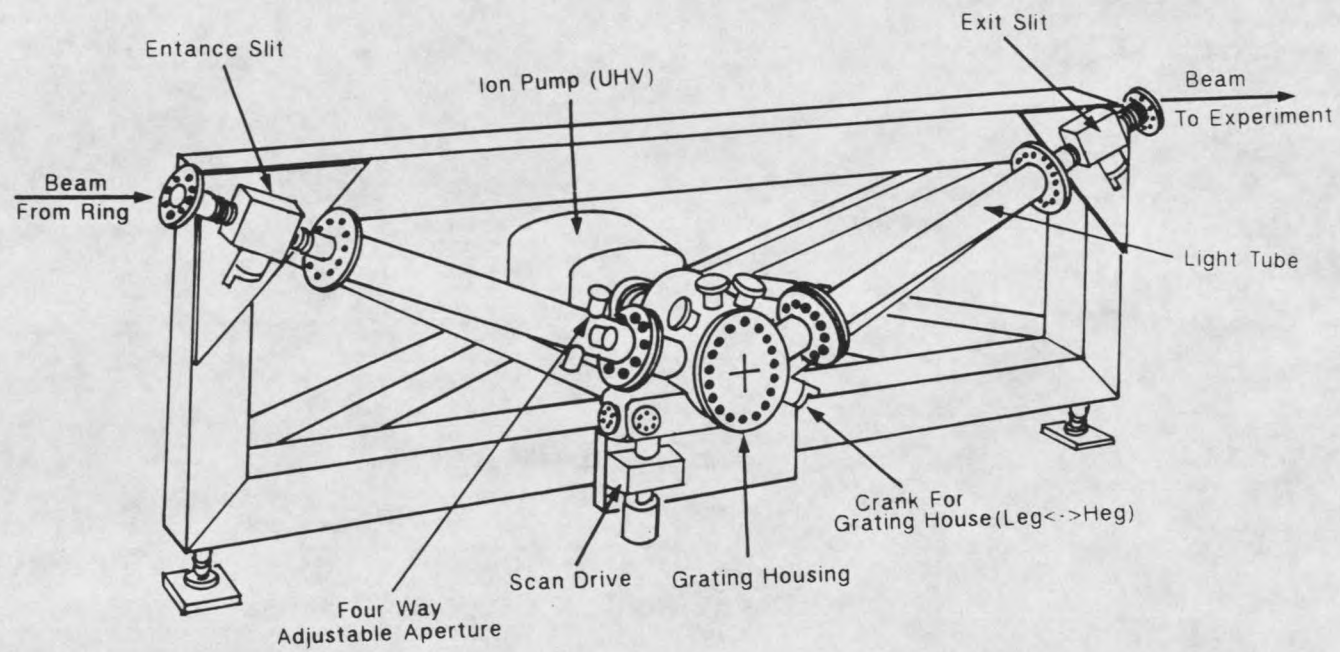


Figure 16 Three-meter toroidal grating monochromator.

Figure 17 is a schematic of the photoemission system showing the system's layout during measurement operations. The main ultra-high vacuum (UHV) experimental chamber attaches to an aluminum mounting structure. This mounting structure has various adjustment features which allow for kinematical motion during optical alignment.

On top of the UHV chamber is a sample manipulator (built in-house) which transports the crystal from the upper diagnostic level (for LEED, XPS, ELS and AES) to the lower analytical level (for photoemission studies). The sample manipulator also allows the crystal to move in the horizontal plane and rotate about a vertical (V) axis and a horizontal (H) axis for changes in the polarization angles of the synchrotron radiation, *i.e.*, the angle between the crystal lattice and the radiation vector potential $\vec{A}$. A plane mirror analyzer (PMA) is housed in the lower level of the chamber and mounted on a twin-axis goniometer which, in turn, is attached to the base Wheeler flange. The twin-axis goniometer allows rotation about a primary (P) and secondary (S) axis which permits positioning of the PMA at any emission angle with respect to the sample. An angle-resolving cylindrical mirror analyzer (CMA) inserts with a bellows drive assembly into the lower level and is also used for photoemission studies. Light from the storage ring is dispersed at the monochromator (right-hand side) and, via an exit mirror, the radiation is redirected to the main experimental chamber. Upon leaving the exit mirror, the light is refocused with a ellipsoidal mirror. Following the refocusing, the light passes through a tungsten diode (for flux measurement) and is directed to a 1 mm spot on the sample at the analysis point. The photoelectron analyzer, either the PMA or CMA, is also aimed at the analysis point for measurements.

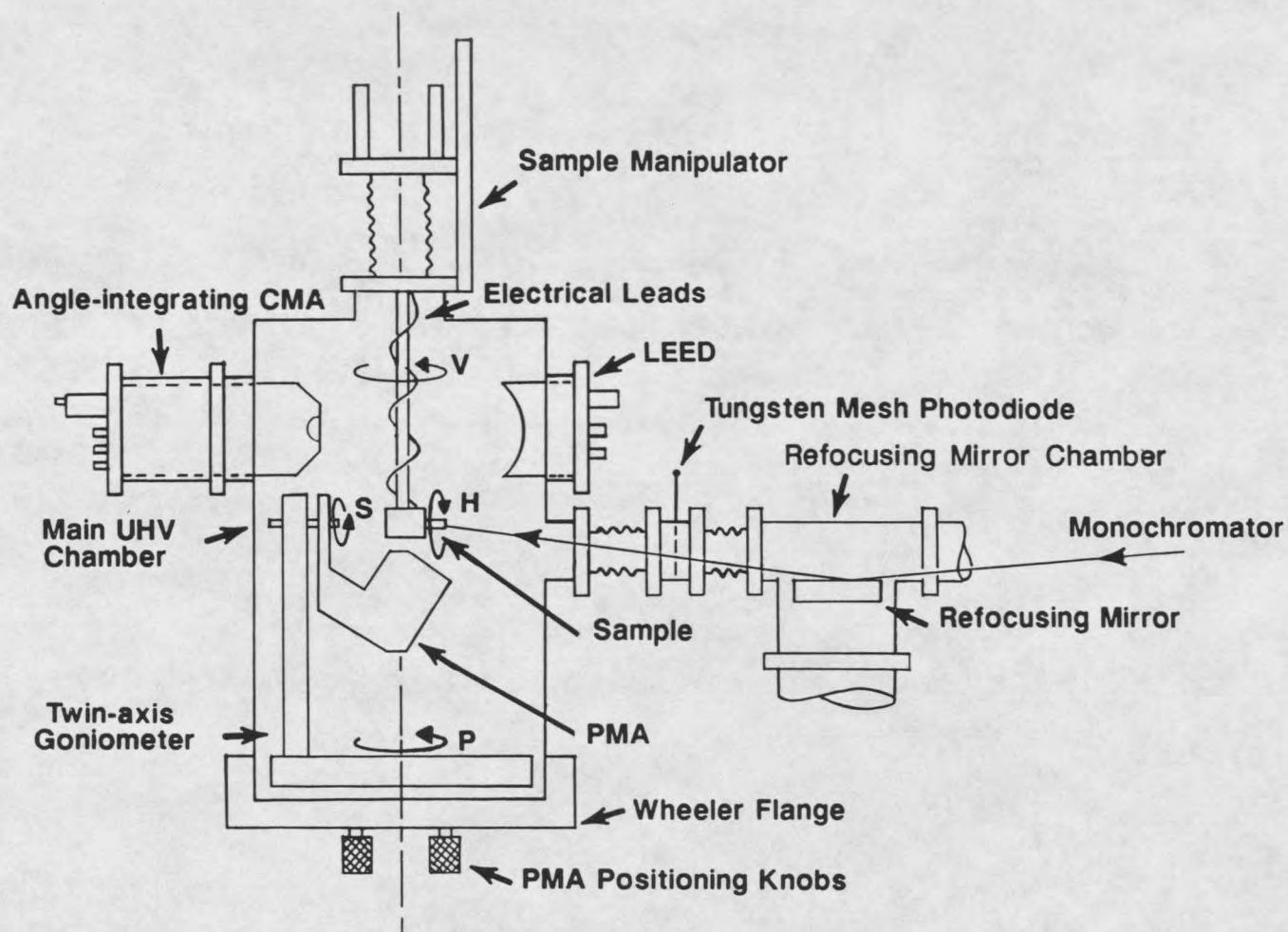


Figure 17. Schematic of photoemission system.

Chamber Design

The main ultra-high vacuum (UHV) experimental chamber, shown in Figure 18, was built to our specifications by Varian Associates, Inc. (Palo Alto, CA). The stainless steel chamber is a bell jar with an outer diameter of 12 inches. Design specifications called for 31 ports, including a 12 inch Wheeler flange (copper wire seal) which holds the plane mirror analyzer (PMA) and goniometer movement. Also included in the port arrangement was six 8-inch ports to house the various spectrometers and the turbomolecular pump, one 6-inch port for the sample manipulator, two 4-1/2 inch ports, and twenty-two 2-3/4 inch ports for various purposes. A 1/8-inch thick mu-metal canister with port hole cutouts was inserted inside the chamber to provide shielding of the earth's magnetic field.

The main experimental chamber is a bi-level design where (1) the upper level (AA') would be used for diagnostics with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), x-ray photoemission spectroscopy (XPS), and electron energy loss spectroscopy (ELS) and (2) the lower level (CC') would allow for angle-resolved photoemission (ARPES) with either a double-pass cylindrical mirror analyzer (CMA) with a angle-resolving drum or a custom-built plane mirror analyzer (PMA) mounted on a twin-axis goniometer. Transport of the sample between the diagnostic level and the analytical level was handled by a custom-built sample manipulator with 11 inches of vertical travel. Sample preparation, including cleaving and evaporation, occurred at BB' or CC' levels. Various pumping hardware, including an ion pump, a turbomolecular pump, and several sorption pumps, was attached at the DD' level.

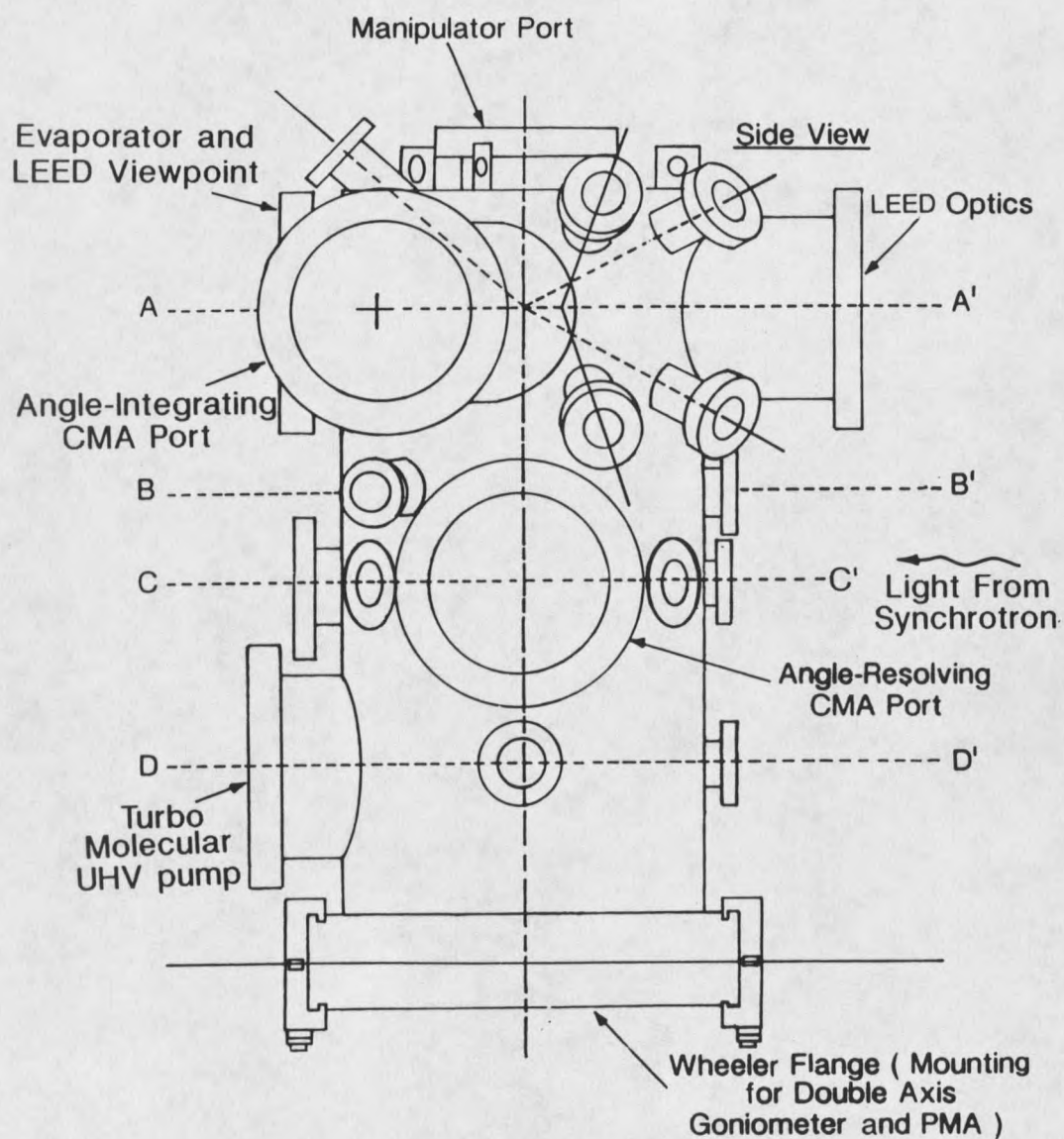


Figure 18. Main experimental chamber for photoemission. The AA' level is for sample diagnostics and photoemission measurements occur at level CC'. The manipulator was inserted from the top and the PMA from the bottom.

Ultra-high Vacuum Pumping

Figure 19 shows the UHV-pumping configuration. The two vacuum chambers are the main experimental chamber and refocusing mirror chamber. Main pumping for the main experimental chamber is a 550 liters per second (l/s) turbomolecular pump (Leybold-Heraeus Vacuum Products Inc.).

The forepump circuit includes a pneumatic valve, molecular sieve, and oil-sealed rotary vane pump (Leybold-Heraeus). Initial pump down from atmosphere is accomplished with a carbon vane rotary pump and LN_2 sorption pumps. After the chamber pressure reaches about 1×10^{-6} Torr, the turbomolecular pump is started. The chamber pressure would rapidly decline to 1×10^{-9} Torr after a 12-15 hour bake at 200°C . (See Figure 20) Before and after bakeout, all filaments were checked and outgased. After firing the titanium sublimation pump (TSP) for 1 minute, the base pressure would fall to the 1×10^{-10} Torr range. The turbomolecular pump was valved off and the system was operated on the 60 liters per second ion pump when left unattended, as protection against accidental venting. The mirror box chamber had its own ion pump and provided differential pumping between the sample and the synchrotron storage ring.

Light Optics (Mirror Box)

Even though it was somewhat tedious to optically align, a refocusing mirror was used between the monochromator and the main experimental chamber in order to obtain a 2:1 light spot size reduction (see Figure 17). The refocusing mirror chamber (or "mirror box") consisted of an ellipsoidal, gold-coated front-surface mirror.

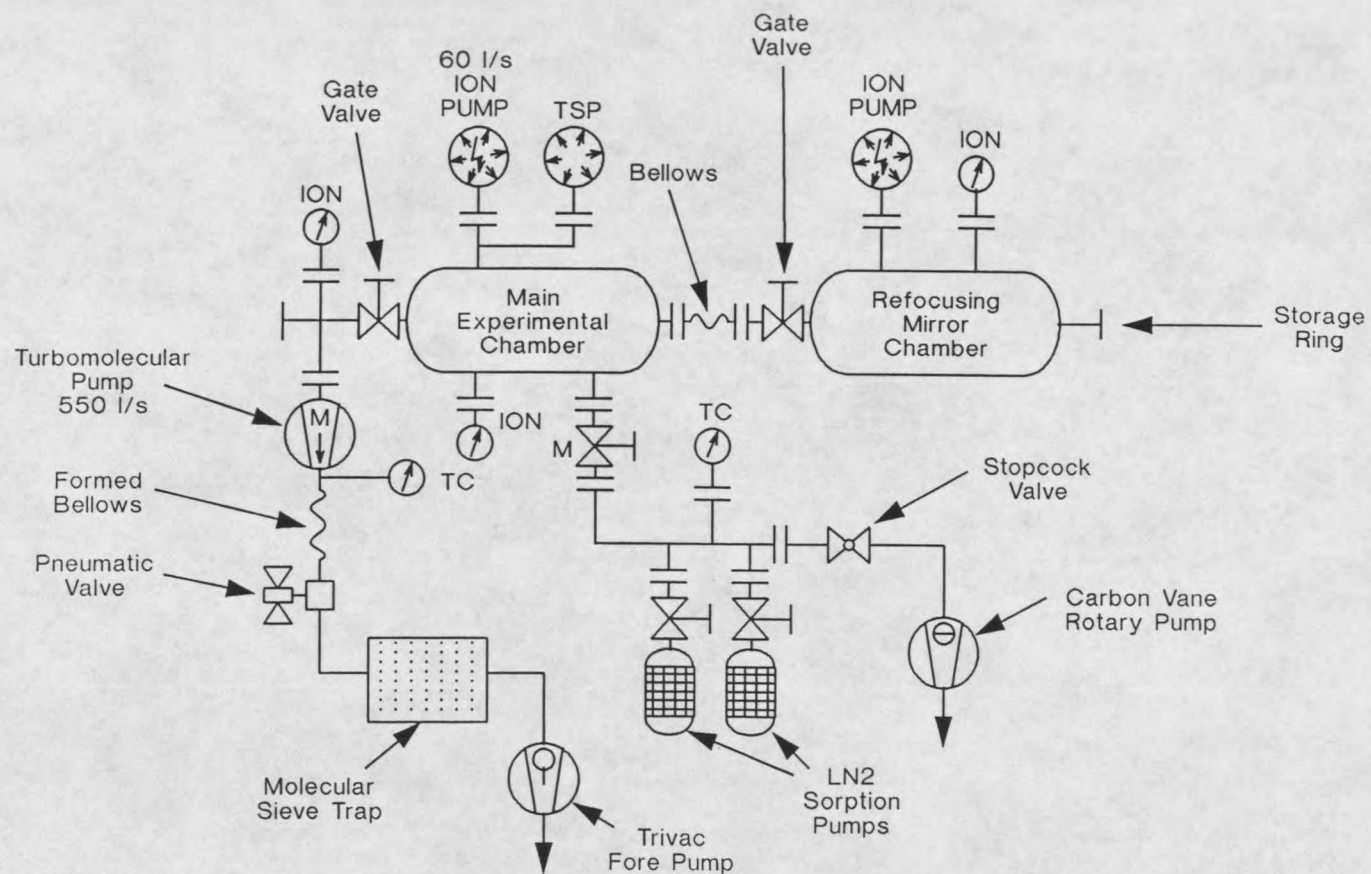


Figure 19. Ultra-high vacuum pumping configuration.

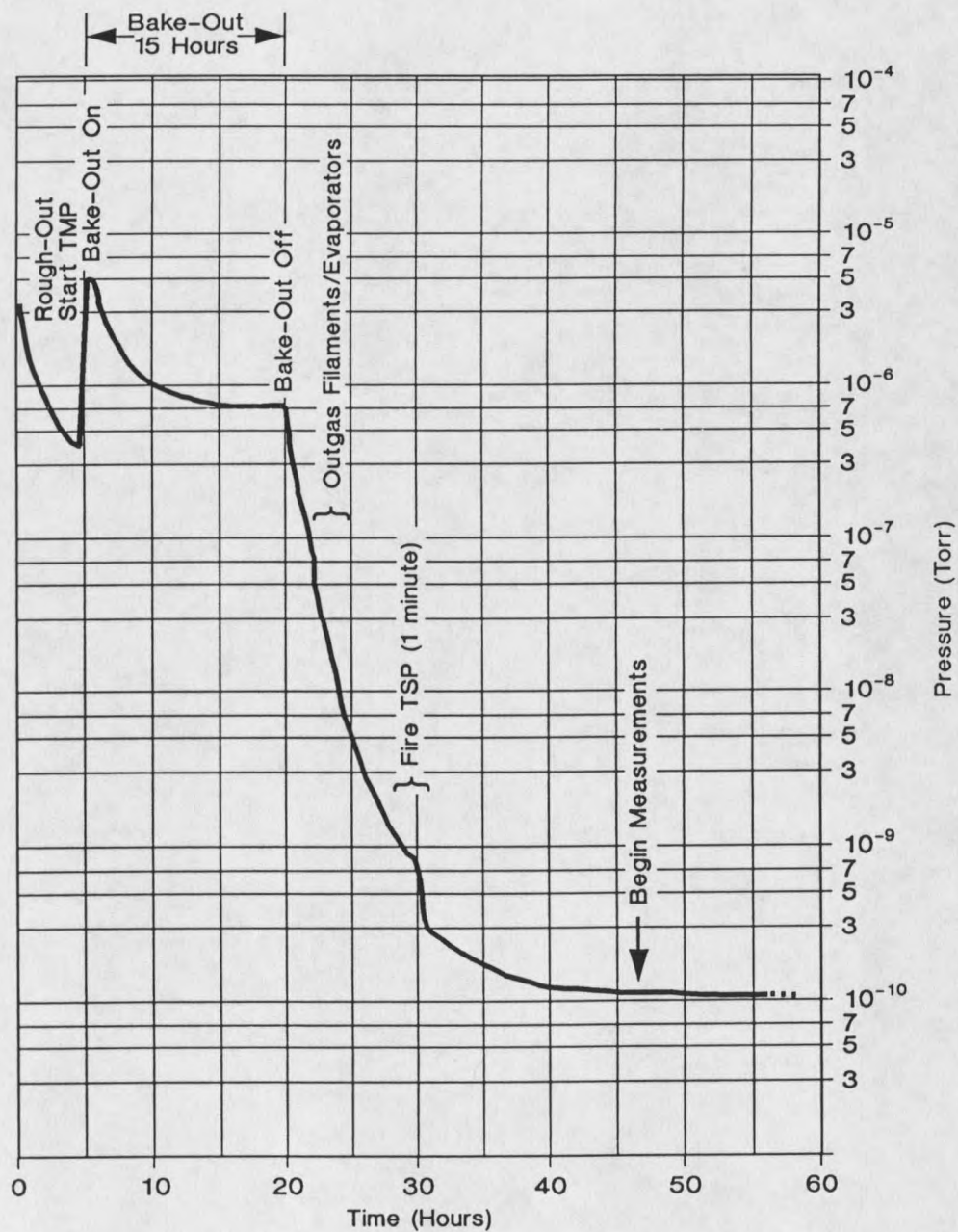


Figure 20. Typical pump-down curve. Pumping down from atmosphere begins at time zero, followed by a bake-out of 12-15 hours, and a 8-10 hour cool down period.

The mirror box also provided differential pumping between the monochromator and the main experimental chamber (Figure 19). A tungsten mesh (90% transmission) was included in the mirror box design to monitor the photon flux. This was used in normalization of the photoemission spectra.

Sample Manipulator and Holder

The sample manipulator (shown in Figure 17) was an integral part of the system design. It allowed for five types of sample motion plus tilt. Samples were transferred between the upper and lower levels of the main experimental chamber by a lead screw and linear bearing arrangement, powered with a small electric motor. Total vertical travel (z) was 11 inches. In addition, horizontal x- and y- travel was approximately 2 1/2 inches and controlled with precision micrometers.

The sample could be rotated about its surface normal from 0° to 360° and beyond (H rotation in Figure 17). Polar rotation of the sample's normal exceeded 360° total (V rotation). Electrical leads for sample bias voltage, heating, and temperature readings were also part of the manipulator. It was possible to attach many different sample holders. The sample holder used in my particular experiment is discussed below.

A high precision sample holder (Figures 21 and 22) was designed and fabricated to meet special requirements of these measurements:

- (1) Secure sample holding was required so that bench-made alignments would be preserved during cleaving and data collection. This is quite important, since the sample was often rotated about its surface normal and any wobble would affect the results. The sample holder performed very well in preserving sample orientation.

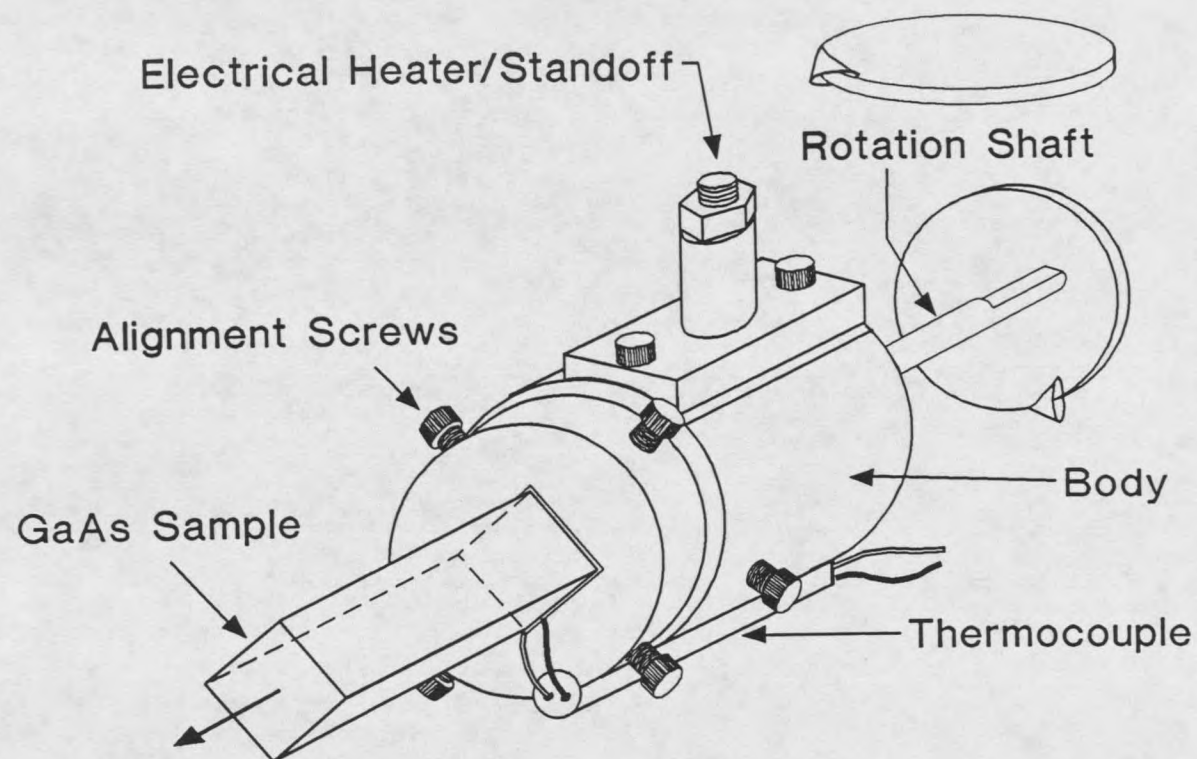


Figure 21. GaAs sample holder (perspective view). Rotation shaft inserted into the manipulator allowing for two orthogonal rotation axes. Alignment screws secure the crystal and provide for adjustments.

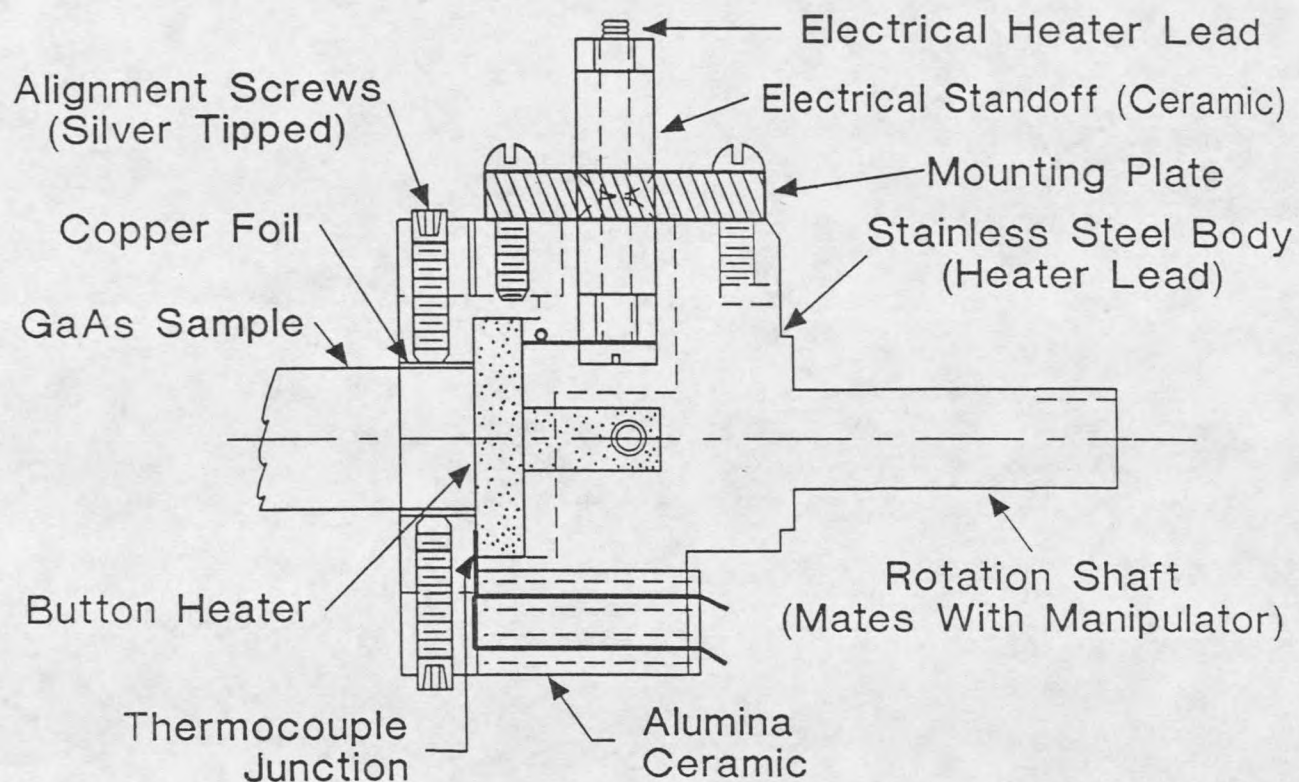


Figure 22. GaAs sample holder with heater (cross section). The button heater had good thermal contact with the sample's base. A thermocouple allowed for temperature monitoring during sample heating.

- (2) Somewhat contrary to the first requirement, a certain flexibility was needed to allow the sample to move slightly during cleaving. This would compensate for any small misalignment in the cleaver. It would also accommodate differential thermal expansion during sample heating and system bakeout.
- (3) Sample heating to about 350° C (as measured at the free end of the crystal) was needed.

The holder had a cylindrical body (stainless steel-304) with a rotation shaft (1/8") which mated with the sample manipulator (Figure 22). The cross-sectionally square GaAs crystals were inserted into a square receptacle in the holder's end, and four screws (silver-tipped) provided restraint and alignment capability.

In order to protect the brittle crystals from the force of the alignment screws and also allow some movement, consistent with requirement (2) above, the butt end of the sample was wrapped with 1 mil thick molybdenum foil to prevent alloying of the samples with the holder during heating. It was then wrapped with thicker copper foil for cushioning before insertion into the holder. This proved to be a reliable and accurate means of holding the samples.

Home-wound heaters had proved unreliable, so sample heating was provided with a commercial "button heater" (Model #292, Spectra-mat Corp.). The front surface of the button heater contacted the butt end of the sample and ensured good thermal conduction. (see Figure 22) At 27 watts (and 8 volts) which is 90 % of its maximum power rating, the temperature of the holder's thermocouple was 450° C. At this temperature, the heater cavity is 'yellow-hot'. Using a Pulsar-II IR photometer, a sample surface temperature of 388°C was measured, assuming a surface emissivity of 1 and a measurement distance of

24 inches. The heater can and stem was molybdenum (no alloying problems) with a aluminum oxide filler containing a tungsten/rhenium filament (0.008 "). This heater was very reliable.

Sample Cleaving Equipment

The cleaving method was the standard knife-and-anvil technique where a flat copper anvil is positioned flush against the side of the sample and a tungsten carbide blade is located against the opposite side. While moderate pressure was applied to both the knife and anvil, a gentle tap against the knife initiated cleaving. Even with careful laser alignment, the ratio of usable cleaves to total cleaves was less than 40%.

Antimony Evaporator Equipment

The setup included a Sb evaporation source with shutter and a thickness monitor, permitting *in-situ/in-vacuo* overlayer preparation (Figure 23). Overlayer growth was controlled very well by this apparatus.

The antimony evaporation source was a small (mouth diameter=11 mm) conical crucible of molybdenum sheet metal (thickness=0.008 ") surrounded by a tungsten filament. The evaporator was charged with about 5 g. of Sb and the end of the crucible was covered with tungsten mesh to keep the Sb ingot from falling out. This is because during the evaporation, Sb sublimes from the solid state (at 903° K), rather than the molten state. A chromel/alumel thermocouple was attached to the crucible to monitor evaporation temperatures and a shutter was available for interrupting the beam.

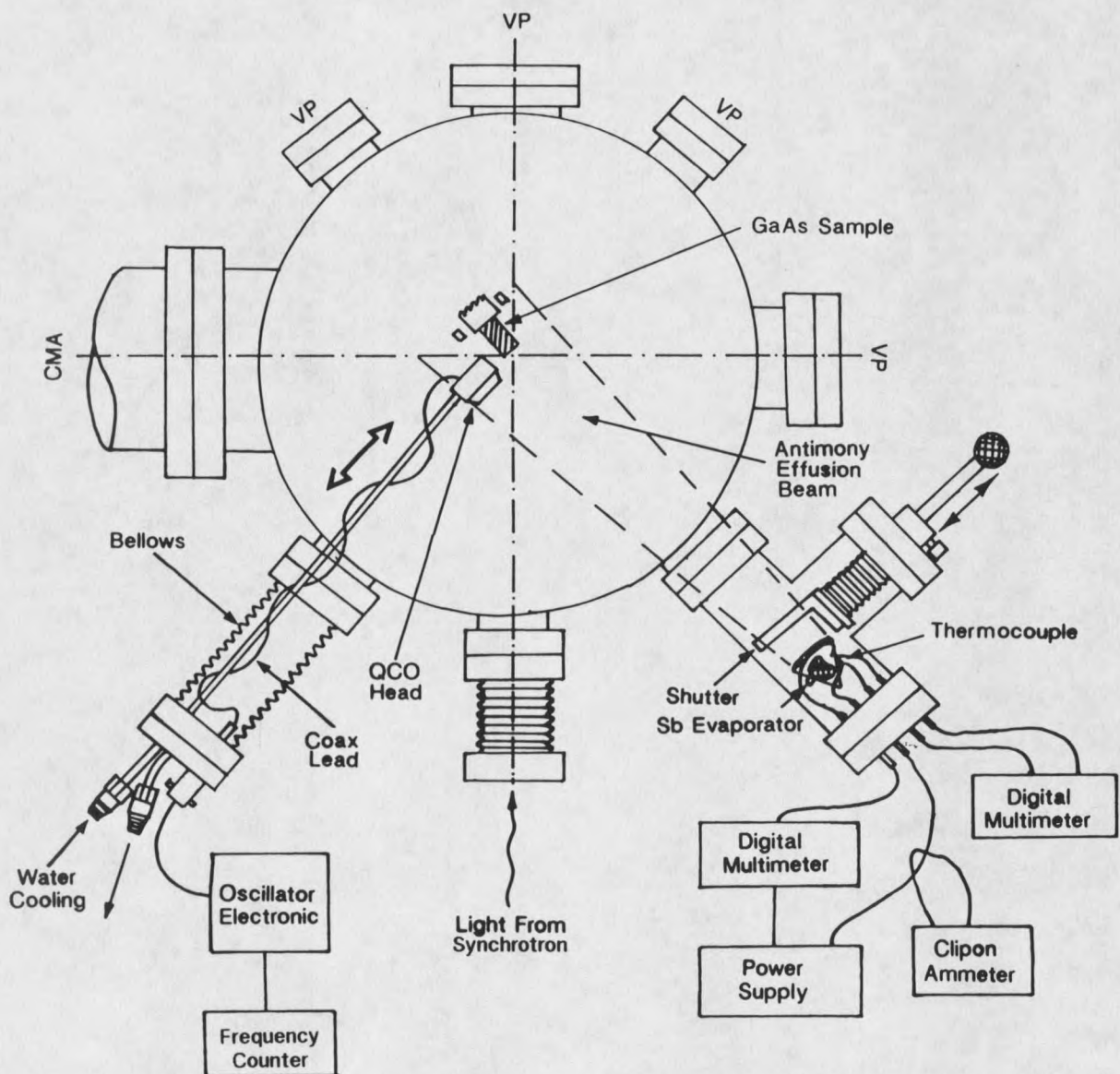


Figure 23. Setup for antimony evaporation for overlayer growth. Thickness monitoring apparatus shown on left-hand side and evaporation setup on the right. Overlayers could be grown *in-situ* with photoemission measurements.

Evaporator performance was very well behaved and reproducible. Figure 24 shows a plot of evaporator thermocouple voltage versus time for a typical evaporation. The filament current is annotated along the curve, showing the parameters necessary for approaching the evaporation conditions without overshooting. The thermocouple voltage measured at evaporation was always 22.4 mV, while the filament current was 9.2 amperes. During deposition, chamber pressure would rise to the low 10^{-9} Torr range.

The antimony overlayer thickness was measured during the evaporation process with a water-cooled quartz crystal oscillator (QCO). The QCO (Sloan Technology Corp.) is a piezoelectric resonator which works on the principle that any mass evaporated onto the vibrating crystal will result in a predictable shift δf in the resonate frequency. Therefore, a film thickness d of evaporated material (density ρ) is related to the frequency shift by the following:

$$d = -\frac{\delta f}{C_q \rho} \quad (38)$$

where C_q is the calibration constant of the quartz crystal oscillator ($5.65 \times 10^7 \text{ cm}^2 \text{ g}^{-1} \text{ sec}^{-1}$). Equation 38 will give the thickness in Å; however we know from Duke (1982), that the first Sb overlayer is 2.35 Å thick, so that for our sample:

$$\theta = -\frac{\delta f(\text{Hz})}{8.79} (\text{in ML}) \quad (39)$$

This gives the dosage. To convert to coverage, a sticking coefficient of 0.7 is used. The QCO approach proved to be a reproducible means of determining Sb coverage.

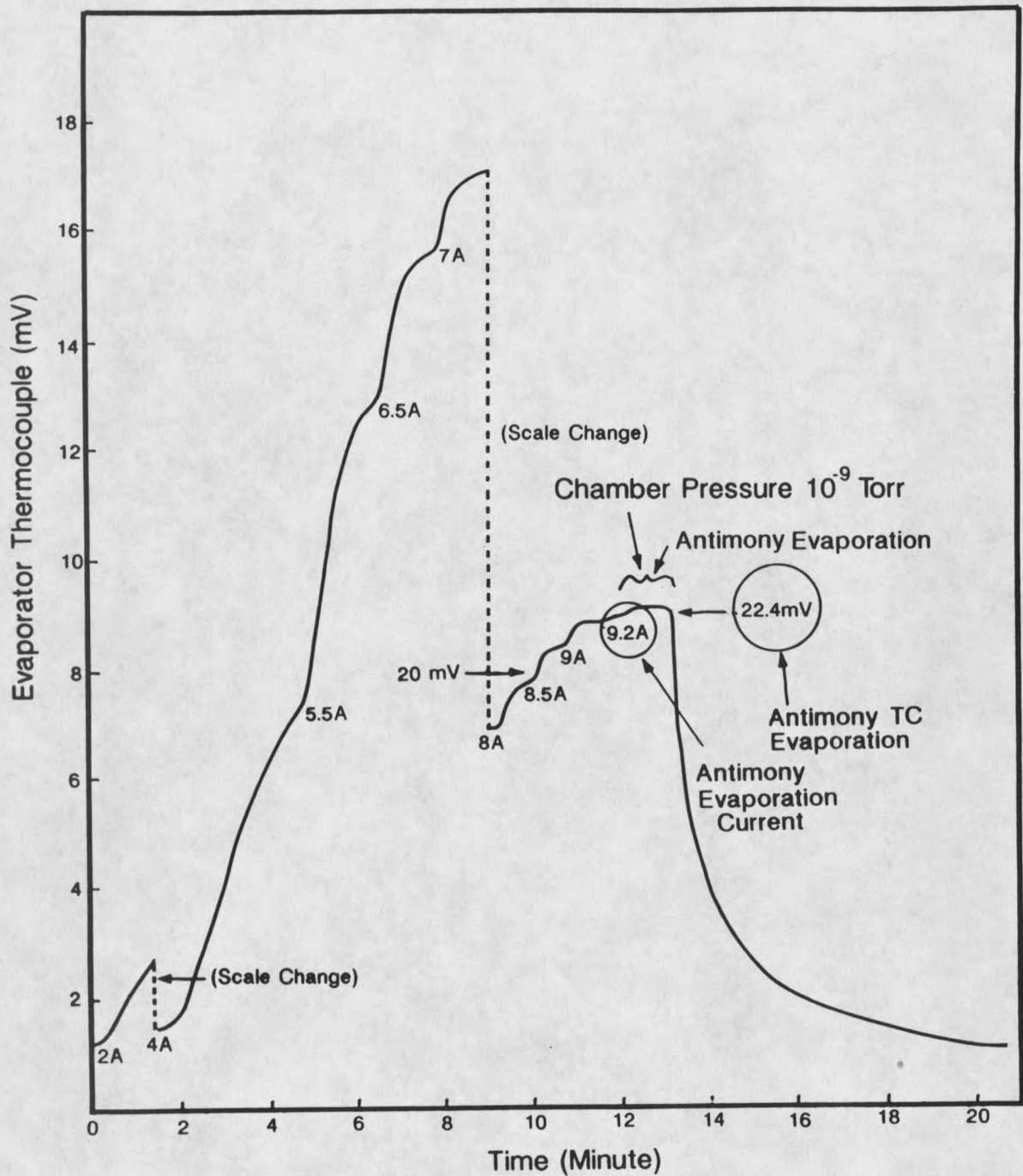


Figure 24. Typical antimony evaporation curve. Evaporation curve of evaporator temperature (thermocouple reading) versus time. The current to the evaporator is noted whenever it is changed. Sb evaporation occurs at 22.4 mV.

The crystal was a 5 MHz quartz wafer housed in a water-cooled holder with a teflon coax signal lead. Baking to 250°C posed no outgassing problems. During filament outgassing after the bakeout, 50-100 Hz (5-10 ML) of Sb was deposited on the quartz crystal oscillator crystal in order to prepare the surface for later sample overlayer growth. This procedure was to ensure that the sticking coefficient between the quartz crystal oscillator crystal and Sb atoms was constant from one experimental setup to another.

LEED and AES Systems

The LEED apparatus was a standard Varian model 981-0127 electron optics and controller and was principally used to orient the sample's mirror plane and provide for confirmation of surface order. LEED could not be done without moving the sample from the photoemission measurement position and therefore was only done when relocation of the crystal would not compromise the photoemission measurements.

Although some AES spectra were taken, this technique was not extensively used because of possible contamination caused by the direct line-of-sight of the electron gun in our apparatus as reported by Zurcher (1982). Instead, use of electron loss spectroscopy (ELS) was pursued as being less surface destructive, probably by virtue of the lower current and lower energy input beams.

ELS System

The electronics for AES and ELS measurements is shown in Figure 25. The CMA was a double-pass model with coaxial electron gun.

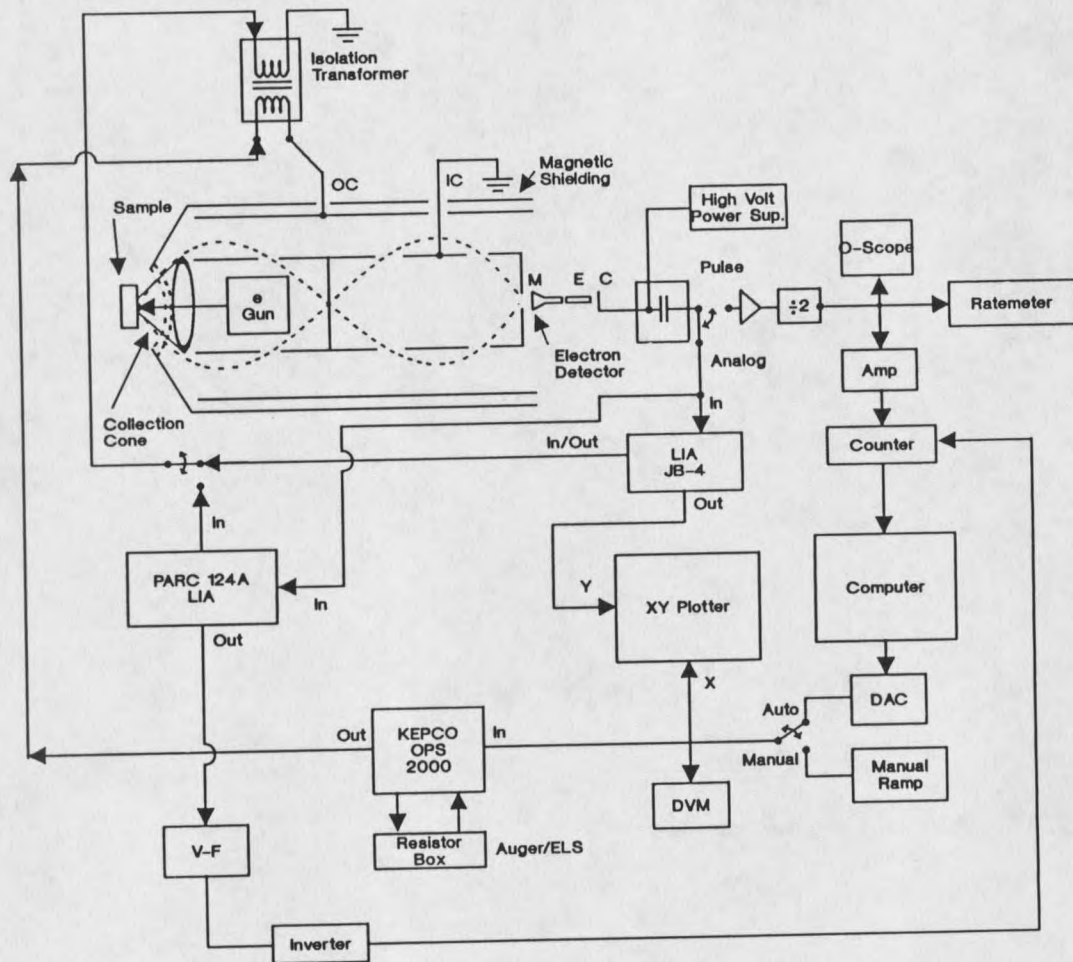


Figure 25. Schematic of the electronics setup for AES and ELS. The CMA and sample is shown in the upper-left hand corner. Data could be acquired in either pulse counting or analog modes.

The sample was oriented normal to the electron beam and the emitted electrons were measured within a collection cone subtended by 42.3° as shown. The electron trajectories pass through the inner cylinder twice and are finally captured at the mouth (M) of the electron detector. The channel electron multiplier is set for large gain and the pulse of electrons is collected (C).

At this point the measurement could be handled either in pulse-counting mode (like PES) or in analog mode using lock-in detection techniques. The pulse counting mode is similar to the PES mode, where the pulse is amplified by a pre-amplifier and then passed to either an oscilloscope (for diagnostics), digital ratemeter (visual monitoring), and another amplifier before going through a counter and into the computer system.

In the analog mode, the large signal was taken into a lock-in amplifier (PARC JB-4). The modulation reference for the lock-in amplifier was connected to the CMA's outer cylinder through an isolation transformer to guard against the high voltage. The lock-in amplifier output was used to drive the Y-input of a XY-plotter.

In the double differentiation mode of ELS, the reference signal with measurement signal from the JB-4 lock-in amplifier was used as input to the PARC 124A lock-in amplifier. This output was passed through a voltage-to-frequency converter. The pulses were polarity inverted and brought into the computer through the counter. One was able to select either first derivative, second derivative, or EDC-type mode.

The voltage ramp for the kinetic energy scanning was provided by the computer through a DAC or by a manually controlled ramp. If the computer controlled the ramp, then multiple sweeps and signal averaging could be used. The output of the ramp was used to drive the X-axis of the XY-plotter as well as the outer cylinder of the CMA. A programmable high-voltage power supply (Kepco OPS-2000) was controlled by the

ramp. For quality control, a DVM was used to monitor the ramp. The resistor box was used to select the gain on the OPS to permit the different scan ranges of high-kinetic energy Auger versus lower-kinetic energy ELS.

Additionally, there were control electronics (not shown) for the electron gun and the electron detector. Besides a selectable filament current, the gun had focus and extractor lens voltages that were adjustable in order to optimize the signal. Typically, the initial sample alignment was done in pulse-counting mode. When the signals became too large for pulse counting, the electronics was switched to analog mode. In all cases, the current collected at the channeltron was below 0.1 microamps. The control electronics on the electron multiplier are the same as in PES.

Electron Energy Analyzers

Electron energy analyzers were used to measure the kinetic energy and direction of the photoemitted electrons. This is accomplished by passing the photoelectron beam, which is formed by the entrance aperture through a well controlled electric field. The resulting dispersion is a function of the particle energy per unit charge. An exit slit selects out of this dispersed beam, those electron which satisfy the energy pass conditions of the analyzer. Following the exit slit is an electron detector. This device is used to produce electron pulses of sufficiently large voltage so that they can be measured with the electronics.

The energy passband ΔE of the analyzer is defined as the full width at half maximum of the peak which appears when the analyzer is scanned across the energy of a

monochromatic beam of electrons. This transmission function normally has a Gaussian shape. The resolution can be approximated from the geometrical dimensions of the analyzer according to Moore *et al.* (1983). In particular, the energy resolution is

$$\frac{\Delta E}{E_{pass}} = aw + b(\delta\alpha)^2 + c(\delta\beta)^2 \quad (40)$$

where E_{pass} is the central energy of the particles transmitted through the analyzer.

w is the entrance and exit slit widths.

$\delta\alpha$ and $\delta\beta$ are angular deviations of the electron beam.

a , b , and c are constants, characteristic of a particular analyzer.

Plane Mirror Analyzers

The chief advantage the plane mirror analyzer(PMA)/goniometer arrangement had over the CMA was its ability to be positioned at any polar/azimuthal angle with respect to the fixed sample. The CMA could accomplish this only with additional motion of the sample, changing the polarization conditions and the resulting photoemission spectra. The PMA was designed as an integral part of the new photoemission system and was based on the Bell Telephone Laboratory design by Traum and Smith (private communication). The energy resolution, $\Delta E/E_{pass}$ was 6%.

Figure 26 illustrates a perspective view of the PMA used for the thesis measurements. It consisted of a lower plate and upper plate which provide the electric field used to deflect and, hence, energy analyze the photoelectrons.

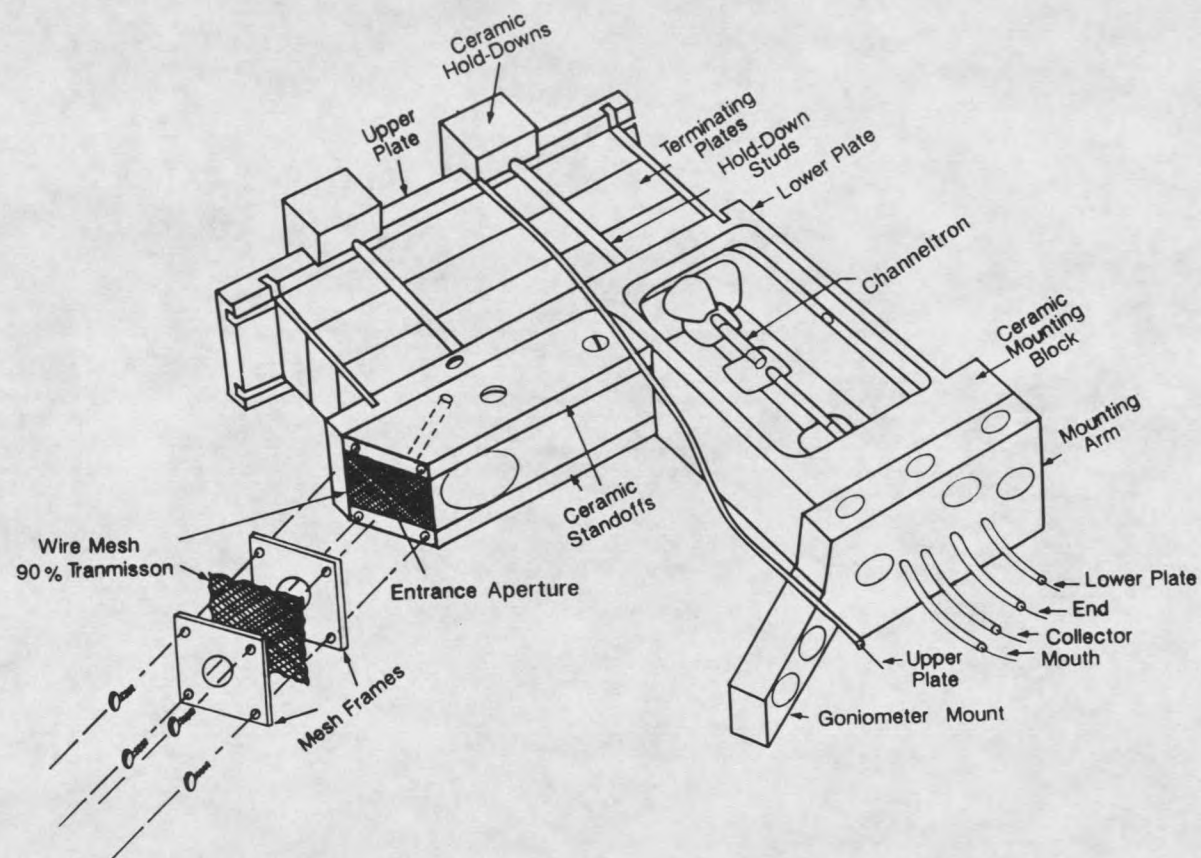


Figure 26. Plane Mirror Analyzer (3-d schematic). Channeltron is housed in the lower plate cavity which is shown open. Wire mesh used to control fringe fields is shown near the entrance aperture.

In order to compensate for fringe fields at the edges of the plates, specially prepared ceramic coated terminating plates were used to hold the lower plate and upper plate in position. The four terminating plates, lower plate, and upper plate were held together with four hold-down studs which attached to ceramic hold-down blocks on the upper plate. In order to insure good electrical contact with the terminating plates, the joints were silver painted.

The lower plate (LP) had three other design functions: (1) house the Channeltron electron multiplier (CEM), (2) provide attachment to the goniometer, and (3) contain the front-end electron optics.

- (1) A standard Channeltron (Galileo Electro-optics Corp.) was attached to a ceramic mounting block inside the lower plate cavity. Five electrical leads (LP,E,C,M,UP) ran down the goniometer structure to an electrical feedthrough at the Wheeler flange.
- (2) A mounting arm was attached to the plane mirror analyzer and attached to the goniometer's polar motion arm at the correct analyzer angle.
- (3) Energy retardation of the photoelectrons was provided by a tantalum wire mesh (90 % transmission) attached to the lower plate. An additional wire grid was held in a metal frame and attached to ceramic standoff side pieces. This grid was at ground potential and ensured a field-free region from the sample to the detector for the photoelectrons. The front end region was a critical part of the design because any stray fields would distort the electron's trajectories into the plane mirror analyzer. Consequently all parts, especially insulators, were carefully coated with Aquadag (Archeson Colloids Co.) to avoid an electrical charging situation. After this procedure, the analyzer performed according to specifications.

In order to avoid fringing fields at the entrance apertures and exit hole (near the Channeltron), tantalum wire mesh was spot-welded to these areas. Although the mesh reduces the fringing field problems, it probably had an adverse effect on the throughput of the analyzer. A line-of-sight hole was put in the back terminating plate, so that the light beam could be pass directly through the plane mirror analyzer for setup and alignment purposes.

Although the plane mirror analyzer is attractive because of its compact size and simple design, it has several problems; (1) the apertures can act as electron lenses, since they are at the boundary of a strong electric field, (2) the wire mesh, positioned over the apertures to curtail fringing fields, lowers the transmission of the device, and (3) focusing of the electron beam occurs only in one plane of the analyzer. Even so, the PMA was very important in doing experiments such as the angle-resolved CFS measurements of Chapter 7, where it is desirable to have variable analysis angles while maintaining constant polarization conditions.

Cylindrical-mirror Analyzers

The cylindrical mirror analyzer (CMA) is analogous to the plane mirror analyzer (PMA) except that the flat deflection plates are coaxial cylinders. This type of analyzer has been used in photoemission spectroscopy for many years and is available commercially from several vendors (Phi or Physical Electronics Corp.). A relative advantage that the CMA design has over the PMA design is double-focusing. Double-focusing means that focusing occurs in both the deflection plane and the perpendicular plane. Two CMAs were used routinely in these thesis measurements. These analyzers were an

angle-resolving CMA in the lower level for photoemission experiments and an angle-integrating cylindrical mirror analyzer mounted in the upper level for ELS-AES-XPS measurements.

The angle-resolving cylindrical mirror analyzer was a commercial device (Phi model #15-250) which was retrofitted with a angle-resolving drum after Knapp, *et al.* (1982). Three angular sizes of apertures were allowed, 4° (diameter:3 mm), 8° (diameter:6 mm), and 360° (angle-integrating). As the drum was rotated, the analyzer swept through a set of emission angles which describe a cone tilted with respect to the crystal normal. In order to measure at another set of angles, the sample would have to be rotated and this would change the polarization of the light with respect to the sample. Uncoupling of these angles was the prime motivating factor in building the plane mirror analyzer system. However, the cylindrical mirror analyzer did have some distinct advantages over the plane mirror analyzer, and at special angles where the CMA was better suited (*e.g.*, normal emission), it was the analyzer of choice. These advantages were higher throughput, better energy resolution, and selectable aperture sizes.

Twin-axis Goniometer

A twin-axis goniometer allowed the PMA to move through a full 4π steradians of solid angle centered about the sample's analysis point. It was a design requirement that the PMA could be reliably repositioned to within $1/2^\circ$. This was accomplished by a high gear reduction ratio in the drive mechanism and kinematic constraints on the motion. Figure 27 shows a 3-d diagram of the analyzer and goniometer.

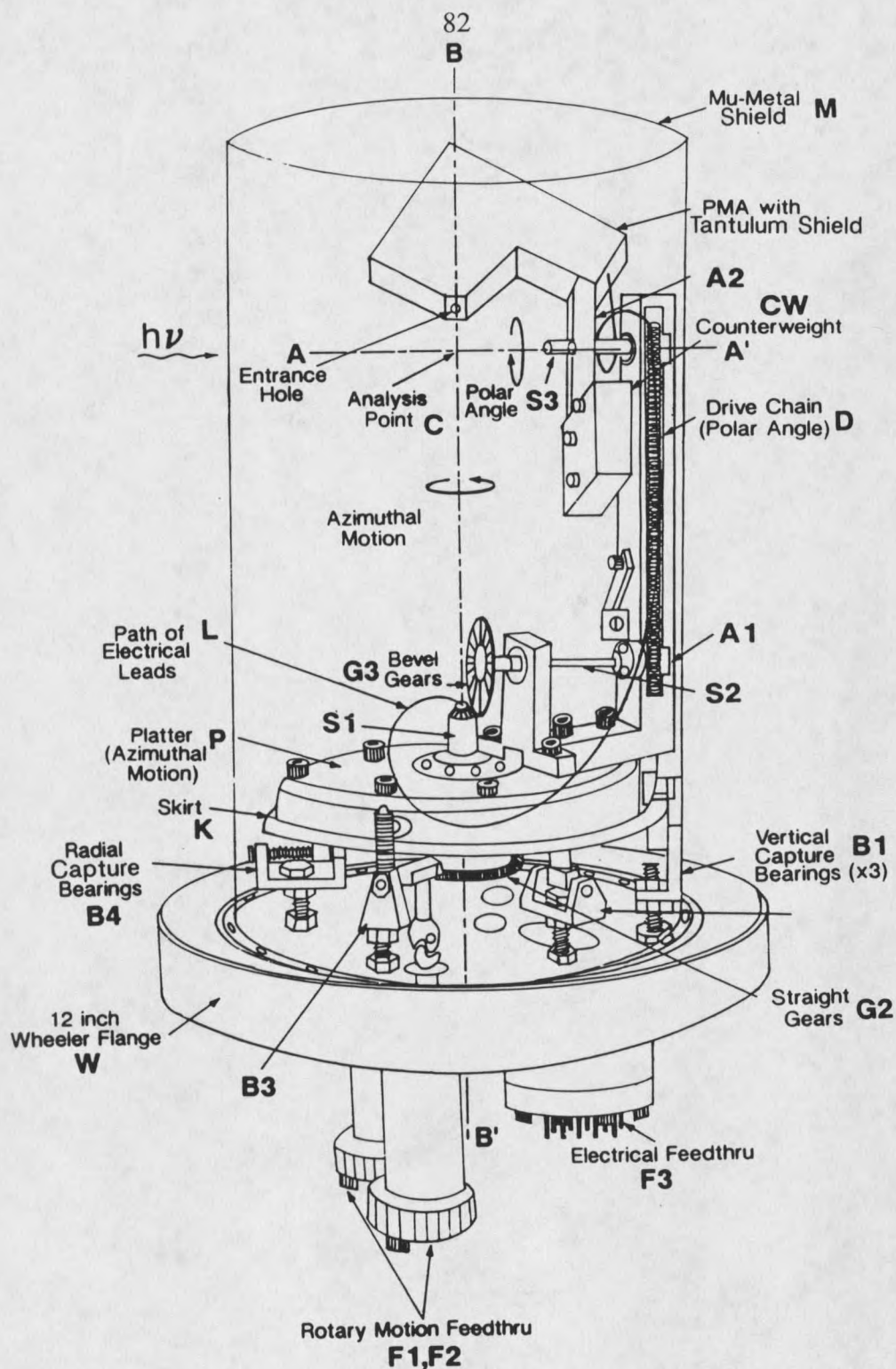


Figure 27. Schematic of PMA and twin-axis goniometer. Analyzer assembly was mounted on the base Wheeler flange where rotary and electrical feedthroughs were attached.

The two angular rotations required were about the polar angle (axis AA') and the azimuthal angle (axis BB'). During operation, the light focus and sample analysis point were located at the intersection of AA' and BB'. In all positions, the entrance hole H had to maintain a constant distance of 1.1 inches from analysis point C.

Azimuthal motion of the PMA was accomplished with platter rotation. This angle was selected by hand through the rotary feedthrough F1 which drove the platter P with a straight spur gear set G1 (gear ratio 18:96). The polar angle could be set with F2 which drove a set of straight spur gears G2 (18:48) connected to shaft S1 along BB'. This motion engaged the set of bevel gears G3 (30:120) which turned shaft S2. The polar angle shaft S3 was connected to S2 by a drive chain D, where the sprocket ratio was constant (all gears from PIC Corp.).

The vertical arm A1 attached to the platter contained the polar angle drive train and revolved inside a mu-metal shield M which kept the entire photoemission measurement region magnetic field free. Ports in the mu-metal shield coincided with the ports in the main chamber in order to bring in the light, sample manipulator, *etc.*

Arm A2 was the mounting piece for the base of the PMA and allowed it to rotate about the AA' axis. A counterweight CW was later removed after it was determined to give no significant benefit.

The platter was captured with a set of six bearings so as not to over-constrain its motion and cause binding. Bearings B1, B3, and B5 (Dalc Corp.) held the platter vertically on the skirt K. Radially positioned bearings B2, B4, B6 (120° apart) constrained the platter's horizontal motion. All of the bearing assemblies were mounted to the 12 inch Wheeler flange which formed the structural base of the device.

Five electrical leads followed the path L from electrical feedthrough F3, through the center of S1, up along A1, looping around A2 to connect with the PMA. The wiring was commercially available braided coax with Teflon insulation (RG-178 B/U 50 Ohm, 30 AWG stranded conductor, Belden Corp.).

All material was non-magnetic stainless steel 304, except for the bearings which were BeCu high precision mini bearings lubricated with molybdenum disulfide (New Hampshire Ball Bearing Corp.).

Data Acquisition Electronics

Pulse Counting Electronics

Figure 28 shows a block diagram of the electronics used by our system for general photoemission data acquisition. The Tantalus storage ring (upper left corner) generates a broad spectrum of light which was monochromatized with either the toroidal grating monochromator or the Seya monochromator.

The monochromator grating could be positioned or scanned in real time by the computer. Consequently, the monochromator's wavelength setting was user-selectable through custom coded software.

The light at a selected energy $h\nu$ passes through a tungsten mesh diode used to monitor the synchrotron photon flux. The loss of charge due to photoemission on the mesh was measured with a picoammeter (Keithley model 471) and digitized with an analog-to-digital converter before being read by the computer (Tektronix 4051).

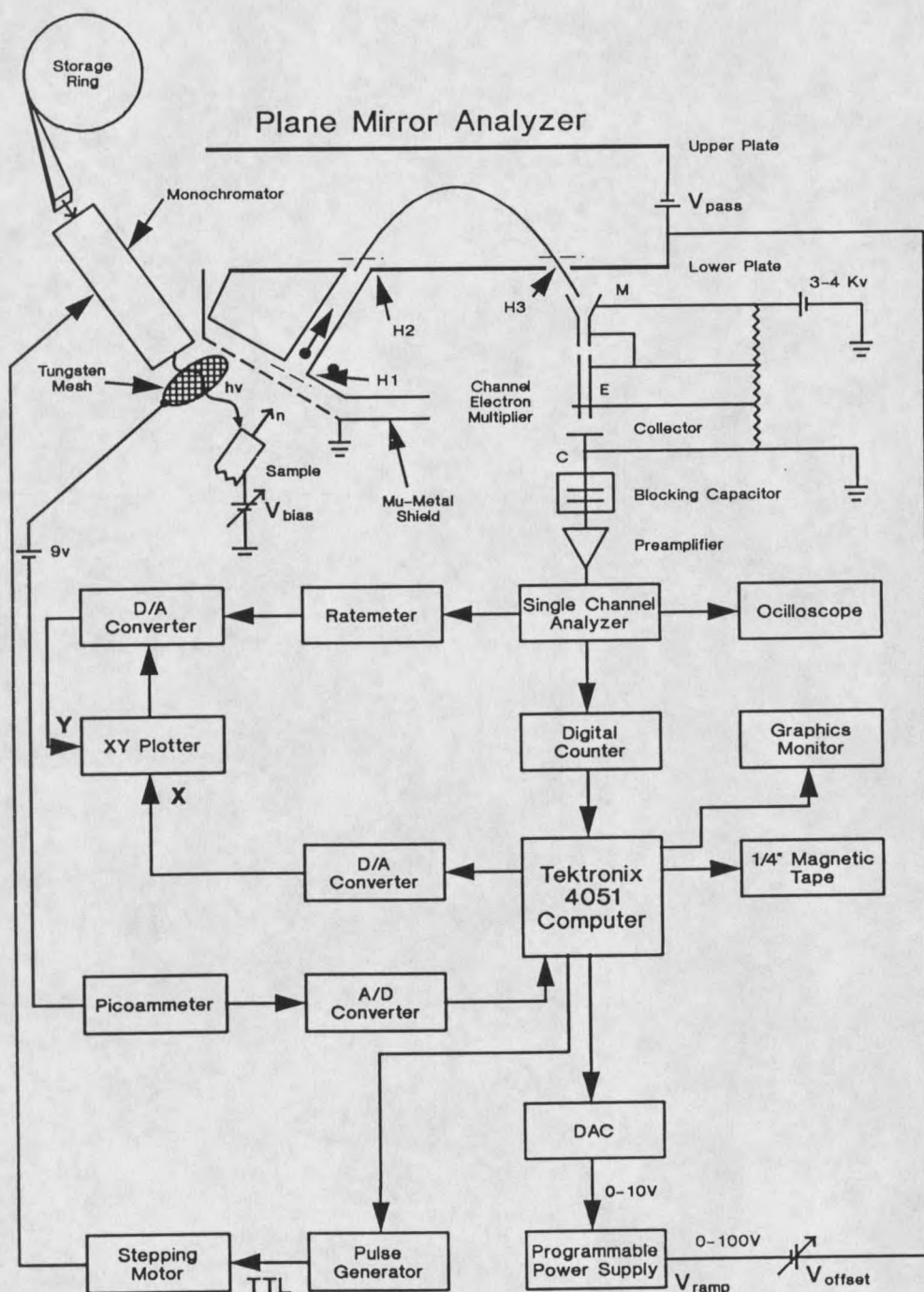


Figure 28. Block diagram of photoemission acquisition electronics. The photoemission setup is shown at the top. Hardcopy of data was recorded with an XY-plotter and stored in the computer for later analysis.

In this manner, a single flux reading could be taken for each EDC spectra, or, in the case of CIS/CFS spectra, flux readings were taken for each spectra point. This information was used to normalize the measurements to the light flux.

The radiation, which was focused on the sample, induced photoemission. The photoelectrons entered the analyzer (PMA in this case) through a mesh on the grounded tantalum shield. The analyzer operated in retarding field mode, such that potential on the lower plate would reduce the electron kinetic energy until it could pass through the pre-selected pass energy of the analyzer, E_{pass} . This energy window ΔE could be scanned with a ramp voltage V_{ramp} (lower right corner) which could vary between 0-100 volts. A programmable power supply was used to amplify the 0-10 volt output of the computer by a factor of ten.

After entering the PMA's cavity, all electron trajectories were bent along parabolic paths by the constant electric field between the plates. Only those electrons which have the proper kinetic energy, would make it out the exit hole H3 of the analyzer. With a 100 volt positive bias on the mouth of the Channeltron (CEM), one is assured of collecting all photoelectrons which pass through the analyzer. A positive bias applied across the CEM was used to produce the required gain of approximately 10^6 . A metal collector at 3-4 kV potential captured the CEM pulses and routed them out of the vacuum through a electrical feedthrough.

Immediately outside the main experimental chamber, was a DC-blocking capacitor which passed only the high frequency pulses. After being amplified with a preamplifier (LeCroy model 510), the pulses were a few hundred millivolts in height. A single channel analyzer acted as a pulse height discriminator rejecting background noise pulses which were much lower in voltage.

The signal was split three-ways following the single channel analyzer:

- (1) An oscilloscope was used to monitor the quality of the pulses from the experiment.
- (2) A digital ratemeter (Tennelec) was used to count the number of pulses over a selected gate time (0.1-2 secs). The ratemeter signal passed through a digital-to-analog converter (DAC) and drove the vertical axis on a xy-plotter. The computer, through a DAC, was able to scan the horizontal axis on the plotter.
- (3) A digital counter (Transera model 730) processed the single channel analyzer signal and passed it into the computer. The computer plotted the data, in real time, on a graphics monitor and stored it on 1/4-inch magnetic tape (Scotch DC-300).

Sample Preparation

The GaAs samples were purchased from Laser Diode Inc., oriented and cut to the required size and shape. They were Zn-doped (*p*-type) bar-shaped samples measuring about 5x5x15 mm. The antimony was in the form of high purity ingots. In order to minimize uncertainties in sample preparation, several diagnostic procedures were used. First we will discuss the preparation of the GaAs(110) samples and follow that with procedures for the GaAs(110)+Sb,*p*(1x1) preparation.

Clean Sample Preparations

The steps involved in preparing a sample were: (1) the bromine etch test to determine direction of Ga dangling bond, (2) sample holder orientation, (3) orientation of mirror plane (MP) with the use of LEED, and (4) Ga dangling bond checking with CIS spectra.

- (1) A bench test determination of the Ga dangling bond direction (by convention, the $\phi_A \equiv 0^\circ$ direction) was conducted by etching the sample in a bromine-methonal solution. Various concentrations were tried and the best recipe was the color of "medium-strength tea". Immersing the sample for about 1 1/2 minutes resulted in a definitive etch. Of the four sides of the bar sample, the very strongly etched side was the As side and the matte side was the Ga direction.
- (2) While the sample was mounted in the holder and the manipulator was still on the clean room bench, a laser alignment was performed. By reflecting a He-Ne laser beam off the (110)-face and onto the opposite wall (about 10 feet away), the crystal could be aligned precisely often to about 1/2° wobble in a full 360° rotation.
- (3) LEED was performed on the sample *in vacuo* to ascertain the mirror plane orientation. This was compared with the bromine test and was convenient for setting the zero positions on the manipulator dials. It was also used to check qualitatively the condition of the surface.
- (4) Finally, by measuring constant initial spectra of the Ga exciton peak as the azimuthal angle of the crystal was changed, the mirror plane could also be determined. In addition, the Ga exciton peak was a good indicator of surface cleanliness. Consequently, quality control CIS curve were periodically taken.

Overlayer Sample Preparations

In a typical overlayer preparation, the QCO head was positioned next to the sample so that it was within the Sb effusion region. (Figure 23) The QCO frequency was optimized and a pre-evaporation reading was taken on the frequency counter (Eldorado Electronics Model 1615). Thermal loading from the heating source would drive the

frequency up a few Hz, however deposition of Sb would cause the frequency to ultimately decrease. Because the source was monitored closely, the behavior of the QCO would parallel that of the source, allowing the entire process to be very tightly controlled. After deposition, a new frequency reading was again taken with 0.1 Hz resolution. A frequency change of 8.79 Hz corresponds to 1 ML with a unity sticking coefficient. One could readily determine the overlayer thickness.

As a check on the QCO-determined overlayer thickness, core level spectra were taken at a photon energy of 110 eV. This energy was chosen in order to establish a correspondence with overlayer calibration measurements taken by Skeath (1982). The ratio of core amplitudes versus Sb dosage from Skeath is plotted in Figure 29. Skeath defines dosage D as the number of Sb atoms adsorbed onto the Sb-covered QCO crystal. This is in distinction to *coverage* θ which is the number of Sb atoms adsorbed onto the GaAs(110) sample. The difference would be accounted for by the difference in the sticking coefficient between Sb-Sb on the QCO and Sb-GaAs on the sample.

In order to determine the sticking coefficient S versus dosage, necessary to convert the dosage amount into a coverage, Skeath calculated the coverage from the standard attenuation formula:

$$\frac{A_{Sb}}{A_{Ga}} = k(\exp(d/\lambda) - 1) \quad (41)$$

Based on the ratio of Sb-4d to Ga-3d peak areas (1.7:1) on GaSb(110) and the fact that there are twice as many Sb atoms per cm^2 in the overlayer than in GaSb, gave $k = 2 \times 1.7 = 3.4$. From the universal escape curve, $\lambda = 7.3 \text{ \AA}$ for a kinetic energy of 100 eV. Using these data, we can assemble the following calibration table.

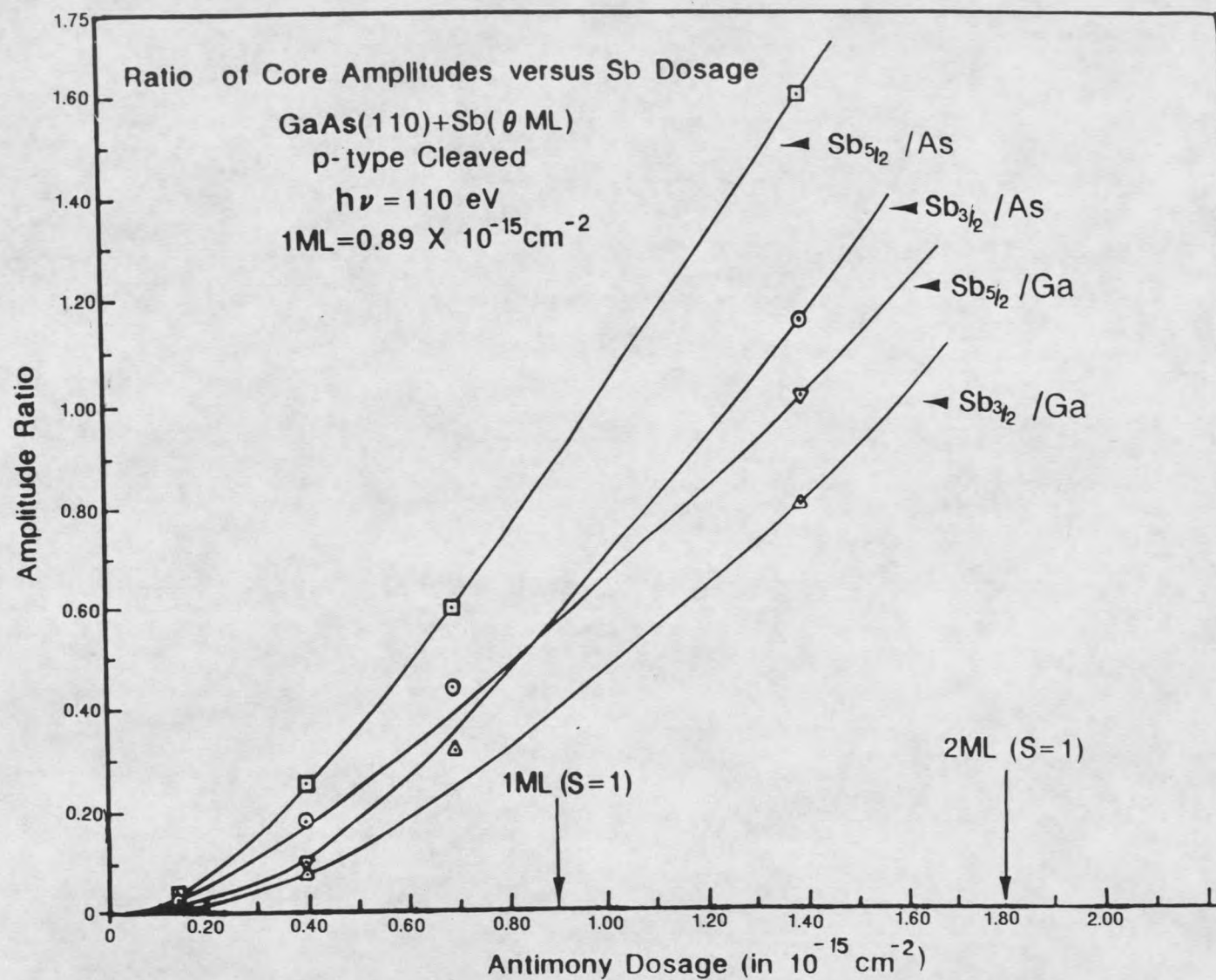


Figure 29. Ratio of Core Amplitudes Versus Sb Dosage.

Table 6. Antimony Overlayer Calibration Data.

Surface Concentration $\sigma_{\text{Sb}} \text{ (a)}$	Surface Concentration $\sigma_{\text{GaAs}} \text{ (a)}$	Coverage $\theta \text{ (b)}$	Sticking Coefficient S
0	0	0	n/a
0.07	n/a	n/a	n/a
0.14	0.03	0.034	0.21 (c)
0.40	0.20	0.225	0.50 (c)
0.70	0.50	0.562	0.71
1.40	1.00	1.124	0.70
7	n/a	n/a	n/a
30	n/a	n/a	n/a

a units of 10^{15} atoms/cm².

b $\theta = \sigma / 0.89 \times 10^{15}$ atoms/cm²; units are in ML.

c Possibly in error (Skeath)

After evaporation of the Sb overlayer, ratios of the various Sb spin-orbit split peak amplitudes versus the Ga or As peak amplitudes are calculated and plotted on Figure 29. From this data, an average antimony dosage is determined. This can be converted into units of monolayers using 0.89×10^{15} atom sites /cm² for the (110) surface. Then multiplying by the S at that dosage will produce the proper coverage. Skeath generally found that $S = 0.7$; however below $D = 0.8$ ML, S seems to drop rapidly to about 0.2 ($D = .16$ ML).

CHAPTER 6

CORE LEVEL MEASUREMENTS

In general, the core electrons of a material have distinctly different attributes than the valence electrons. Their binding energies are more characteristic of the constituent atoms than of the solid itself, since the major contribution to their energies is due to Coulomb attractions with the nucleus of the host atom. Consequently, their orbital character is atomic-like and the spatial extent of the orbitals is localized on the host atom. However, energy perturbations and wavefunction interaction can occur with neighboring nuclei and, more important to us here, with the valence electrons.

Because core electrons are generally understood and because they couple with the solid's electronic structure, they can help to understand the chemical and electronic nature of the interface. This core electron coupling can occur via (1) Coulomb interactions with the valence electrons or as (2) electronic excitations between core and valence states. The first effect involves core level binding energy shifts caused by the charge transfer associated with the formation of the interface region (chemical shift effect). The second phenomenon, electronic excitations between core levels and empty surface-related states, can occur as well and is termed the core threshold effect. Both effects are used to derive information about valence states which are associated with the interface formation between Sb and GaAs(110).

In order to explore these effects in the GaAs+Sb interface system, a variety of spectroscopic measurements were applied to the core levels. High-resolution core lineshape measurements were conducted to study the core level binding energy shifts; and electron energy loss spectroscopy (ELS), angle-resolved CFSs, and photoelectron yield spectroscopy (PYS) were carried out to investigate the Sb core threshold effect.

Figure 30 shows an overview set of EDC spectra for the d-core levels of GaAs(110), *as-cleaved* and with the Sb overlayer. The energy axis is referenced to the VBM and the location of the VBM is determined from the normal emission EDC study on the same sample (see Chapter 7). The binding energy obtained is 18.8 eV for the Ga-3d core and 40.7 eV for the As-3d core. These energies agree with values reported elsewhere (Eastman *et al.* 1982). The upper spectrum obtained after Sb deposition was shifted by about 300 meV to compensate for the surface Fermi level pinning caused by the Sb. This band bending shift is consistent with Skeath's (1982) observations for sub-monolayer Sb coverages on GaAs(110). From the energy separation of the Ga and Sb peaks, we obtained values for the binding energy of the Sb-4d core state, whose spin-orbit splitting is easily observed. These binding energy values are summarized in Table 7.

Table 7. Binding energies for Ga-3d, Sb-4d, and As-3d cores*.

Sample	Ga-3d	Sb-4d(5/2)	Sb-4d(3/2)	As-3d
GaAs(110)+Sb	18.80	31.36	32.60	40.70

* Energies in eV referenced to VBM.

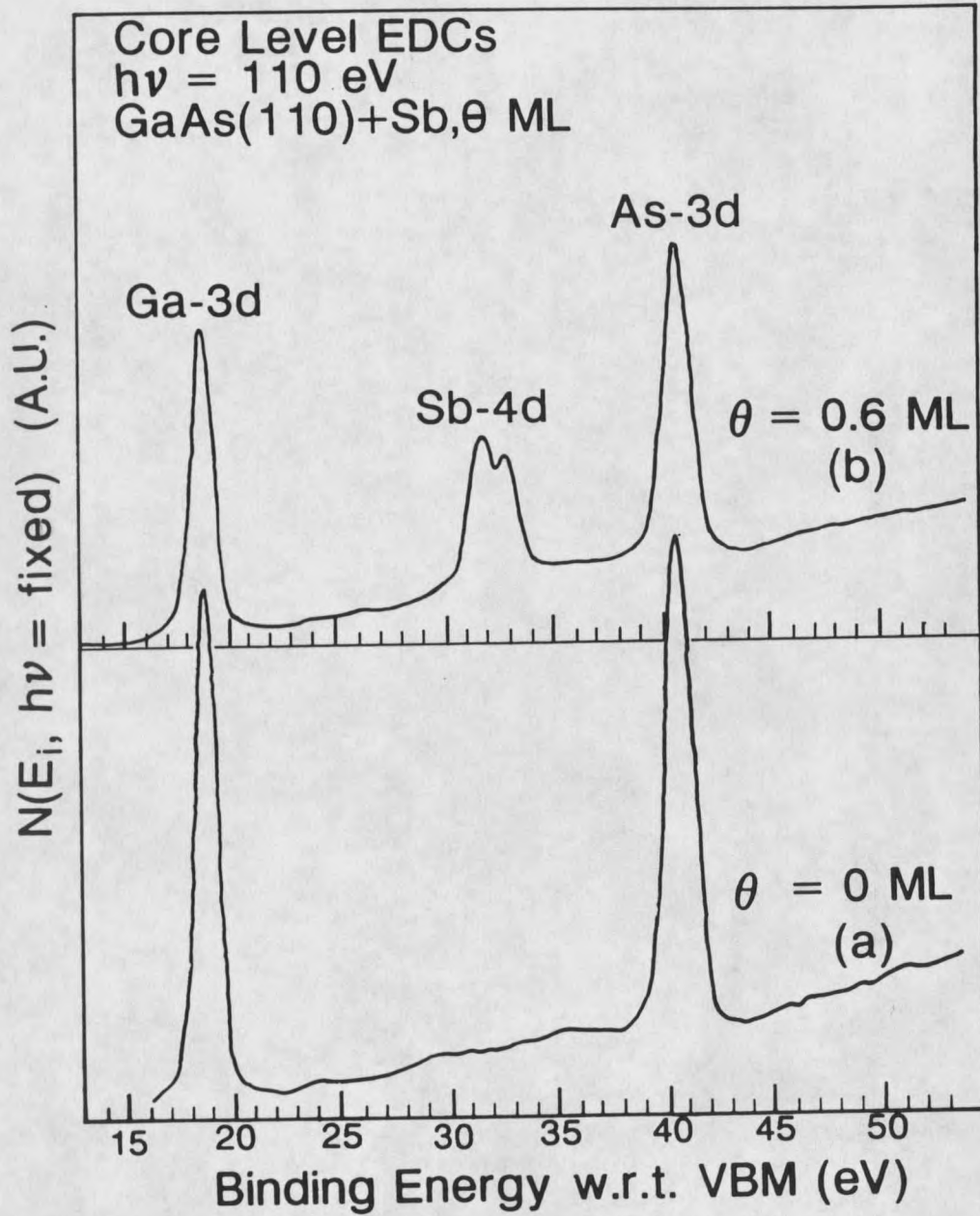


Figure 30. EDC spectra showing Ga-3d, Sb-4d, and As-3d cores. The curve (b) has been shifted to lower binding energy by 300 meV to compensate for Fermi level pinning due to the antimony.

High Resolution Core Lineshape Study

The Sb-4d core doublet in curve (b) of Figure 30 was examined with higher energy resolution so details of its lineshape could be studied. Several angle-integrated EDC spectra of the antimony core taken at a photon energy of 73 eV are seen in Figure 31, in which the background due to the secondaries has been subtracted from the spectra. Curve (a) is the room temperature *as-deposited* GaAs+Sb sample (#7111) with an Sb coverage of 0.6 ML. The doublet character of the spectrum is due to spin-orbit splitting inherent in the antimony core. The middle spectrum of the figure, curve (b), is sample #7112 composed of a much thicker Sb layer ($\theta = 4ML$) prepared by an additional deposition. As a final step, heating of the crystal to about 350° C allowed thermal desorption of the thicker Sb layer and spectrum (c) results. Determination of the overlayer thickness of 1.4 ML for sample #7113 was done by examining the relative amplitudes of the core levels (see Chapter 5).

These high-resolution core EDC spectra were taken with a double-pass CMA spectrometer and a toroidal grating monochromator (see Chapter 3) with a combined instrument resolution of approximately 125 meV. Preparation of this sample is fully discussed in the normal emission EDC study of Chapter 7.

Relative to the thick Sb overlayer sample, the *as-deposited* sample shows a rather complex lineshape with individual peaks having roughly twice the width of those seen in curve (b). This observation suggests that curve (a) is a composite curve made up of several lines with different binding energies. The thick Sb overlayer sample exhibits a simple Lorentzian lineshape, indicative of a single spin-orbit split pair of core states. When most of the thick Sb layer was desorbed, the complex lineshape returns as seen in curve (c).

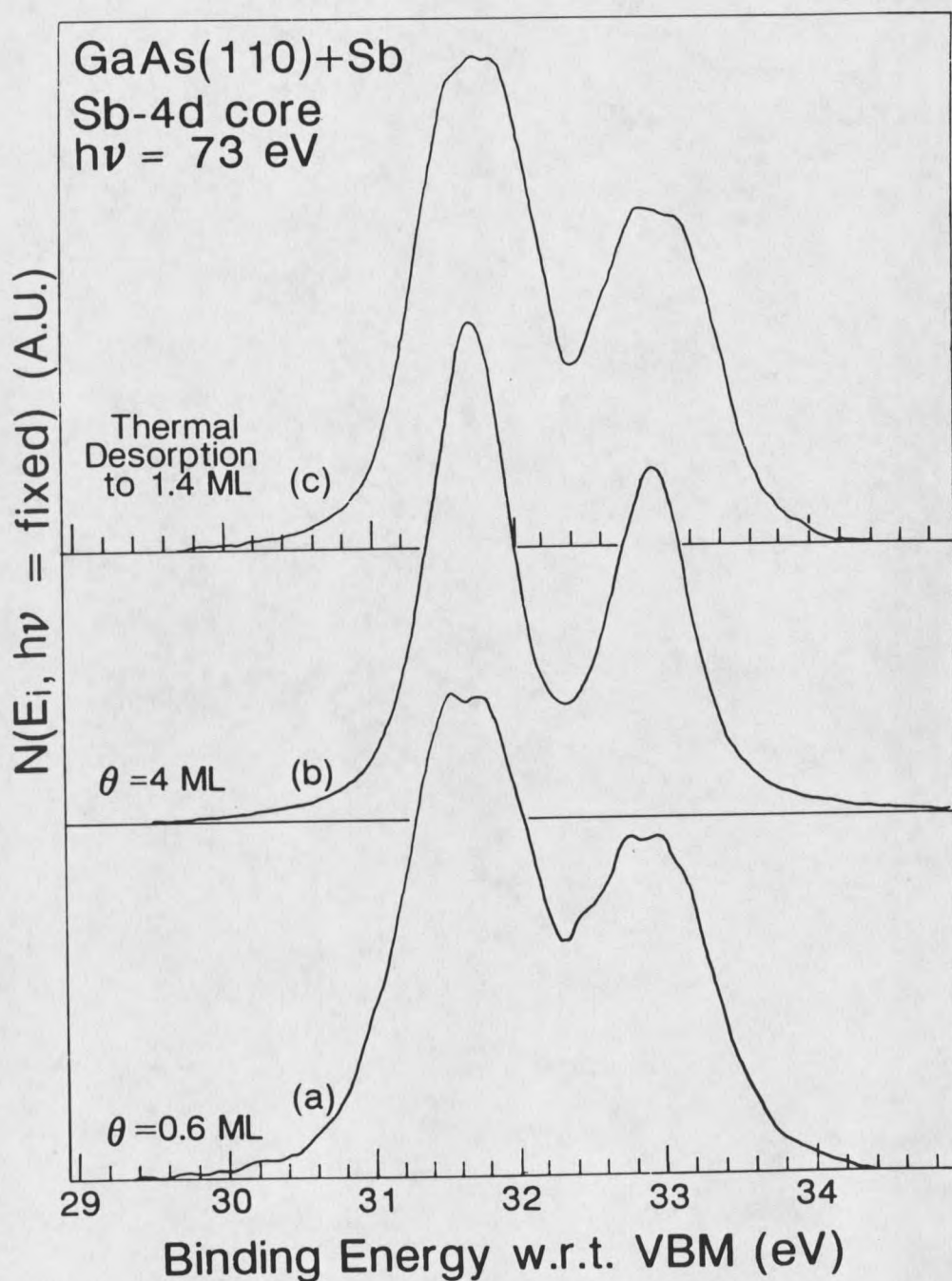


Figure 31. High-resolution EDC spectra of the Sb-4d core. Curve (a) is for 0.6 ML of Sb, *as-deposited*, curve (b) has a thicker Sb overlayer of 4 ML and curve (c) has 1.4 ML of Sb as a result of thermal desorption of sample #7112.

Lineshape Fitting of Sb-4d Core

After starting with a survey set of core level EDC spectra, we examined the lineshape dependence of the Sb-4d core versus overlayer thickness. In order to study the data more precisely, we employed a curve-fitting procedure to study the details of the Sb-4d core lineshape. It is found that the lineshape for the thick Sb sample could be fit very well with Lorentzian functions. The fitting gave a spin-orbit splitting of 1.25 eV with an amplitude ratio of 0.66. The full width at half maximum for the $J = 5/2$ peak is 0.5 eV and that for the $J = 3/2$ peak is 0.51 eV. The high quality of the Lorentzian fit is attributed to the fact that the instrumental resolution was small compared to the linewidths observed; hence any instrument effect is not manifested in the lineshape.

The *as-deposited* Sb lineshape, curve (a), was then studied with the curve fitting procedure. The component curves used in this procedure are the Lorentzian lines derived from the thick film analysis. Curve (a) was found to have two component lines as is shown in Figure 32. The two components are separated by 0.38 eV and have almost equal amplitudes. Existence of two component lines in the spectrum means that the Sb atoms sit in two inequivalent sites on the cleaved GaAs(110) surface, viz., the Ga and As bonding sites. The observation of two inequivalent Sb sites is consistent with the structural model for Sb overlayers on GaAs(110) obtained from a dynamical LEED analysis (Duke *et al.* 1982). In that model, the Sb bonding sites are approximately those that would be occupied by the next layer of Ga and As atoms if the bulk lattice was imagined to be continued. For the Ga-Sb bond, there is a charge transfer from the electropositive Ga to the electronegative Sb which increases the screening of the core potential around the Sb atom, resulting in a lower observed binding energy for this core state.

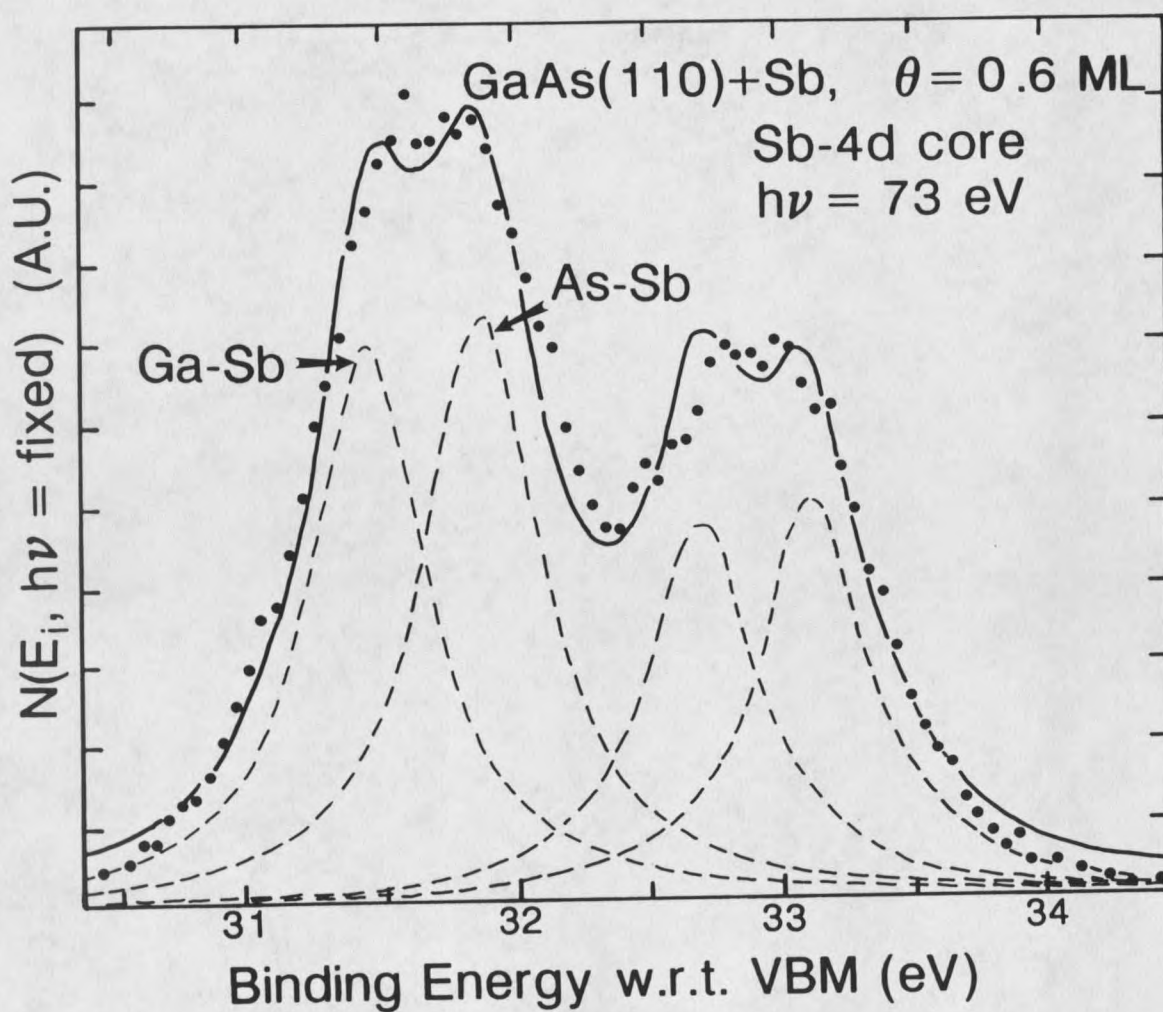
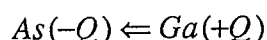


Figure 32. Antimony core levels with Lorentzian line fits.

Hence the component line on the left-hand side of Figure 32 is attributed to the Sb bonded to a surface Ga atom. Conversely, the Sb bonded to the surface As atom has an decreased valence charge density due to the charge transfer towards the arsenic. This screening reduction of Sb core potential then produces a higher measured binding energy. The component on the right-hand side in Figure 32 is assigned to the Sb bonded to a surface arsenic atom (*i.e.*, As-Sb).

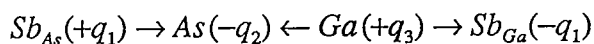
It is well established (Duke *et al.* 1980) that the relaxation of the clean GaAs(110) surface after cleaving causes electronic charge to be transferred from the surface Ga atom, with a Pauling electronegativity $\chi = 1.6$, towards its neighboring As atom ($\chi = 2.0$). This can be schematically written as a two-atom cluster:



where the double arrow indicates a relatively large electron charge transfer from the Ga to the As and the $\pm Q$ denotes the residual charge density on each atom. Because of this charge redistribution, the Ga atom for the clean surface has an empty dangling bond orbital while the orbital on the surface As is fully occupied. This charge imbalance drives the surface relaxation, resulting in the Ga atom moving inward and the As atom moving outward as seen in Figure 12.

When the Sb overlayer is forming and a Sb atom covalently bonds with a surface As atom, each of these atoms contribute a single electron to the bond. For As, this means it has an extra electron, in addition to the two it started with, not participating in the As-Sb bond. However, an Sb atom which tries to bond with the surface gallium, finds only an empty dangling bond orbital on the Ga atom. In order to complete the Ga-Sb bond, an additional electron is needed and is provided by the neighboring As atom. Therefore, the large charge imbalance which was responsible for the surface relaxation

of *as-cleaved* GaAs(110) is reduced substantially. A charge distribution more like the bulk is obtained. Consequently, the relaxation of the cleaved surface is essentially healed out with the adsorption of Sb. This four-atom cluster can be written as



where the single arrows indicate the direction of electron charge transfer and the $\pm q$'s denotes the residual charge density on each atom. In general, $q \ll Q$ for any of the q 's, making a more evenly arranged charge distribution.

This argument is also consistent with the structure model derived from LEED analysis, which places the surface Ga and As atoms in the GaAs+Sb interface essentially in their bulk positions (Duke *et al.* 1982). Hence it should be possible to see changes in the core lineshapes of Ga and As with Sb adsorption. The lineshapes for the cleaved Ga and As surface have been studied by the Eastman *et al.* (1980,1982), who observed a component to the lineshape due to atoms on the surface by choosing a photon energy which yields high surface sensitivity. The largest shift reported by Eastman *et al.* is for the arsenic core level, which moves to lower binding energy by 370 meV. Conversely, the Ga-3d surface component shifts to higher binding energy by 280 meV. The direction of the shift is easy to understand by the prior discussion of charge transfer and screening of the core potential.

We also measured the As-3d core at a photon energy of 80 eV for maximum surface sensitivity. The signal/noise in this data is not optimal because of photon flux available in the beamline was low and because the arsenic emission was attenuated by the Sb overlayer. The lineshapes were analyzed with the curve fitting routine. However, the results were poor, because of the limited signal-to-noise, and have not been reproduced here. Some qualitative observations of As-3d core can be made, however.

First, the gross shift in the lines is due to Fermi level pinning and band bending. The spectrum from the *as-cleaved* surface is slightly broader than that for the overlayer case and does not have a well resolved minimum between the two spin-orbit partners. This is because the surface component of the line is shifted to lower binding energies. With the adsorption of Sb and the healing out of the clean surface reconstruction, the surface component is almost totally removed and a slightly narrower line is observed with a single spin-orbit split component.

Results

We have now seen how the adsorption of the Sb to the GaAs(110) surface occurs at two electronically inequivalent bonding sites, *viz.*, the Ga and As surface atoms. This results in two chemically distinct surface bonds (*i.e.*, Ga-Sb and As-Sb) each having different electron charge distributions, which can be qualitatively understood on the basis of the respective electronegativities of the atoms. The extra electron which the surface As atom had for the cleaved system is transferred back to help complete the neighboring Ga-Sb bond. The redistribution of the electron charge, eliminates the reconstruction of the clean surface, and restores the Ga and As atoms, more closely to their bulk positions. Therefore any binding energy shift due to valence charge transfer is reduced and consequently, the surface component of the As core line disappears, almost as if there was no surface at all. When several monolayers of Sb are deposited, the surface Sb atoms then occupy just one bonding site, *viz.*, that of the previous Sb layer, and a single Lorentzian component is observed. When these outer Sb atoms are thermally desorbed, allowing the interface Sb atoms to be measured again, the two Sb core lines reappear, almost as before.

Core and Surface State Interaction Study

To observe all the possible photon induced emission processes, particularly the enhanced emission at core threshold, several constant final state spectra were measured. The use of CFS spectra was described previously in Chapter 3. The CFS is measured by fixing the final state energy and scanning the photon energy (see Table 1). In Figure 33, several angle resolved CFS spectra (ARCFS) are shown for normal emission (*i.e.*, $\theta_A = 0^\circ$) and p-polarized light. In this case, the radiation A vector is oriented in the same direction as the Ga dangling bond (*i.e.*, $\phi_A = 0^\circ$). The spectra shown are taken at a final energy for which the various peaks in the spectra are well separated.

The sample conditions for the spectra shown in Figure 33 are as follows: the lowest curve is for the *as-cleaved* GaAs(110) surface, followed by the curve for a coverage of 0.6 ML, the third curve is for a coverage of 4 ML, and the upper curve is obtained by thermal desorbing the multilayers of Sb leaving 1.4 ML. These curves are respectively labeled a, b, c, and d. The samples with the various coverages are the same as those discussed earlier in connection with the discussion of Figure 31. The curves have been corrected for the spectral dependence of the light from the monochromator (light curve).

The advantage in taking CFS spectra is that it is possible to observe both the direct emission and emission due to core hole decay at the emission threshold. This emission is referred to as core threshold enhanced emission. The resulting spectra are rather complex because, in addition to the valence band emission, there are three shallow cores, marked with solid triangles.

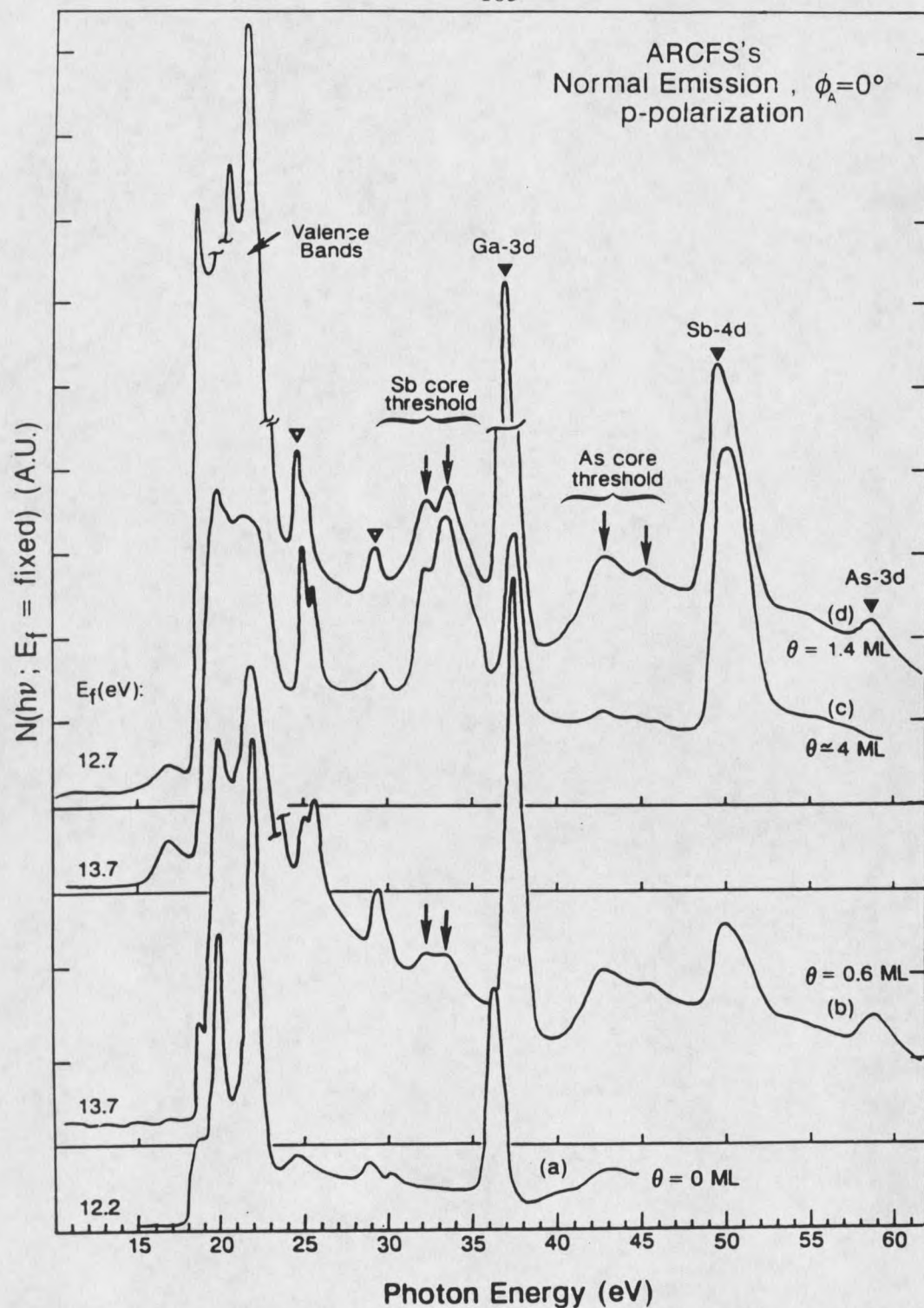


Figure 33. ARCFS spectra showing Sb core threshold effects. The open triangles denote second-order core emission, while the solid triangles mark direct emission from the same cores.

Because the monochromator had moderate levels of second-order radiation, we also observe another set of core peaks, indicated with open triangles. The emission at low photon energy on the left of the valence band threshold is also caused by second-order light.

Two classes of emission features are noted on the figure. First, the direct emission starting from the left is the valence band emission followed by the Ga-3d, Sb-4d, and As-3d cores, the latter being somewhat weak. All of the core threshold features are present. The core threshold for the Ga-3d, as a result of the final energy parameter selection, is located near the VBM; and it has been studied previously (Lapeyre and Anderson 1975). The As core threshold, in the neighborhood of 43 to 46 eV, has also been previously studied (Zurcher 1981). However the Sb core threshold doublet, located at photon energy of 32.5 and 33.75 eV, is newly observed and will be discussed shortly in some detail.

The core threshold features just noted are easy to identify and can be distinguished from the direct emission because core threshold features always occur at the same photon energy. Hence, when the final state energy parameter is changed, the threshold features do not appear at a different photon energy in the spectra, while the direct emission features do. This effect is exemplified in the lower two curves. When the final state energy changes by 1 1/2 eV from 12.2 to 13.7 eV, the energy of the Ga-3d core changes by a 1 1/2 eV, while the core threshold emission for the arsenic at about 42 eV is unchanged. This test also allows identification of features due to second-order radiation from the monochromator.

The enhanced emission at the Sb threshold is of interest in these spectra and we will examine it in more detail. The two peaks noted at photon energies of 32.5 and

33.75 eV are separated by the spin-orbit splitting of the Sb core state. The latter emission due to decay of the core hole can also be seen by other spectroscopic techniques, which are summarized after a presentation of the theory of recombination or core hole decay.

Theory of Recombination

The mechanisms by which recombination (valence or core hole decay) can occur are either radiative or non-radiative. In the latter case, the recombination results in electron emission. It can be considered like the inverse of impact ionization, because instead of an excited electron which creates a electron/hole pair, it is the electron/hole pair which excites an electron above the vacuum level to be measured by the spectrometer. Two principal non-radiative mechanisms exist for the decay of the core hole. They are direct recombination (DR) and Auger decay (see Figure 34).

On the right-hand side of Figure 34 is an energy scale referenced to the VBM, which shows relevant energy levels. The core level energies are those obtained from the high energy EDC spectra shown in Figure 30 and tabulated in Table 7. Above the VBM are two empty states S_7 and S_8 which have been calculated (Mailhoit *et al.* 1985 and Bertoni *et al.* 1983).

Shown on the left is excitation of the Sb-4d core states into an empty state above the VBM, labeled S_7' . These excitations occur when $h\nu = 32.5$ or 33.75 eV. A particular Auger recombination is shown. The core hole (open circle) is filled by a VB electron (square). Because of the Auger interaction, another VB electron is emitted from the solid with a final energy of Δ_1 equal to the energy gained in the decay, if no energy relaxation is assumed.

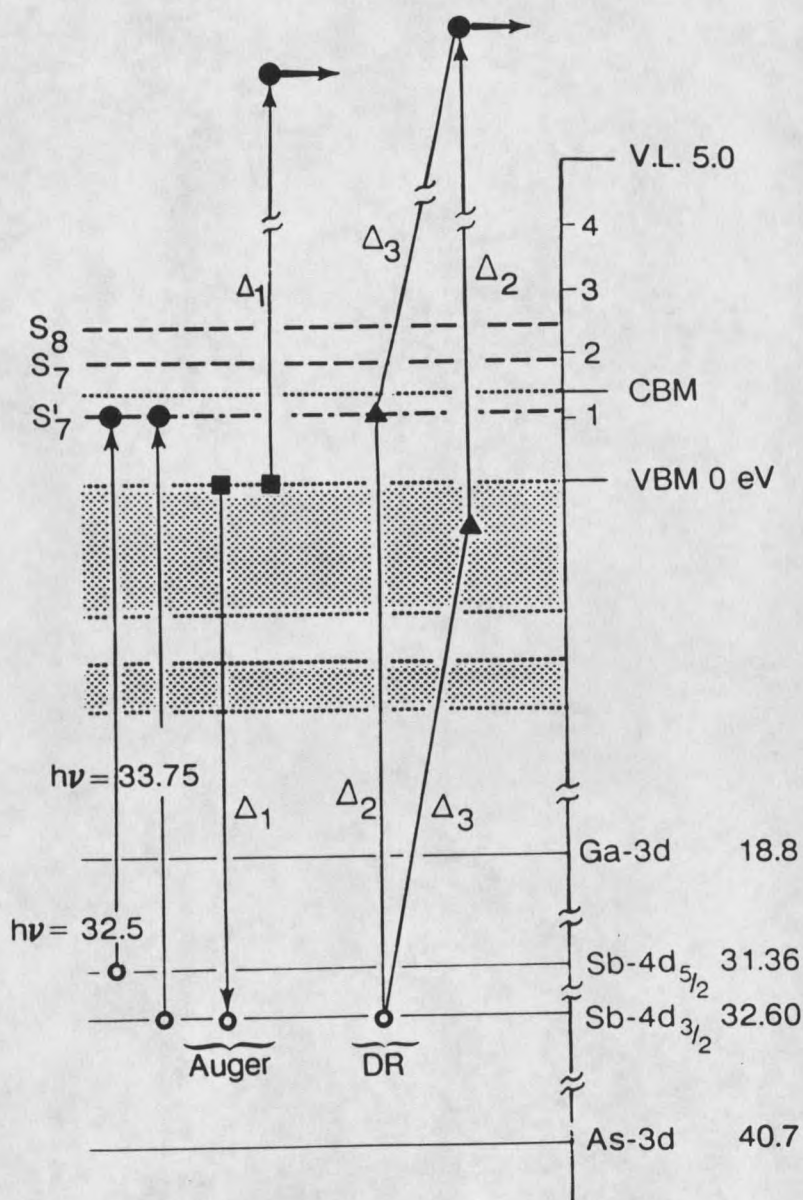


Figure 34. The energetics of core hole decay mechanisms. The creation of the Sb-4d core holes is illustrated on the far left. Auger and direct recombination (DR) processes are shown as possible core hole decay mechanisms.

The maximum final energy E_f is obtained when both transitions originate from the top of the valence band density-of-states. Consequently, the maximum kinetic energy E_k for the enhanced electrons are just E_f less the threshold value of 5.0 eV.

Also shown in the figure is the direct recombination (DR) process. As the name implies, an excited electron which came from the core (triangle) fills the core hole and exchanges Δ_2 energy with a valence band electron. This decay occurs when the electron and hole interact as an exciton, which can be thought of as a somewhat stable entity analogous to a hydrogen atom. This DR mechanism is energetically indistinguishable from direct valence band photoemission. When the enhanced electron originates from the valence band maximum, the maximum kinetic energy for the emitted electrons are obtained. Another possible view of direct recombination, which is quantum mechanically equivalent, is having the valence band electron fill the core hole exchanging Δ_3 energy with the originally excited core electron.

Because both direct emission and direct recombination (from states near the VBM) produce enhanced emission with the same kinetic energy, enhanced emission ought to be observed near the valence band maximum. One way to test for this enhanced emission is to examine a constant initial energy spectra (CIS) where the initial energy parameter is selected to be near the valence band maximum. This measurement was performed, but no enhanced emission was detected within about 1 eV of the valence band maximum. This suggests that the antimony core threshold evolves only by an Auger decay mechanism. Furthermore, if the hole/electron was excitonic, its long lifetime would give a very narrow linewidth in the photon energy scan. In fact, the peak width is large compared to the Ga core exciton. With no excitonic binding, the final state energy is simply the excitation energy less the core binding energy.

For the Sb-4d_{5/2} state, $E(S_7) = 32.5 - 31.36 = 1.18$ eV above the valence band maximum. But the state could be anywhere between about 1.00 and 1.38 eV depending on the relative participation of the two antimony bonding sites which was previously seen to have binding energies split by 0.38 eV (see Section 1 of this chapter).

Photoemission Yield Spectra

If the photoemission quantum yield or total photocurrent from the sample is monitored by scanning the photon energy through the core threshold, another measurement of the antimony core threshold effect can be taken. Figure 35 shows this data. The three lower curves (a,b, and c) are the photoemission yield curves taken for various orientations of the radiation vector potential $\vec{A}$ with respect to the Ga dangling bond, viz., $\phi_A = 0^\circ, 90^\circ$, and 180° , the $\vec{A}$ is parallel to the Ga dangling bond, whereas for $\phi_A = 90^\circ$ it is perpendicular to the bond. The photon range was from $h\nu = 15$ to 60 eV and the radiation geometry is p-polarized. The photoelectron yield measurement shows some of the principal energy excitation channels which exist in the solid.

The top curve (d) is the tungsten light curve, as measured by the photodiode mesh in the beamline, which is indicative of the spectral intensity properties of the monochromator. It is these properties which gives each yield curve its general shape, low on each end and high in the middle. No strong polarization effects are seen, since each peak in the yield curve is seen with the same intensity for each polarization.

The strongest features in the yield data are those due to the core threshold enhancement at antimony and arsenic threshold. As in the constant final energy spectra (CFS) data, the antimony core threshold shows two peaks at 32.5 and 33.75 eV.

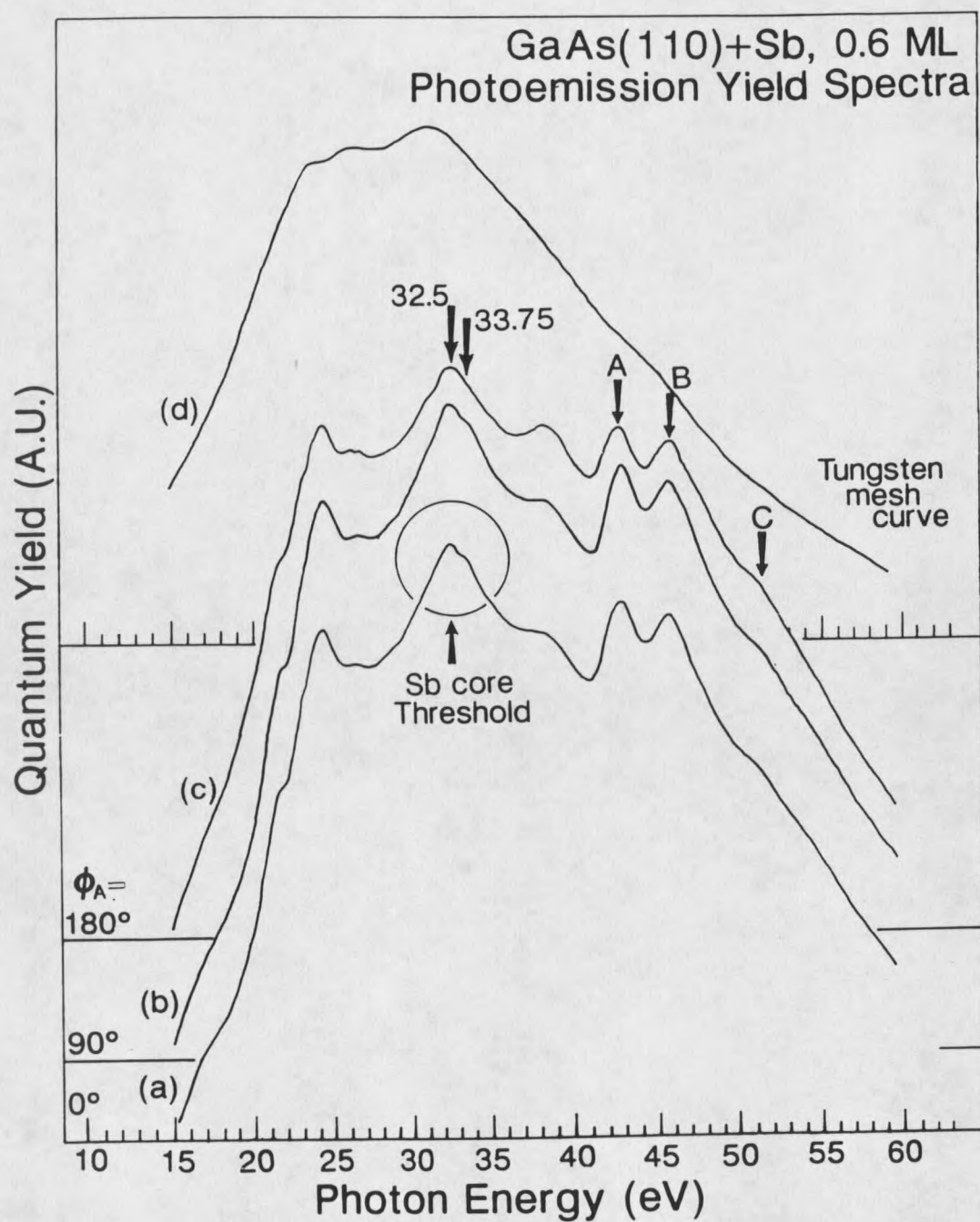


Figure 35. Polarization-dependent photoemission yield spectra. Sb and As core threshold effects occur at all polarizations.

In these data, one notes there is no polarization dependence for the excitation process at core threshold as is the case for the arsenic threshold which has been reported earlier (Zurcher *et al.* 1981).

ELS

Electron energy loss spectroscopy (ELS) was also used to investigate the Sb core threshold phenomena, because of its high surface sensitivity (about 5 Å for a primary energy of 100 eV). For present purposes, it can be regarded as another means of creating the Sb-4d core holes which subsequently decay.

The source was a coaxial electron gun of a angle-integrating double-pass CMA and normally was set to 100 eV primary energy. For a discussion of the equipment and procedures regarding ELS, see Chapter 1. The loss mechanisms of ELS generally involve single particle excitations from filled to empty states. ELS investigates the DOS of the empty levels, both of surface and bulk origin, quite analogous to PES. However, unlike PES, ELS only provides energy transition differences.

Typically, a primary beam energy of 100 eV is used, and the second derivative of the spectra recorded. Spectra obtained for *as-cleaved* GaAs(110) (#6120) and with 0.9 ML layer of Sb (#6121) are shown in Figure 36. The latter spectrum generally contained features due to all elementary excitations. The peaks on the right-hand side of the figure are of the kind generally seen at small loss energies due to interband transitions and shallow core levels. Note, for example, the presence of the bulk plasmon at 16 eV and the surface plasmon at 10 eV. The other features are interband transitions. On the left-hand side of the spectrum we have a structure attributed to Auger transitions.

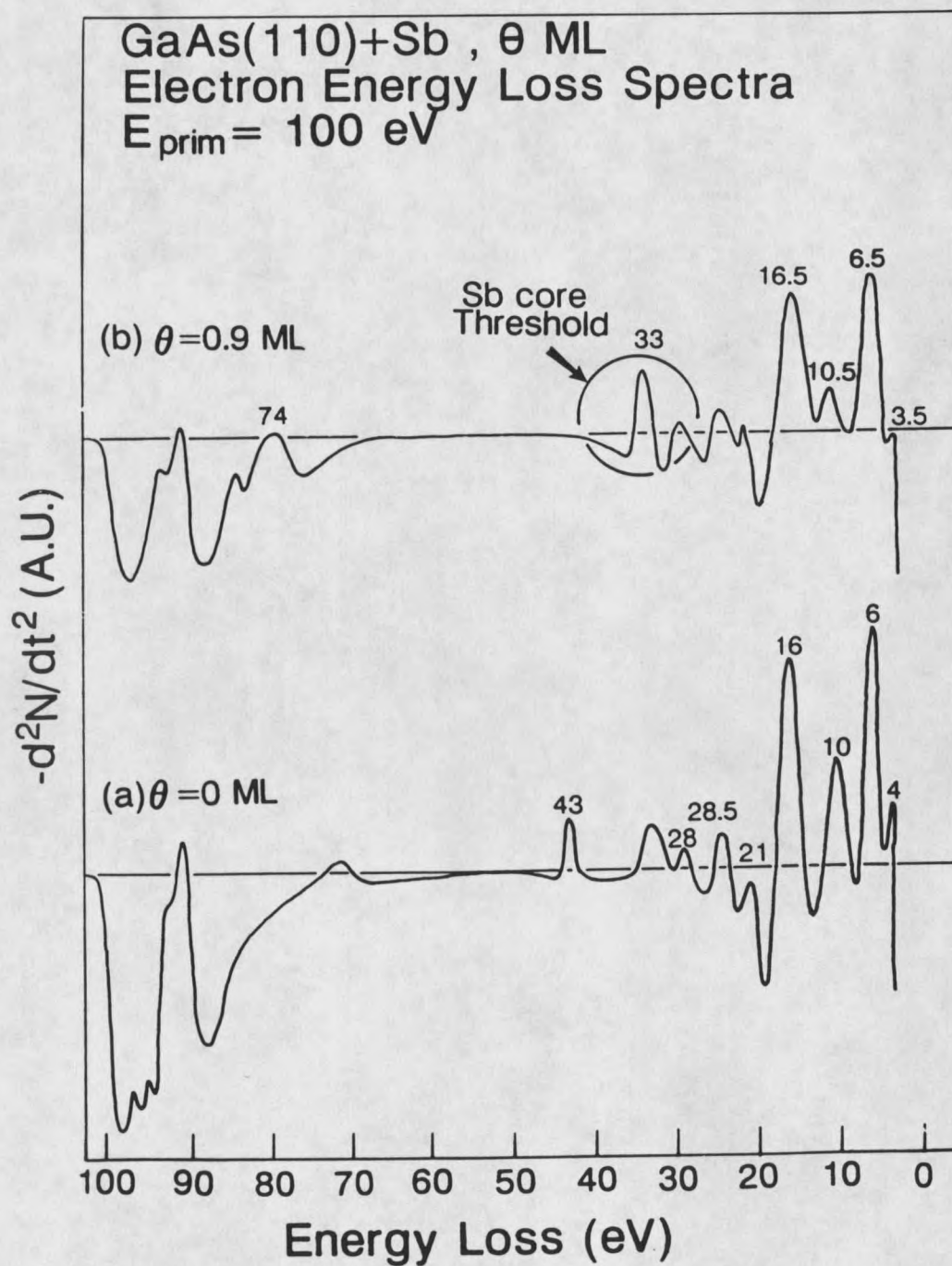


Figure 36. Antimony core threshold effect shown in ELS data.

The feature of interest in this study is the loss peak at 33 eV which appears in the presence of the Sb overlayer. This is due to the losses which result from the excitations of the Sb-4d level at threshold and hence this peak provides additional evidence of the core threshold transition noted in the yield data and CFS data presented earlier. As in the CFS study, the intensity of this peak is proportionally related to the amount of Sb on the surface until it saturates at approximately 1 ML. At the resolution used to obtain the spectra in Figure 36, the feature does not reveal the spin-orbit splitting. However, on other spectra when the modulation voltage was reduced to about 0.5 volts peak-to-peak, two peaks at 32.5 and 33.75 eV loss energy were clearly seen. The photoemission and energy loss experiments both show the core threshold excitation at the same energy. The presence of the threshold emission in the photoemission experiment is due to decay process of the core hole but the creation of the core hole is not dependent upon the source of excitation.

The clean data shows the surface plasmon transition at 10 eV loss, which is shifted by 0.5 eV when the Sb is applied. More significantly, the amplitude of the surface plasmon is greatly attenuated, being reduced by a factor of about 3 (#6121) and still more for the double coverage (#6122). The surface plasmon is due to collective excitations of the conduction electron gas near the surface. It can be regarded intuitively as the entire electron sea oscillating with respect to the ion cores. Typically,

$$\omega_s = \frac{1}{\sqrt{2}} \omega_p \quad (48)$$

This holds approximately for our samples. The bulk plasmon occurs at 16 eV loss for the clean sample and at 16.5 eV for the Sb-covered sample. This phenomenon is

similar to its surface counterpart, but is controlled by the volume charge density of the system. It is not altered by the overlayer since being a bulk-related phenomenon, it is not surface sensitive.

The Ga surface exciton occurs at an energy loss of 21 eV, but at the experimental resolution, the Ga spin-orbit splitting cannot be seen in the spectrum.

Note that only one peak of the As-3d core threshold is present in the clean spectrum along with the Ga exciton. When Sb is grown on the surface, both peaks are eliminated. This is consistent with the hypothesis of Zurcher (1981) which says that this transition of the As core threshold transitions is actually into the Ga empty surface state. Because of bonding with the antimony atoms, the empty Ga dangling bond is filled and both of these transition are consequently eliminated.

Even though the cleave quality of sample number #6120 did not permit good photoemission data, it produced usable electron energy loss spectra. This can be understood in terms of photoemission. The cleave was macroscopically stepped, meaning that visible steps and terraces existed on the surface. These would cause difficulties obtaining a good focus condition (analyzer and light) for angle-resolved photoemission, but did not produced any problems for the flood-like electron gun and an angle-integrating CMA in ELS. In any case, the ELS spectra showed many surface-related features with this sample, both for the clean and overlayer preparations, including the surface plasmon and Ga surface exciton. The conclusion here is that the criteria for a sample with a good surface is very different for electron energy loss spectroscopy than for photoemission spectroscopy.

Results

In a photoemission experiment, the enhanced emission observed at core threshold involves two processes: the creation and the decay of the core hole state. Thus we suggest that the core threshold peak at 32.5 eV is due to an empty Sb-derived surface state, and with our measurements we can infer the energy location of this empty state.

The origin of the final state measured above at 1.18 eV above the valence band maximum is attributed to an Sb-derived surface state. We suggest a state S_7 or S_8 which is reported by theoretical studies of the Sb overlayer systems. This puts us slightly below the conduction band minimum. New states for the cleaned GaAs surface have been discovered in the gap and hence the energetics of those observations support the interpretation of Sb derived surface state. The second peak at 33.75 eV is probably due to excitation of the $J = 3/2$ state into this same final state. However, such a structure could also be enhanced by excitations of the $J = 5/2$ state into higher lying surface or bulk conduction band states. Because of this degeneracy no straightforward means exist to resolve it.

CHAPTER 7

ELECTRONIC STRUCTURE MEASUREMENTS

In general, our goal as stated in Chapter 1 is to study the effects and properties of ordered overlayers on semiconductors. The strategy taken involved measuring the photoemission response of these systems before and after overlayer growth using polarization-dependent angle-resolved photoemission spectroscopy (PARUPS). These photoemission data are related to the microscopic phenomena occurring at the interface. For reasons outlined in Chapters 2 and 4, the model system chosen for study was GaAs(110)+Sb(θ ML) where the overlayer coverage, θ is from 0 to 2 monolayers (ML). This allows for examination of the ordered overlayer-semiconductor interface at its initial formation, when the overlayer can be thought of as a perturbation on the electronic structure of the substrate.

Our specific objectives were two-fold; we looked for (1) overlayer-induced electronic states and for (2) non-uniform bulk band energy shifts caused by the overlayer.

(1) As noted in Chapter 4, overlayer-induced electronic states can be classified into three main types; overlayer states, chemisorption-induced states, and substrate surface states.

(2) The non-uniform band shifts were reported by Zurcher *et al.* (1982) for the GaAs(110)+Ge system. This phenomenon involves energy shifts of bulk interband

transitions beyond the rigid band-bending shifts due to Fermi level pinning at the surface. This effect is non-uniform insofar as different valence band-to-conduction band transitions have different energy shifts, unlike the rigid band-bending model, where all bands are shifted by equal amounts. It is important to examine the generality of such an unusual effect by studying similar systems, such as GaAs(110)+Sb.

Discrimination of two-dimensional surface-related states and intrinsic three-dimensional bulk band states is crucial in finding overlayer-induced electronic states. An important distinction between these states is their wavenumber dependence, *i.e.* $E(\vec{k})$. Since surface states are localized in the surface plane, they do not have a wavenumber component normal to the surface, but only a parallel component, $k_{||}$. Along a bulk Brillouin Zone line of constant $k_{||}$, like the Σ -line (see Figure 12), the energy of two-dimensional states will be constant ($E_i(k_{||}) = \text{constant}$). On the other hand, three-dimensional states have both perpendicular and parallel wavevector components. If $k_{||}$ is fixed in photoemission spectra, but $k_{\perp}$ permitted to vary, then the peaks which show different initial energies from spectrum to spectrum can be classified as bulk electronic states and those at a constant initial energy may be thought to be possible surface-related electronic states. An additional criteria for these surface electronic states is their sensitivity to surface conditions of the sample. *i.e.*, the presence of foreign atoms.

Experimentally, this search for overlayer induced surface states can be carried out in two ways: (1) normal emission angle-resolved EDC spectra (AREDC) and (2) angle-resolved CFS spectra (ARCFs).

(1) For normal emission EDC spectra, $\theta_p = 0$, making $k_{||} = 0$. A geometrical representation of how this works is seen in Figure 12. At normal emission, the detector is oriented straight-down the Σ -line in k -space.

(2) As the photoemission detector is moved away from normal emission, the surface analysis point in momentum space moves away from Γ according to Equation 25. For a fixed non-zero polar angle ($\theta_p = \text{constant} \neq 0$), scanning the kinetic energy E_k moves the analysis point along, in general, a quite complicated energy surface in the Brillouin Zone. Therefore, not only is the initial energy changing in an EDC spectrum measured at an emission angle off the surface normal, but the photoelectron's momentum is also changing. In interpreting these EDC spectra measured off-normal, it is difficult to assign interband transitions to the peaks; the data do not allow for a definitive discrimination between two-dimensional and three-dimensional states since they will both exhibit dispersion. However, in angle-resolved CFS experiments the final energy E_f and the detection angle θ_p are constant, but adjustable parameters. Therefore within a family of ARCFS spectra, $k_{||}$ (or $p_{||}$) can be held constant if θ_p and E_p are correspondingly adjusted according to Equation 25. In Figure 12 this means the measurement will sample the bulk band structure along a constant $k_{||}$ -line parallel to, but not on the Σ -line. Consequently, this technique will measure the surface electronic structure at a single surface Brillouin Zone point. We have therefore successfully fixed the analysis point in momentum space. Setting the acquisition parameters according to Equation 25 was the *modus operandi* of the angle-resolved CFS project.

The remaining parts of this chapter are divided into the two approaches taken to investigate antimony-induced electronic phenomena as discussed above, namely, the normal emission EDC study and the angle-resolved CFS study acquired in the off-normal emission configuration.

Normal Emission EDC Study

Experimental Approach

The general experimental procedures discussed in Chapter 5 apply to the work presented in this section. Clean (110) surfaces were prepared by *in situ* cleavage of a *p*-type GaAs crystal (Zn-doped, $N=3.2 \times 10^{18}/\text{cm}^3$). As a result, GaAs sample #7110 had an extremely high quality surface which was optically flat and without visible fractures. The chamber pressure at the time of cleaving was less than 3.5×10^{-10} Torr. Antimony overlayer preparation went well, resulting in a coverage of 0.6 ML for the GaAs+Sb sample (sample number #7111). LEED analysis after Sb evaporation showed a sharp 1×1 pattern with a low background. This is indicative of an ordered overlayer.

The monochromator and electron analyzer used in this experiment are fully discussed in Chapter 5. Synchrotron radiation was dispersed with the toroidal grating monochromator (TGM), which has higher resolution and throughput than the Seya monochromator. The electron spectrometer used was the angle-resolving double-pass CMA, which also has higher resolution and throughput than the PMA. The combination of these instruments allowed for the high signal-to-noise apparent in the spectra.

Data Processing and Reduction

To aid in the detailed energy band analysis of transitions observed in the EDC spectra, several data processing steps were employed. The sheer quantity of data (about 120 curves) and the high analysis precision desired meant that much of the processing and analysis needed to be automated.

Figure 37 summarizes data processing as it was applied to both the clean, GaAs(110) *as-cleaved*, and the covered, GaAs(110)+Sb, data. Here we see a typical EDC denoted as curve (c), from the dataset. The first step was to remove the effect of the secondary electron distribution by modeling it with an exponential curve shown as curve (d). The curve was fit by least squares to the lightly smoothed EDC. The removal of (d) from the original raw EDC (not shown) resulted in curve (b), which was lightly smoothed to produce curve (a). This curve has the contribution due to the secondaries removed and is referred to as a "primaries-only" EDC. Primary peaks result from photoelectrons that have not inelastically scattered during the photoemission process. This primaries-only EDC, called (a), was the starting point in the analysis phase. The spectra were normalized to the photon flux as measured by a tungsten mesh diode (see Chapter 5).

Before bandmapping and amplitude analysis could commence, energy positions and amplitudes of all the EDC valence peaks were determined by computer analysis (note arrows shown in Figure 37).

Determination of Perpendicular Wavevector

As discussed in Chapter 3, $k_{\perp}$ is not conserved in a photoemission experiment. So from the photoemission data alone, the bulk interband transitions cannot be located in momentum space. Various schemes (Chiang *et al.* 1980, Dietz and Eastman 1978, Heimann *et al.* 1979) have been used to determine a value for $k_{\perp}$, but each have limitations and inherent approximations. The most general method for low photon energies is the structure plot method of Williams *et al.* (1986) and is used in this study.

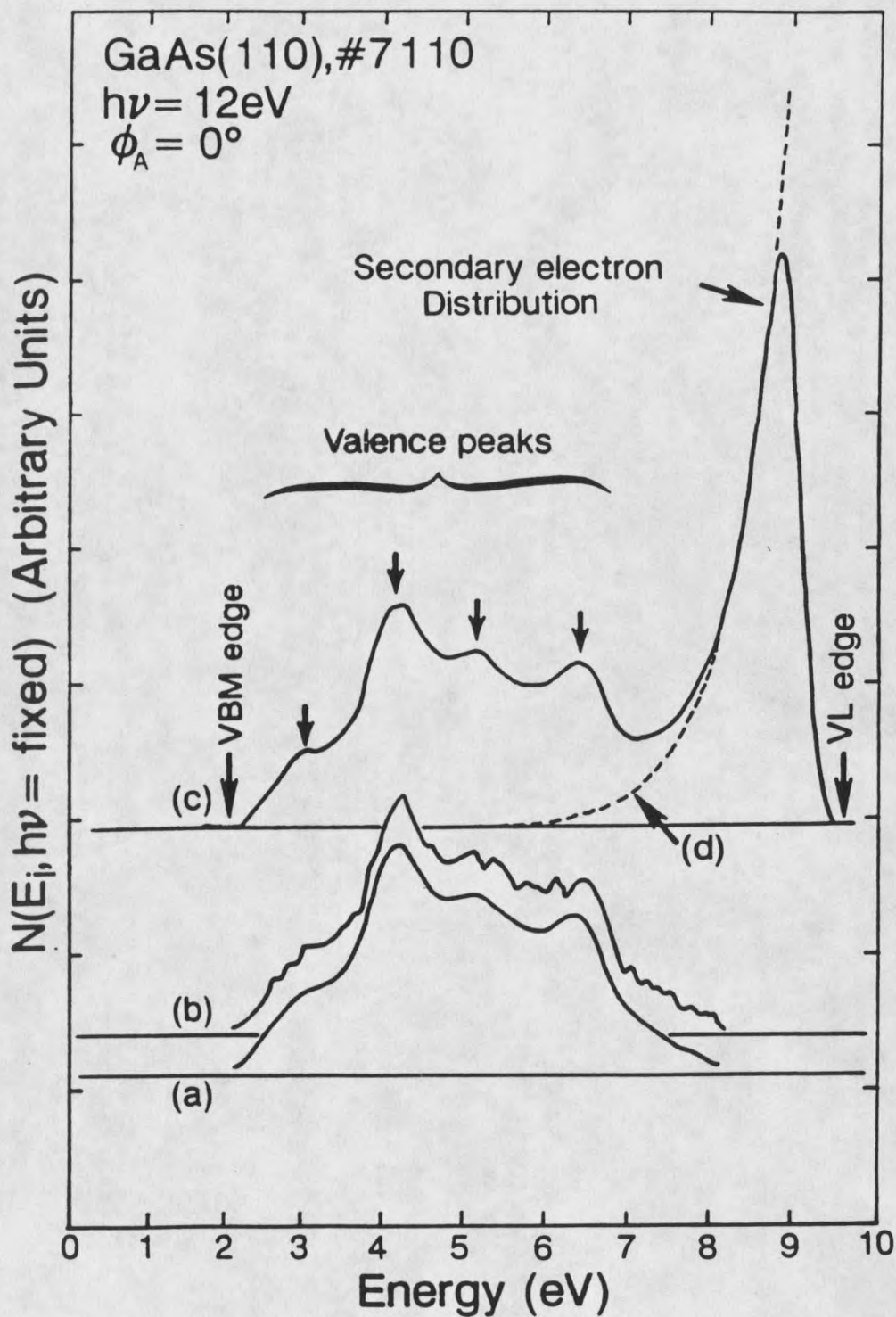


Figure 37. Data processing of normal emission EDC data. Exponential model curve (b), used to subtract the secondary electron distribution resulting in a primaries-only EDC (d), on which the remaining analysis was applied.

The structure plot method provides a way to correlate the experimental results with energy band calculations. In a structure plot, the peaks found in the photoemission spectra are plotted in terms of the dataset's structure, *i.e.*, their initial energy versus photon energy. Given the theoretical energy bands, the same structure plot can be constructed. As a result, close contact between the experiment and theory is obtained. In practice, the theoretical structure plot is placed over the experimental structure plot and correlations are identified, with the result that a $k_{\perp}$ value is obtained for each experimental data point.

Figures 38, 39, and 40 show the theoretical photoemission structure plots, where the pseudopotential calculations of Chelikowski and Cohen (1976) are used for the valence bands (VB) and the conduction bands (CB) are from Pandey's calculations (1986). The vertical axis is initial energy below the valence band maximum (VBM) and the horizontal axis is the photon energy. Each arc on these plots corresponds to a VB-CB pair and can be thought of as the locus of all theoretically possible energy transitions between a chosen valence band and the various conduction bands. Distances along each structure plot arc are related to the $k_{\perp}$ value of the transition. Twenty values of momentum for the Σ -line are noted in the figures, where $k_{\perp} = 0$ at the top of the figure.

When an experimental datapoint did not fall exactly on a theoretical arc, the point was projected onto the nearest arc in the direction of closest approach. This procedure distributes any misfit between the photon energy and the initial energy and is less subject to bias. There is some uncertainty in this procedure because of the non-uniqueness of the initial and final band assignments. These are resolved by using the $k_{\perp}$ value to locate the experiment data point on an energy band diagram and examining the combined experimental and theoretical information for internal consistency.

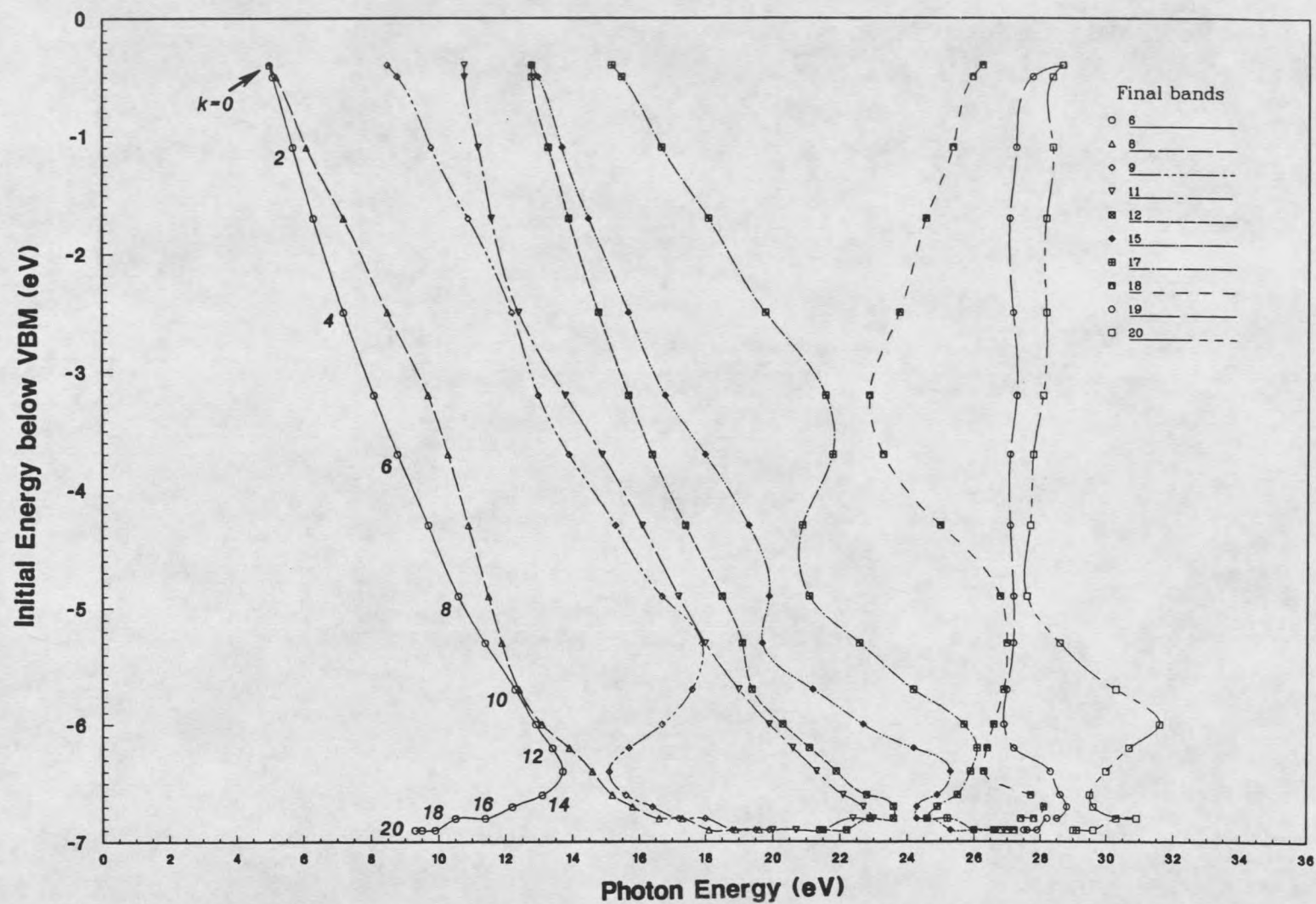


Figure 38. Theoretical structure plot for GaAs(110) for initial band #2. The vertical axis is initial energy below the VBM and the horizontal axis is photon energy of the transition.

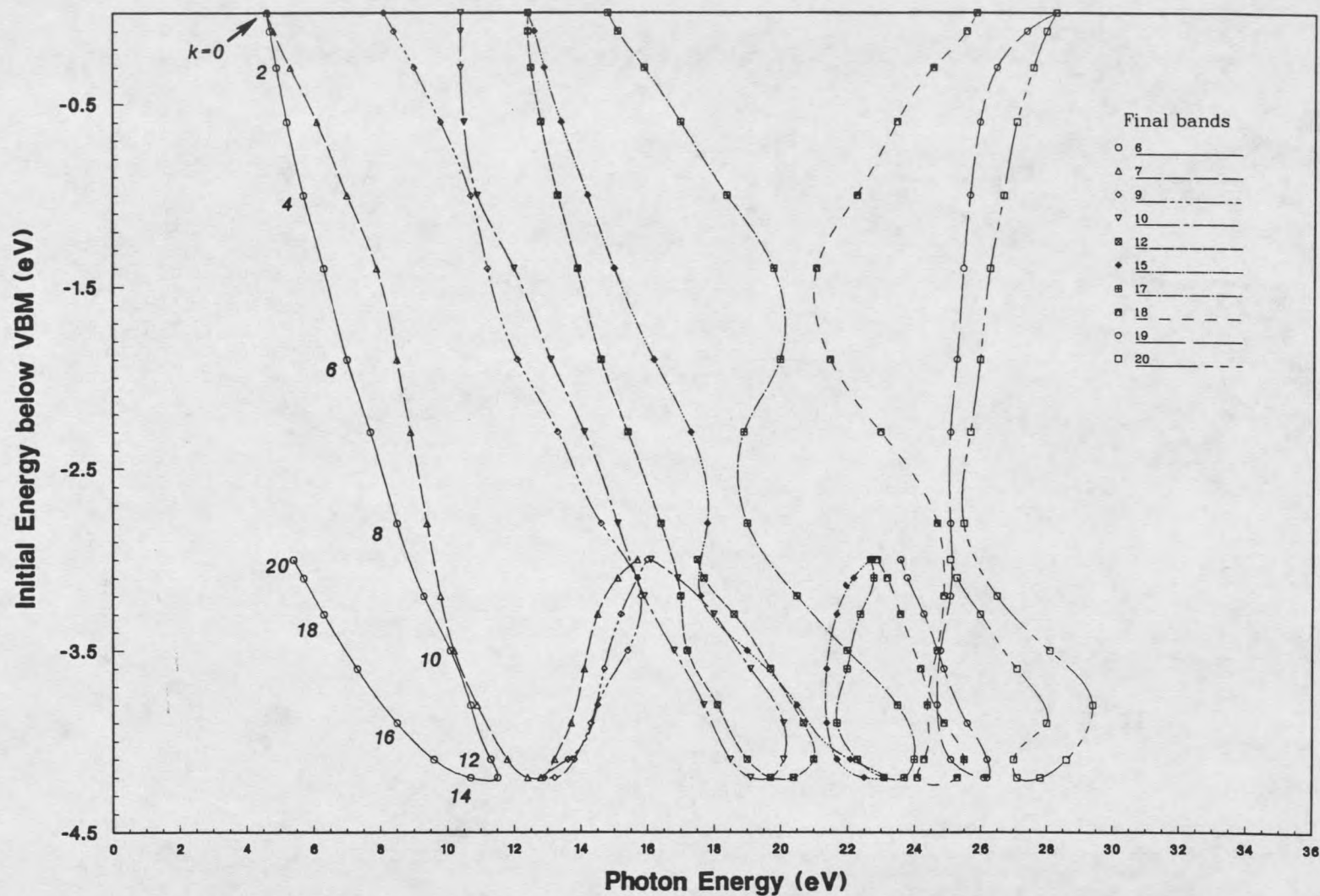


Figure 39. Theoretical structure plot for GaAs(110) for initial band #3. These curves are complicated due to the non-monotonic nature of the initial band.

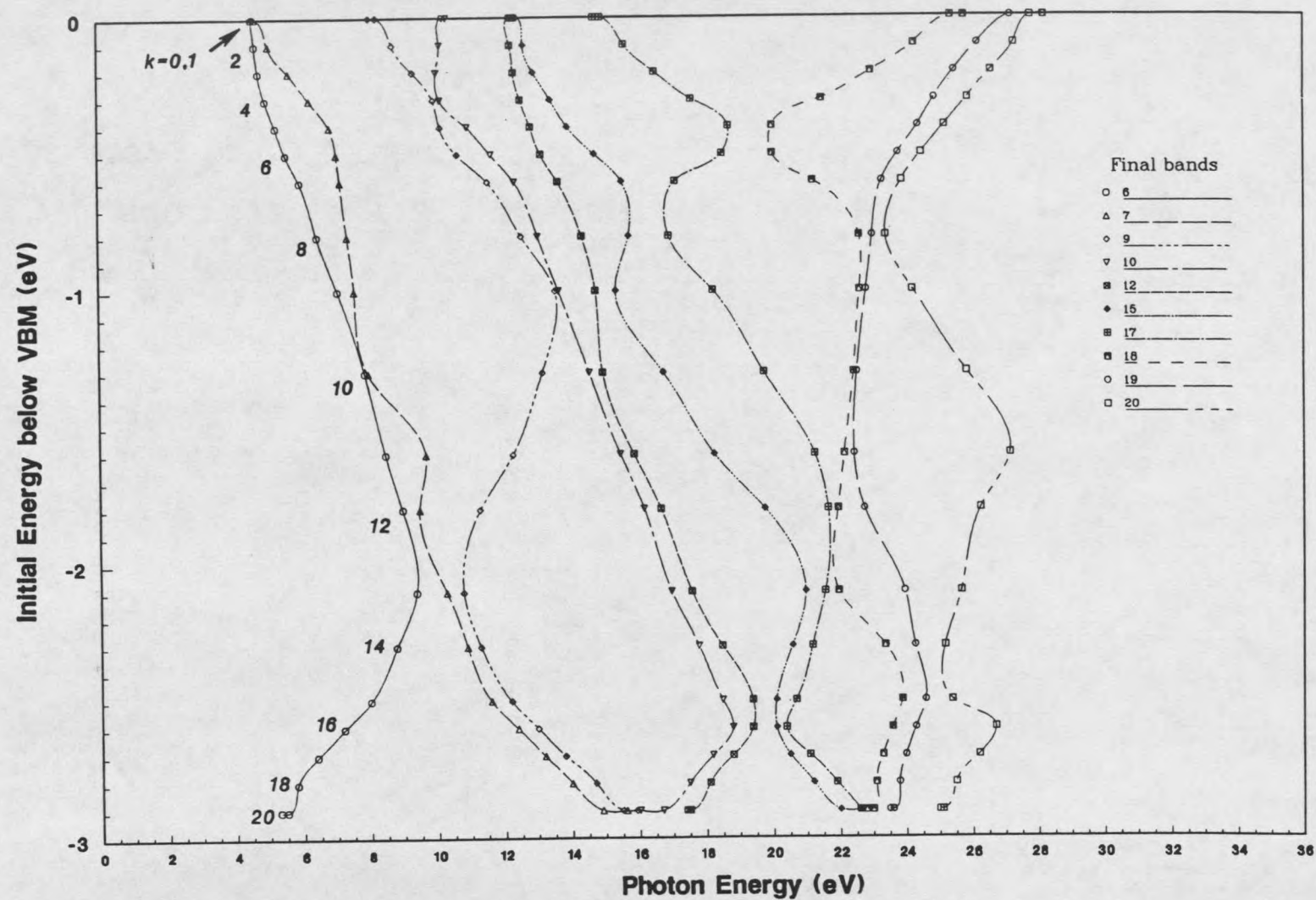


Figure 40. Theoretical structure plot for GaAs(110) for initial band #4. The similarity of these curves with the energy band diagram is due to the monotonic, almost flat nature of initial band.

The experimental structure plot for data obtained under the 90° polarization condition for GaAs(110), *as-cleaved* is shown in Figure 41. This polarization occurs when the optical plane containing the A-vector is oriented at a 90° azimuthal angle with respect to the crystal's mirror plane (MP). Microscopically, this means the light is polarized perpendicular to the Ga dangling bond (see Figures 10 and 11). This dataset will be discussed here in detail. Data and analysis results for the other polarizations (*i.e.*, 0° and 180°) are contained in the Appendices. Once again, in a structure plot the vertical axis is the initial energy of the transition below a arbitrary energy reference and the horizontal axis is photon energy. The VBM is indicated by the horizontal line at $E_i = -2.0$ eV. In Figure 41 the band assignments are also annotated, allowing the data points to be organized into transition groups. The six main transition groups studied (A through F) are noted along with regions, denoted by lower case letters, (a) through (k), of interest regarding Sb-induced modifications to the GaAs electronic structure. We will discuss them later. Each transition family has the initial and final band assignments annotated along it. The critical points, $\Sigma_1^{\min}$, Γ_{15} , and X_5 are marked as well. A concise overview of the transitions at normal emission is seen in the structure plot and detailed discussions of each transition will follow.

Each of the three clean GaAs datasets (polarization 0° , 90° , 180°) were compared with the clean GaAs(110) data of Knapp (1976) and there is good qualitative agreement, considering the different collection geometries used. Transition sequences were similar, even though peak amplitudes were often different. These amplitude variations can be explained by sample dependence and polarization effects caused by different source/sample/detector configurations.

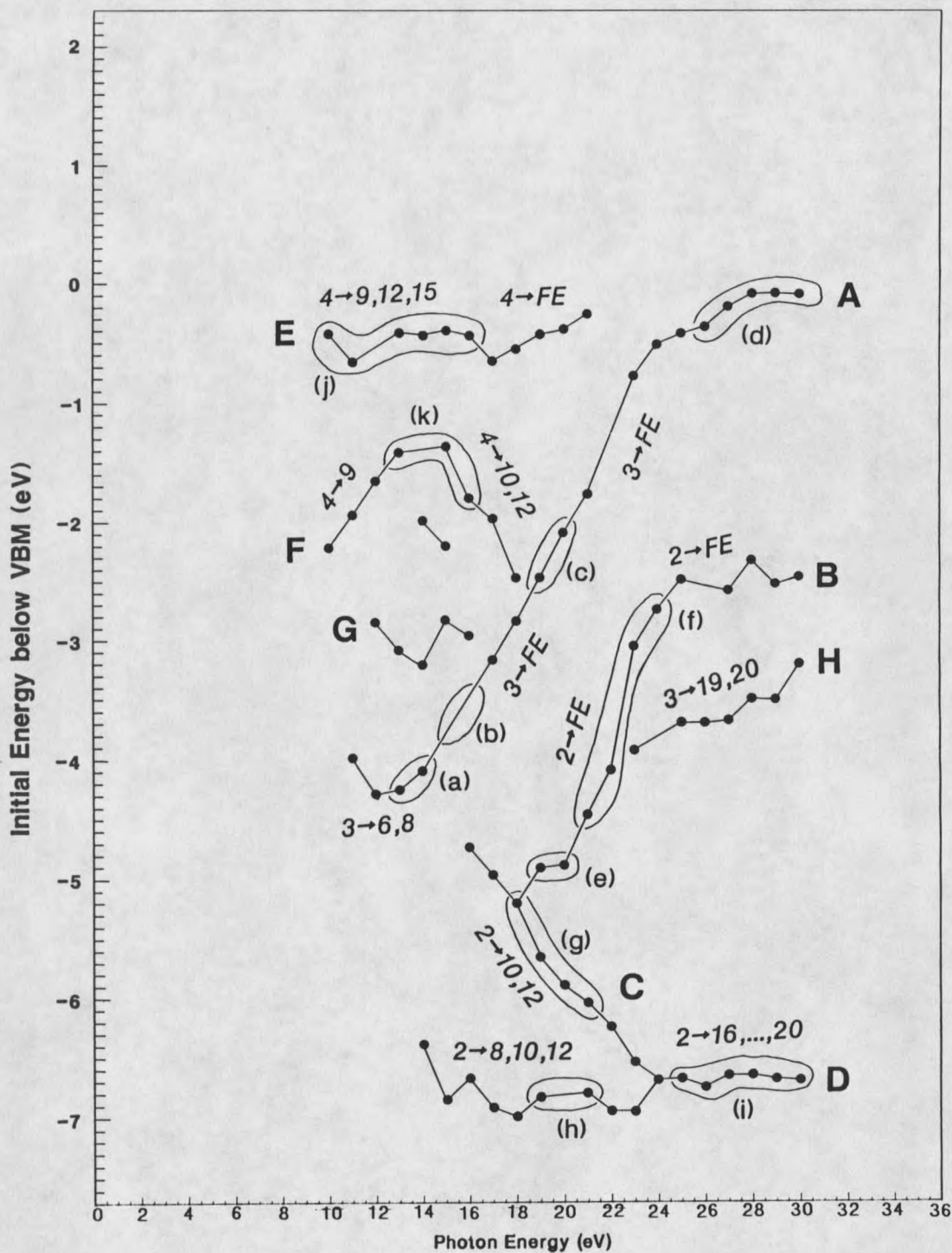


Figure 41. Experimental structure plot for GaAs(110), pol. 90. Transitions A through H are shown with band assignments and regions (a through k) of interest caused by the Sb overlayer.

The structure plot analysis is also done for the Sb covered case. The results are shown in Figure 42. The clean and covered structure plots are generally similar, although many of the transition sequences (*e.g.*, C and J) are less continuous in the covered sample than in the clean sample. The major transition sequences (*e.g.*, A, B, and D) are very consistent when compared before and after Sb coverage. Sequence E showed an interesting overlayer induced suppression. Detailed examination of the differences and similarities of the structure plots will be drawn out in the subsequent discussion.

Data and Analysis

The effects of the Sb overlayer in the normal emission EDC spectra are often subtle and complex. This is due in large part to the complicated morphology of the GaAs spectra, which in turn reflects the large number of bands which can participate in interband transitions. Therefore the ability to determine the $k_{\perp}$ values for the spectral features is essential in quantifying what effect the overlayer has on the substrate.

To assist the reader, the experimental results are presented in a consistent format as typified by Figures 43 and 44. The clean (dashed) and covered (solid) spectra are compared by first, overlaying the EDCs (left-hand side) and second, by taking EDC (clean - covered) difference spectra (right-hand side). The EDC normalization procedure, involving continuously reading of the current from the tungsten mesh photodiode, seems to work quite well since it results in useful difference spectra. The difference curves show features of the clean surface which were attenuated by the Sb overlayer as peaks (denoted by the "-") and clean features which are enhanced by the Sb as troughs (denoted by the "+"). Difference spectra identify trends caused by addition of the overlayer. Each figure contains one transition sequence, marked with arrows.

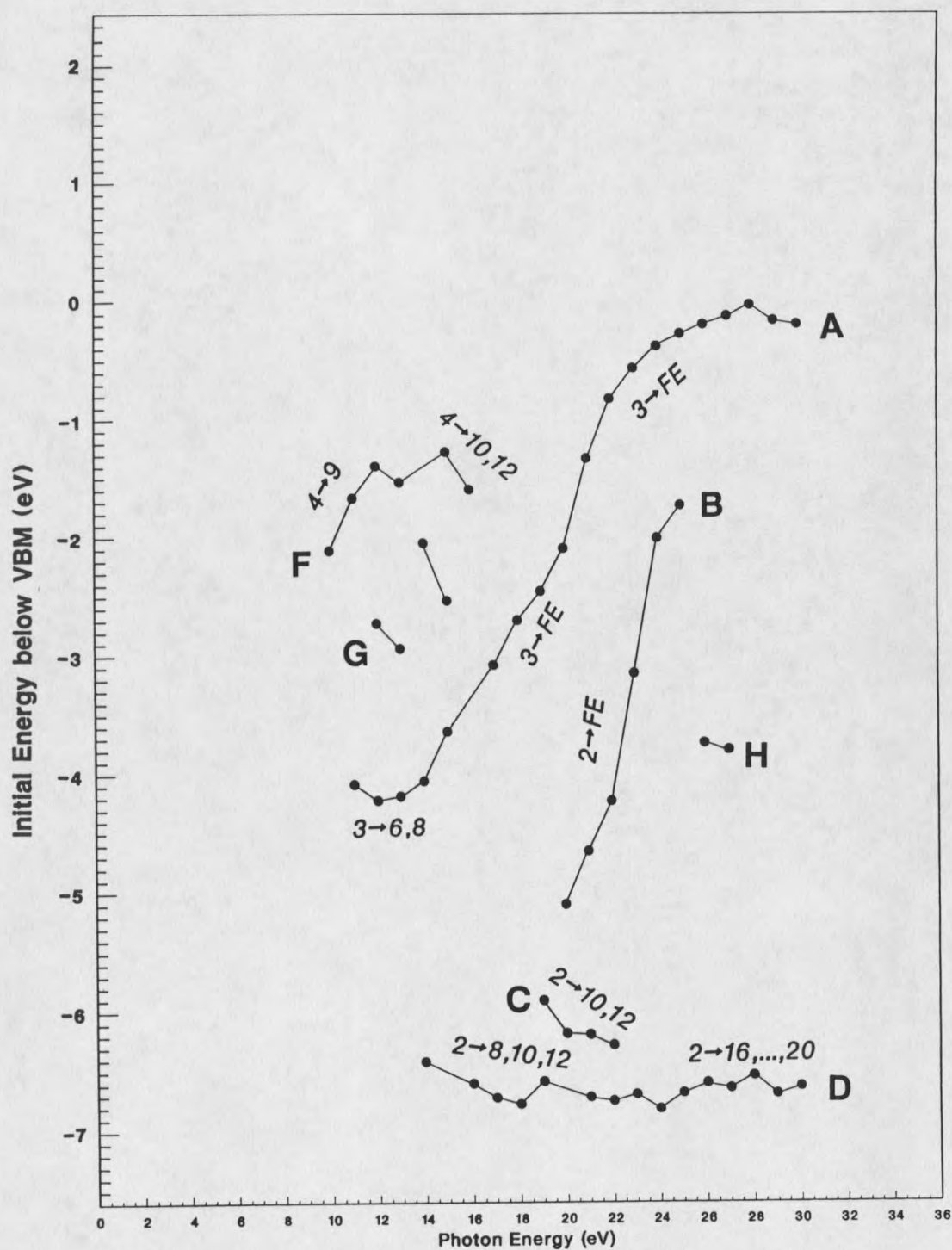


Figure 42. Experimental structure plot for GaAs(110)+Sb(0.6ML), pol. 90. Note the elimination of sequence E and the loss of continuity in C and H transitions.

Direct emission from the Ga-3d core is readily seen at the higher photon energies for all the polarizations. The best example of its presence is seen in Figure 44 from $h\nu = 26$ to 30 eV. The same mechanism shows itself in the lower photon energy regime (Figure 43), $h\nu = 13$ to 21 eV as direct emission from the Ga-3d core due to second-order light from the monochromator.

The figures immediately following the sets of difference spectra are the band structure plots. These show the results of the bandmapping procedure (*e.g.*, Figure 45), which utilized the structure plot method for $k_{\perp}$ determination. Since all measurements are at normal emission, the horizontal axis of Figure 45 is momentum along the Σ -line from Γ , where $k = 0$, to K to X , where $k = 1.57 \text{ \AA}^{-1}$ in the bulk Brillouin Zone. At normal emission, $k_{\parallel} = 0$ so that $k = k_{\perp}$. The vertical axis is energy (in eV) relative to the VBM. The bands are labeled by their energy position at the X point starting with the lowest conduction band. For clarity, the odd parity conduction bands are omitted (7, 11, 13, 14, 17, *etc.*) since they do not contribute to the photoemission. Finally, as an aid to using the plots like Figure 45, the photon energy for each transition is noted next to the conduction band point. Knowing the momentum $k_{\perp}$, initial energy E_i , and final energy E_f of the transitions from the previous analysis, it is possible to locate the transitions on a energy band diagram for both clean and antimony-covered samples. The initial and final states for transition family A are plotted as squares for the clean sample and circles for the Sb-covered sample.

A set of three figures like Figures 43, 44, and 45 is presented for each major transition sequence (A through F). Each transition series (A - F) is discussed below for both clean and covered cases.

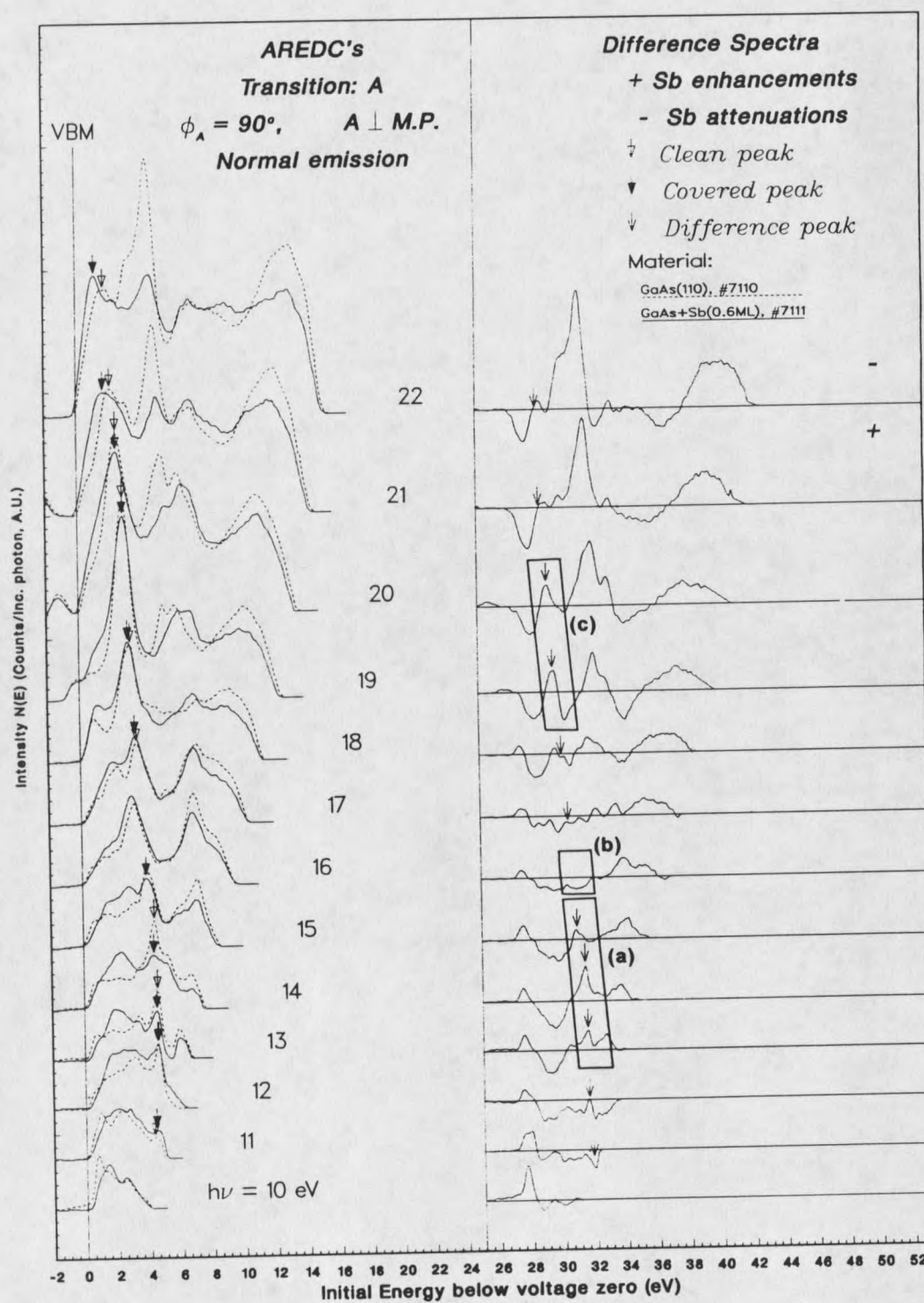


Figure 43. EDC difference spectra, transition A, pol. 90, $h\nu=10-22$ eV. Minor attenuation by the antimony occurs in boxes (a) and (b). The curve at 16 eV is in a hybridization gap.

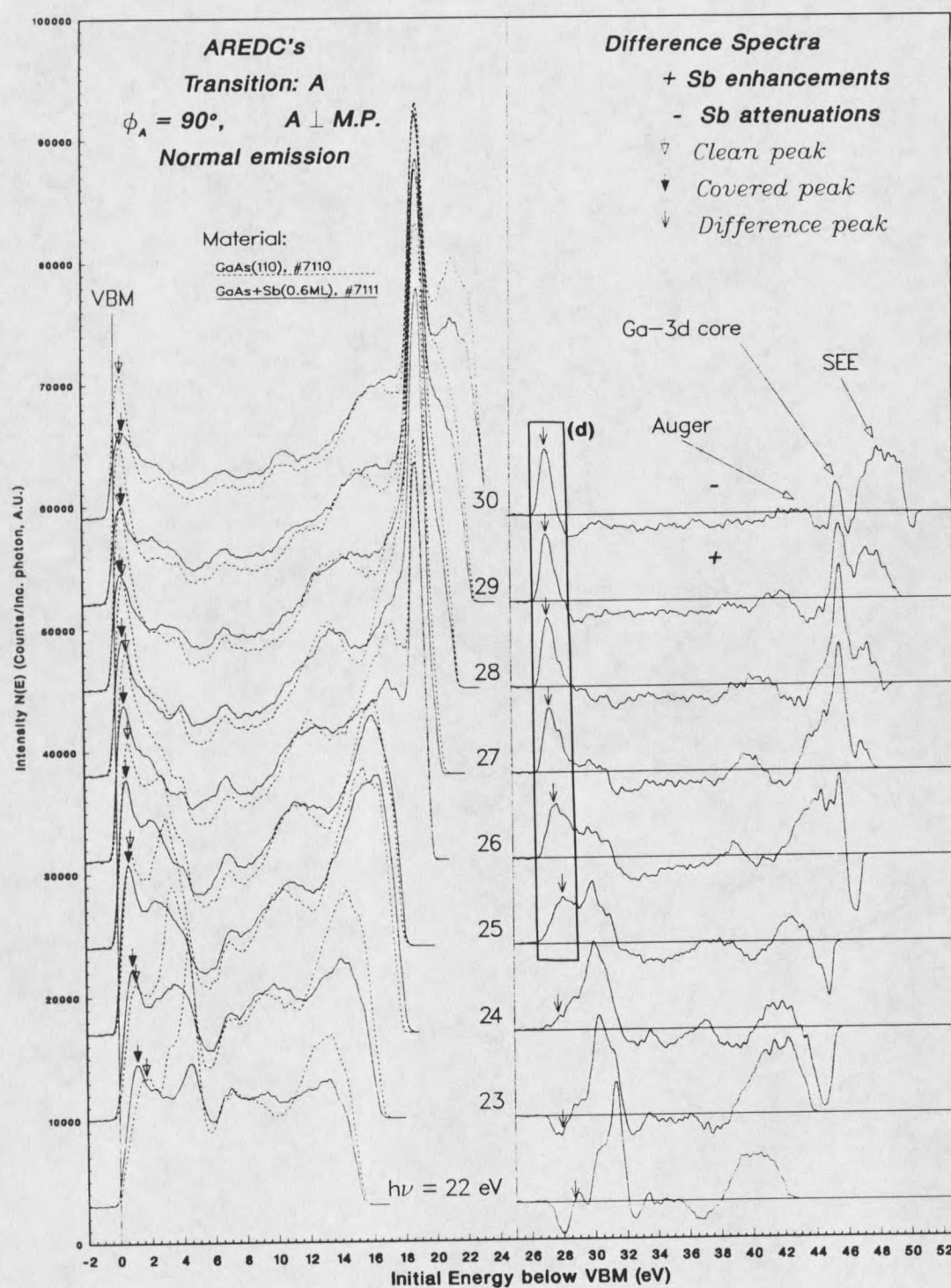
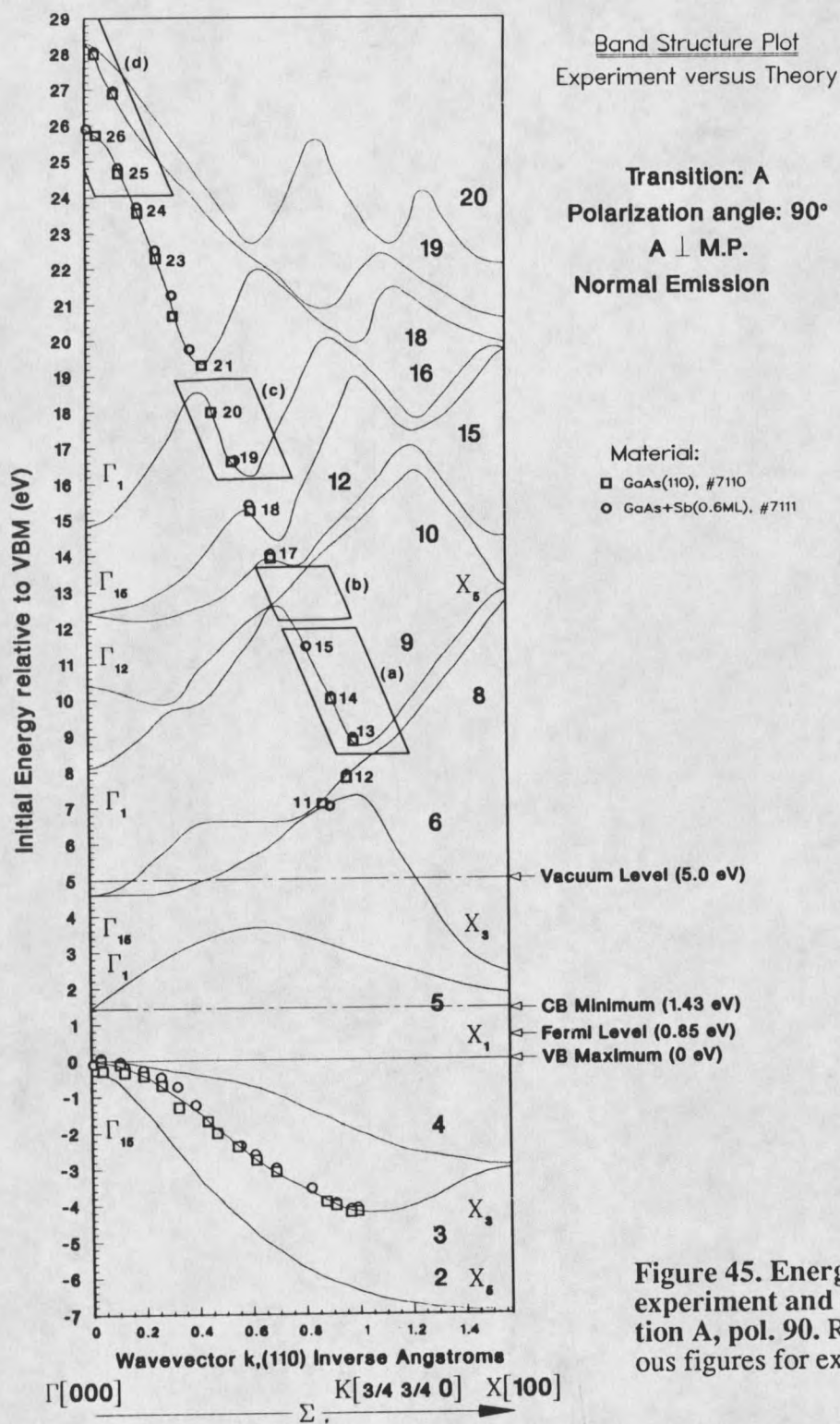


Figure 44. EDC difference spectra, transition A, pol. 90, $h\nu=22-30 \text{ eV}$. Significant attenuation occurs from 25 to 30 eV, box (d), where the initial state approaches the VBM at the BZ center.



Transition A, documented in Figures 43-45, which have already been shown, is the most consistent and well formed sequence of peaks in the normal emission spectra for GaAs(110). The transitions are from VB 3 to the free electron-like conduction band (FE). The initial state starts at Σ_1^{min} and disperses with increasing photon energy towards the VBM at Γ_{15} . The emission from the Γ point of the BZ for photon energies of about 30 eV is consistent with the work of others (Chiang *et al.* 1980, Zurcher *et al.* 1982, and Williams *et al.* 1986).

Interestingly, the Sb overlayer has only a slight effect on transition A. Boxes (a) and (c) in Figure 43 show minor attenuations. Box (b) indicates a hybridization gap near $0.8 \text{ \AA}^{-1}$. As discussed in Chapter 3, the photoabsorption contribution from bulk final states is forbidden in these hybridization gaps; however evanescent final states exist. We note that the Sb overlayer as seen in the difference curves has a very small effect here. The effects of Sb coverage on the amplitude of transition A is shown in Figure 46, which includes the data for polarization azimuthal angles of 0° and 180° . The general trends present in the amplitude curves can be readily understood in terms of joint density of states (JDOS). According to electronic band theory, the JDOS is large if the initial and final bands are parallel or flat and it is small otherwise. Starting at $h\nu = 11 \text{ eV}$, it is seen in Figure 45 that the initial band (VB 3) is not parallel to the final bands (CBs 6 and 8). Correspondingly, the JDOS is small and the resulting peak amplitude shown in Figure 46 is small. Beginning at $h\nu = 13 \text{ eV}$, the CBs move onto the FE band and the valence band disperses towards the BZ center. As transition A approaches the Γ point, the initial band flattens considerably. This increases the JDOS and accounts for the increasing trend of the peak amplitude seen in all the curves of Figure 46.

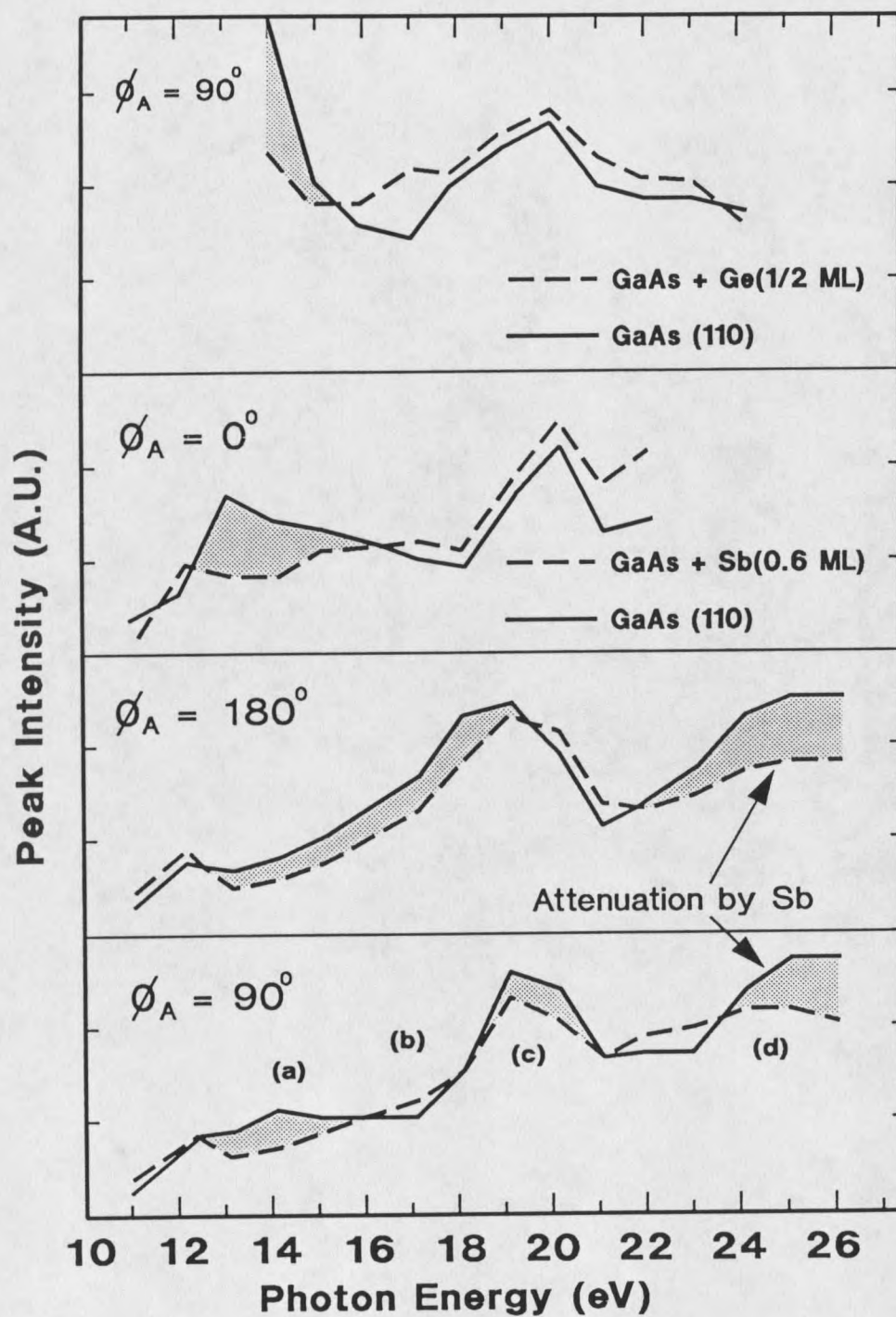


Figure 46. Peak amplitudes of transition A versus light polarization. Comparisons are made for Sb and Ge overlayers (Zurcher *et al.* 1982) on GaAs(110).

The peak amplitude of A from $h\nu = 25$ and 30 eV [region (d)] is attenuated by the Sb, an effect which can be explained by the final states approaching the energy gap at Γ in the CBs. This energy gap is due to Bragg reflection at a Brillouin Zone boundary.

The effects of the Ge overlayer on transition A were examined by studying the data from Zurcher *et al.* (1982). The results are shown in the top panel in Figure 46 where it is seen to have a behavior similar to the Sb case. The photon flux was measured in a different manner for the Sb data and this is probably the reason that the curves for the clean surface have slightly different shape.

The results for transition B are shown in Figures 47 through 50. Here, electrons have been excited from valence band 2 to the free electron-like band (FE), which includes CBs 10 through 20. The clean peak first becomes noticeable around 17 eV (Figure 47), increases in amplitude until about 24 eV, where it diminishes rapidly and becomes dispersionless (Figure 41) as it approaches the Γ_{15} point. Chiang *et al.* report a peak at the same energy as B, but they attribute it to VB emission of band 3 and 4 at the X point. Although there is a large DOS here, which is indicative of the flat bands in this region, analysis shows this transition originates closer to the center of the BZ.

At all photon energies, transition B is affected by the Sb as much as any other peak in the dataset. This can be confirmed either by looking at the difference spectra marked with arrows in Figures 47 and 48 and amplitude plots in Figure 50. Note that, the clean peak is totally eliminated at 18 and 19 eV. This occurs in a region of hybridization gaps, box (e) in Figure 49, where band gap photoemission (see Figure 9) governs the weaker peak and its sensitivity to the addition of a fractional monolayer of foreign atoms.

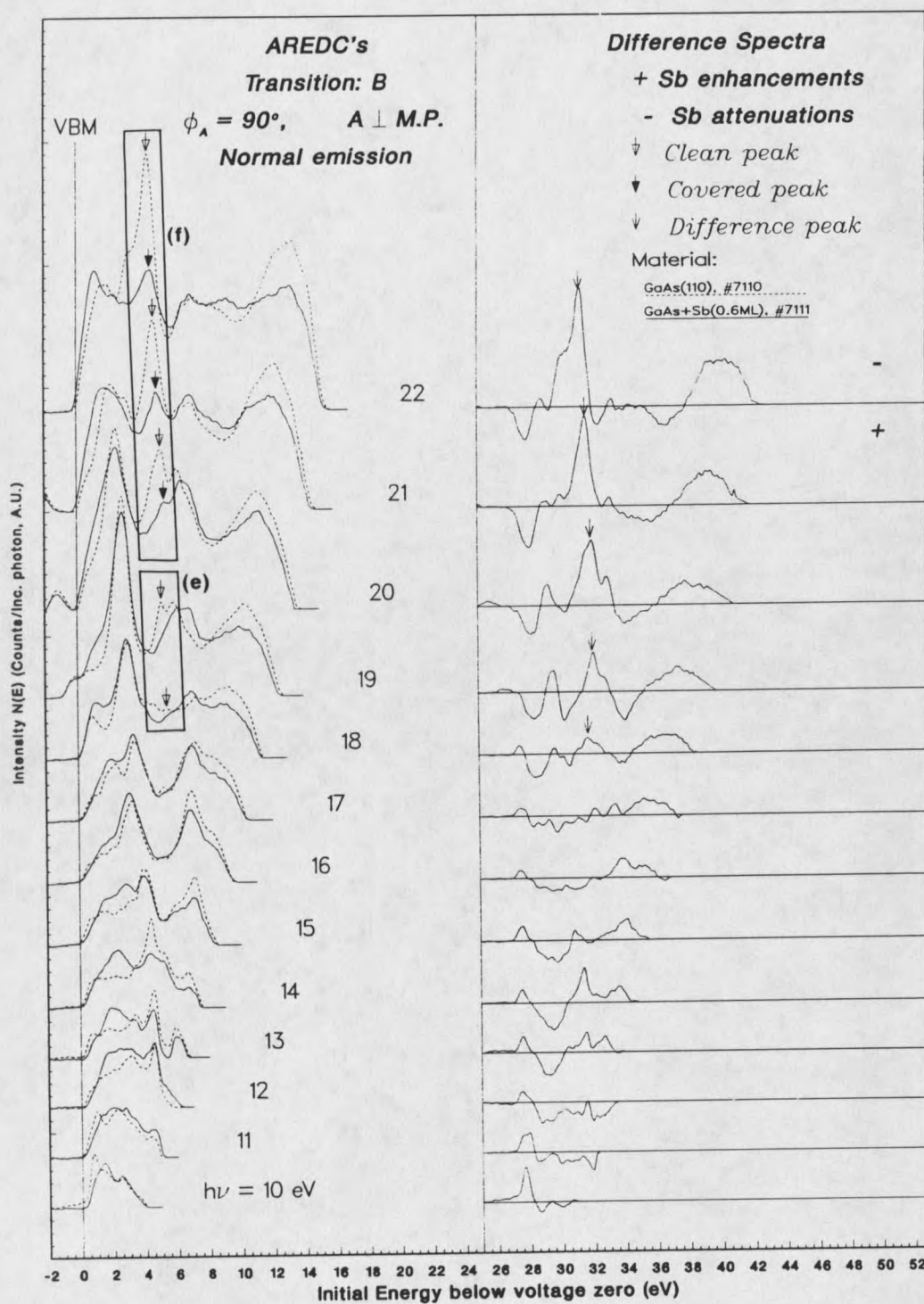


Figure 47. EDC difference spectra, transition B, pol. 90, $h\nu=10-22$ eV. Evanescent vanishing of clean peaks in region (e). Significant attenuation by Sb occurs in box (f).

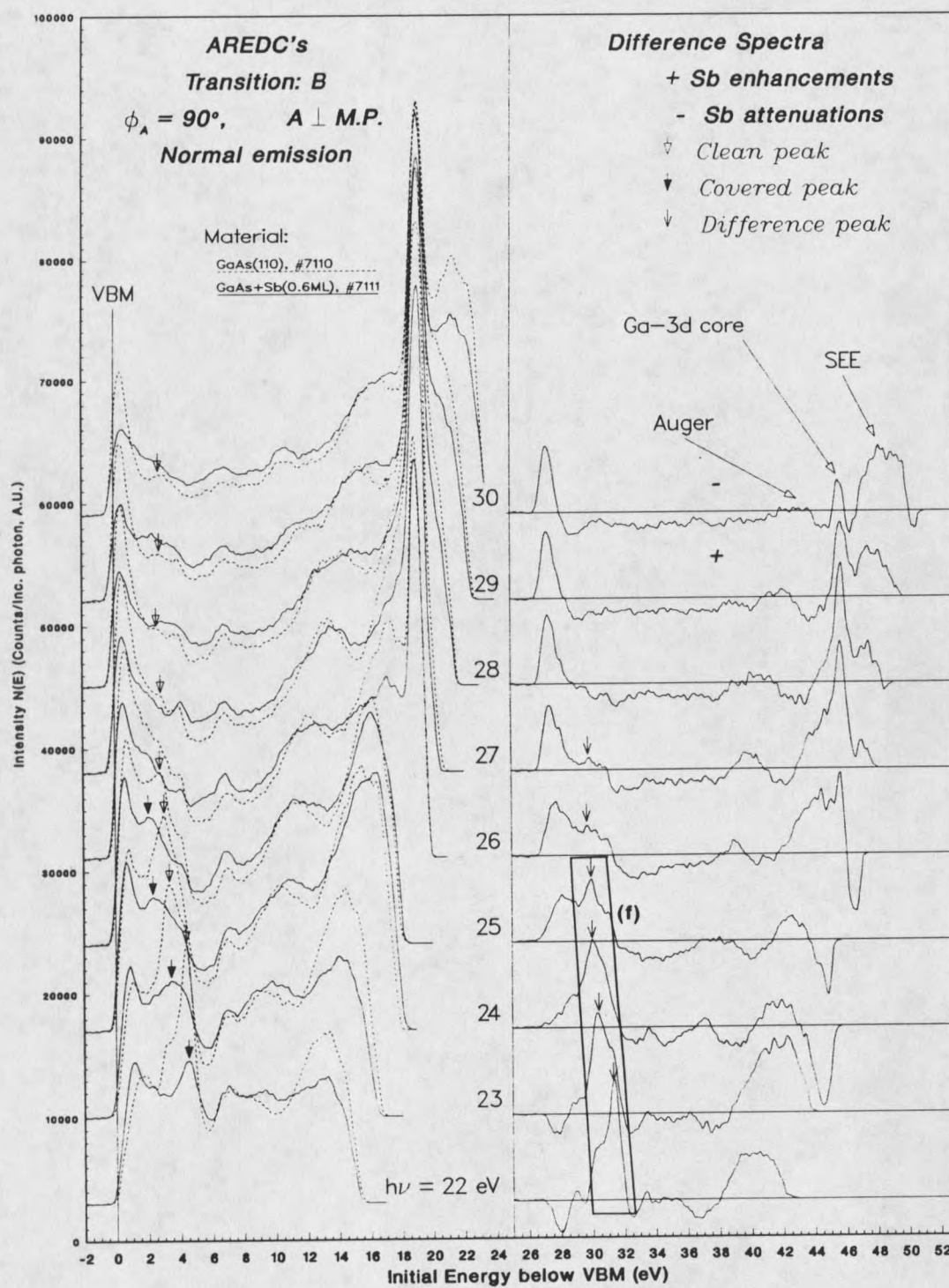
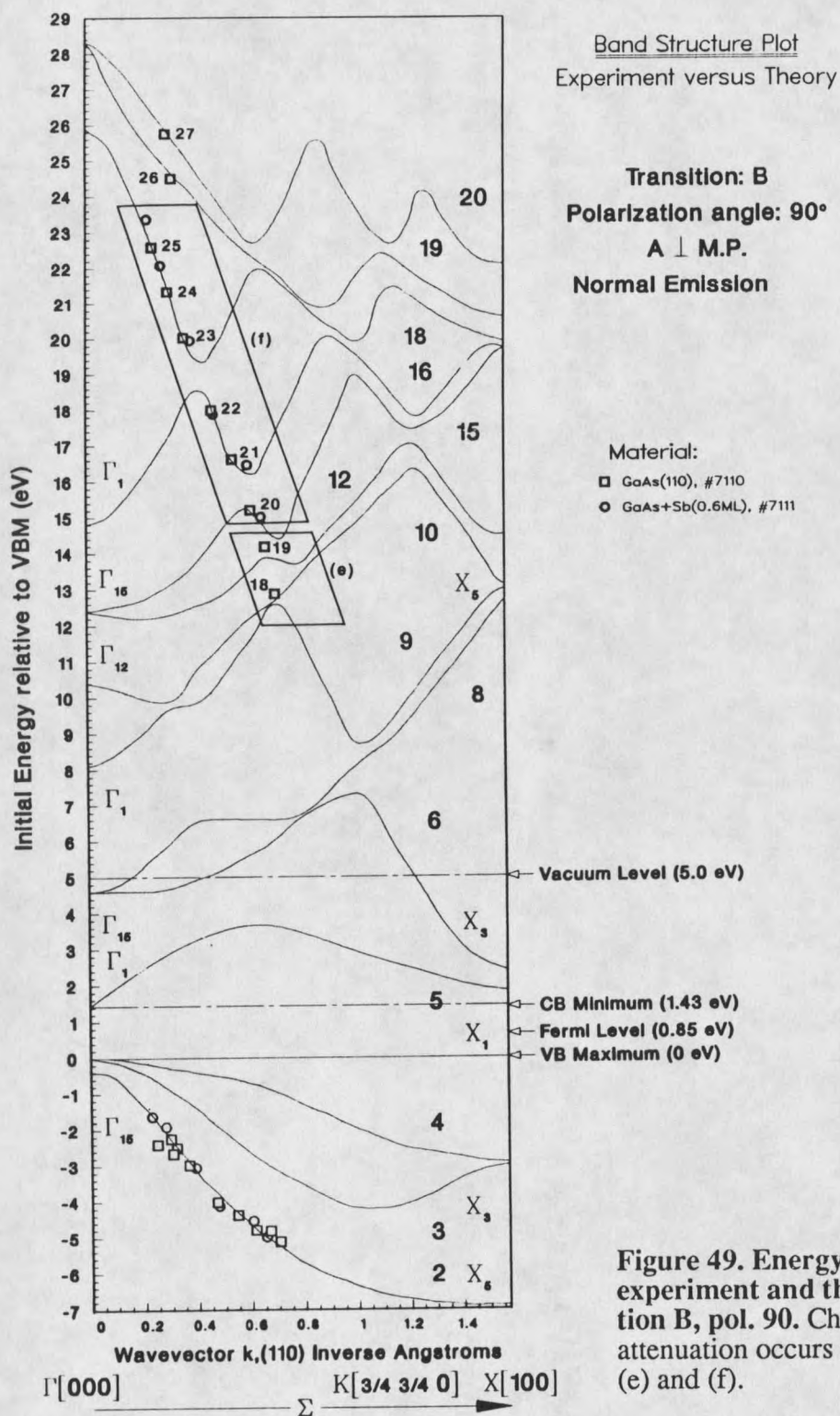


Figure 48. EDC difference spectra, transition B, pol. 90, $h\nu=22-30 \text{ eV}$. Significant attenuation by antimony overlayer occurs for peaks in region (f).



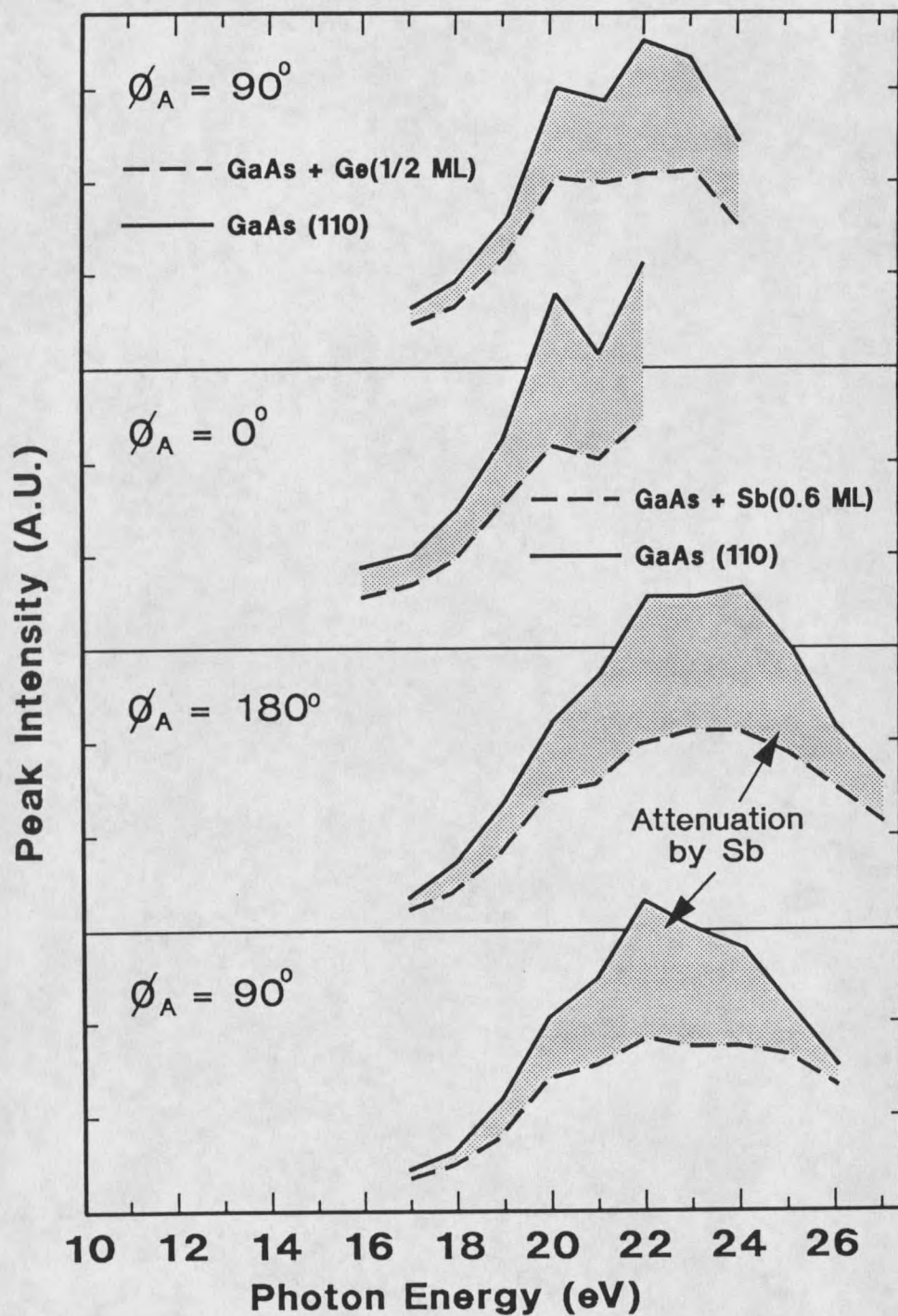


Figure 50. Peak amplitudes of transition B versus light polarization. Comparison of peak amplitudes of transition B for Sb and Ge overlayers (Zurcher *et al.* 1982) on GaAs(110).

The strong attenuation of transition B is a significant discovery which we term the "characteristic amplitude" effect, because it also corresponds to a bulk band transition by virtue of its strong $k_{\perp}$ dependence. Normally, surface-related phenomena and bulk band transitions are considered to be mutually exclusive; yet B shows a dominant effect from the presence of an ordered overlayer. The dramatic differences in the effect which the antimony overlayer has on transition A versus transition B is significant. As we saw, transition A was marginally altered by the overlayer (Figure 46) whereas B showed some of the most extreme overlayer-induced effects in this measurement (Figure 50). Since both transitions have common final states (FE band), the transport and escape steps in the photoemission process ought to be the same. The only difference may occur in the photoabsorption step. Here the dipole matrix element operator will have the same final states, leaving only the initial states which could contain the differences we observe. Therefore we attribute this to an initial band effect. The reason for this behavior is unknown at present. Since this phenomenon occurs in the bulk band photoemission (Figure 9) regime where surface-related effects ought to be minimal, it is difficult to understand the mechanism which drives this overlayer induced attenuation effect.

The behavior of transition B regarding germanium overlayers was examined in Zurcher's data. The results, contained the top panel of Figure 50 indicate a large attenuation due to the overlayer, in agreement with the antimony experiments. Hence this result suggests that the characteristic amplitude effect is more determined by the substrate, *i.e.*, GaAs, bonded with an ordered overlayer, then with specific aspects of the overlayer atom. In fact, the two overlayer atoms are quite different; germanium is a column IV semiconductor, while antimony is a column V semimetal.

The results for transition C are shown in Figures 51 through 53. Like transition B, peak C originates from VB 2. However, instead of final states in the free electron (FE) band as with B, the photoabsorption final state for C is contained on CBs 9, 10 and 12 (Figure 53). As the photon energy increases, the initial state for peak C disperses towards the X_5 critical point in both the structure plot (Figure 41) and the energy band diagram (Figure 53). This feature merges with other VB 2 transitions, *viz.*, transition D around $h\nu = 24$ eV and transition B around $h\nu = 18$ eV. The most significant effect caused by the Sb overlayer occurs from $h\nu = 17$ to 19 eV, outlined by box (g) in Figures 41, 51, and 53. This latter transition occurs in the same part of k -space where transition B was attenuated by the overlayer. Band 10 passes through the hybridization gap of the free electron band and according to the discussion of the one-step model in Chapter 3, the final state wavefunction will have a large admixture from evanescent wavefunctions. This is the component of the signal which is attenuated by the overlayer. This is seen clearly for the polarization where $\phi_A = 0^\circ$ shown in Figure 81. For $h\nu = 16$ to $h\nu = 18$ eV, peak C is almost entirely eliminated, suggesting that in this region the final state wave function is almost entirely evanescent, with little contribution from the bulk component.

The results for transition D are shown in Figures 54 through 56. While the energetics clearly indicate the initial states are from valence band 2, the CB assignments are less obvious than the VB assignments since the VBs have very weak dispersion. The analysis shown in Figure 56 and the structure plots of Figures 41 and 42 support the two qualitatively different behaviors of transition D below and above $h\nu = 19$ eV. The data for $\phi_A = 0^\circ$ and $\phi_A = 180^\circ$ also support this disparity (see Figures 85 and 104 in Appendices). For photon energies up to about 19 eV, we see weak energy dispersion which corresponds to transitions from VB 2 to CBs 8 and 9.

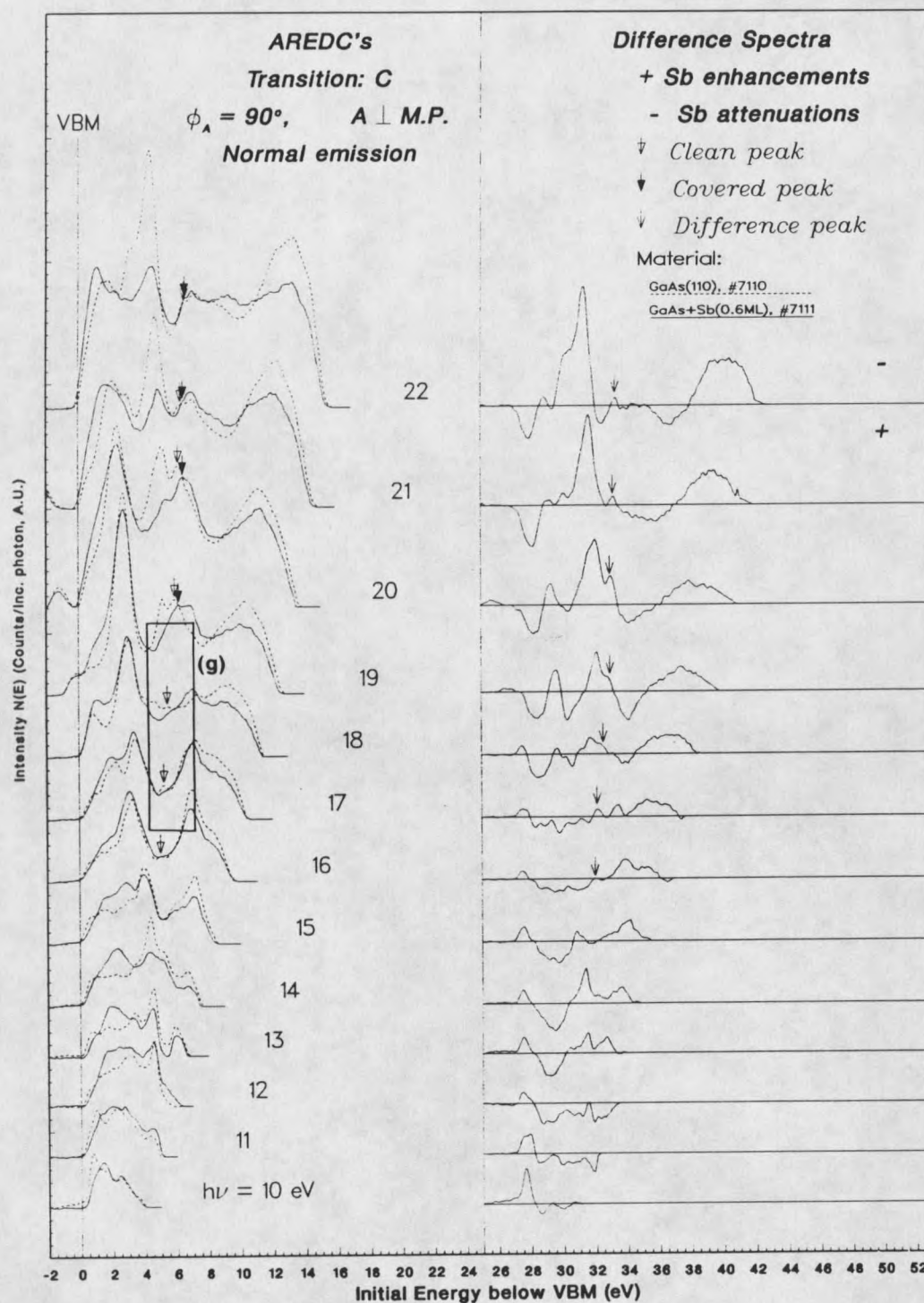


Figure 51. EDC difference spectra, transition C, pol. 90, $h\nu=10-22$ eV. Evanescent vanishing of clean peak occurs in major hybridization gap [i.e., box (g)].

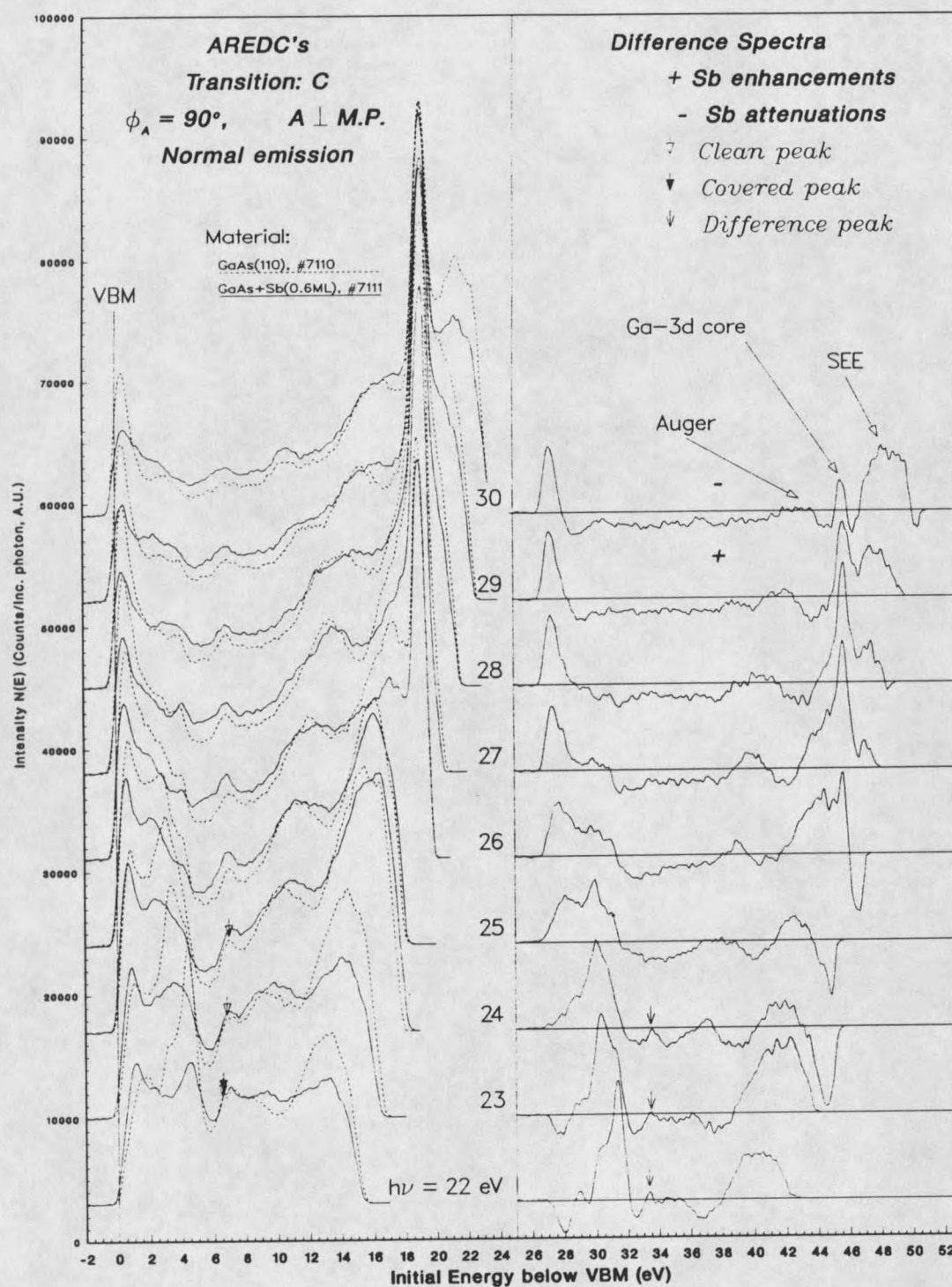


Figure 52. EDC difference spectra, transition C, pol. 90, $h\nu=22-30 \text{ eV}$. No modification of clean peaks occurs in this region. Here transition C merges with transition D.

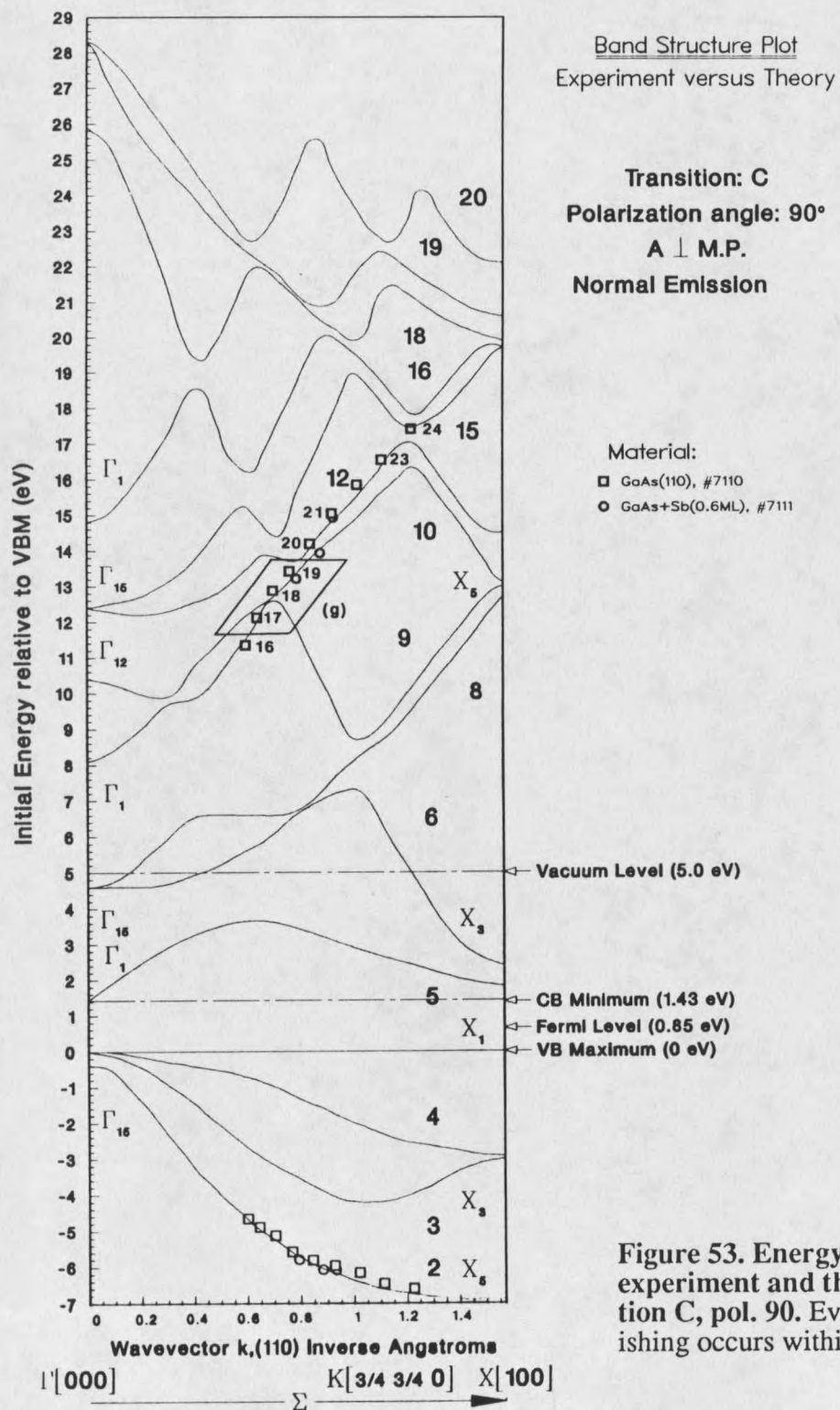


Figure 53. Energy bands of experiment and theory, transition C, pol. 90. Evanescent vanishing occurs within region (g).

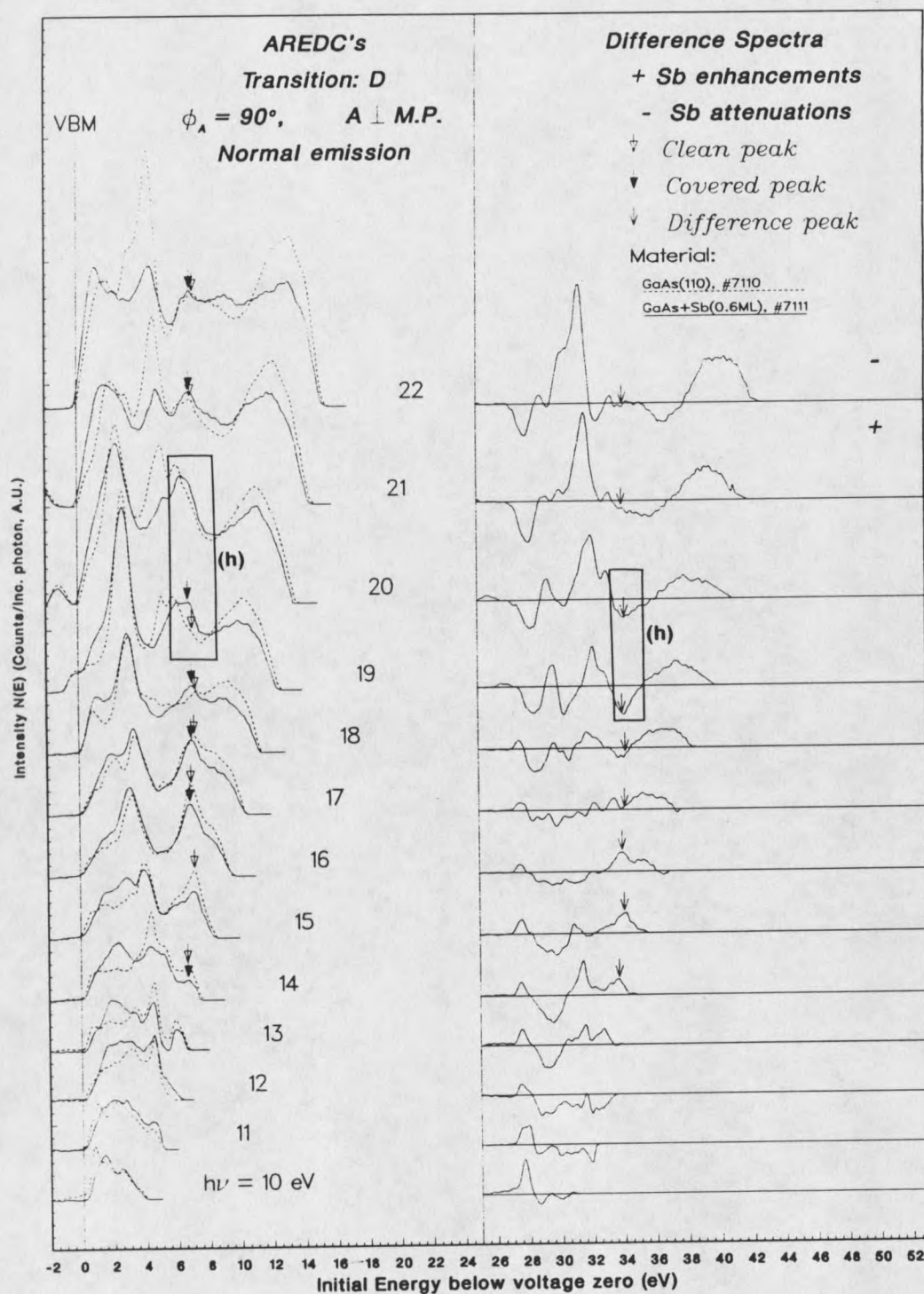


Figure 54. EDC difference spectra, transition D, pol. 90, $h\nu=10-22$ eV. Evanescent enhancement occurs within region (h) for hybridization gap between CBs 9 and 10 (See Figure 49).

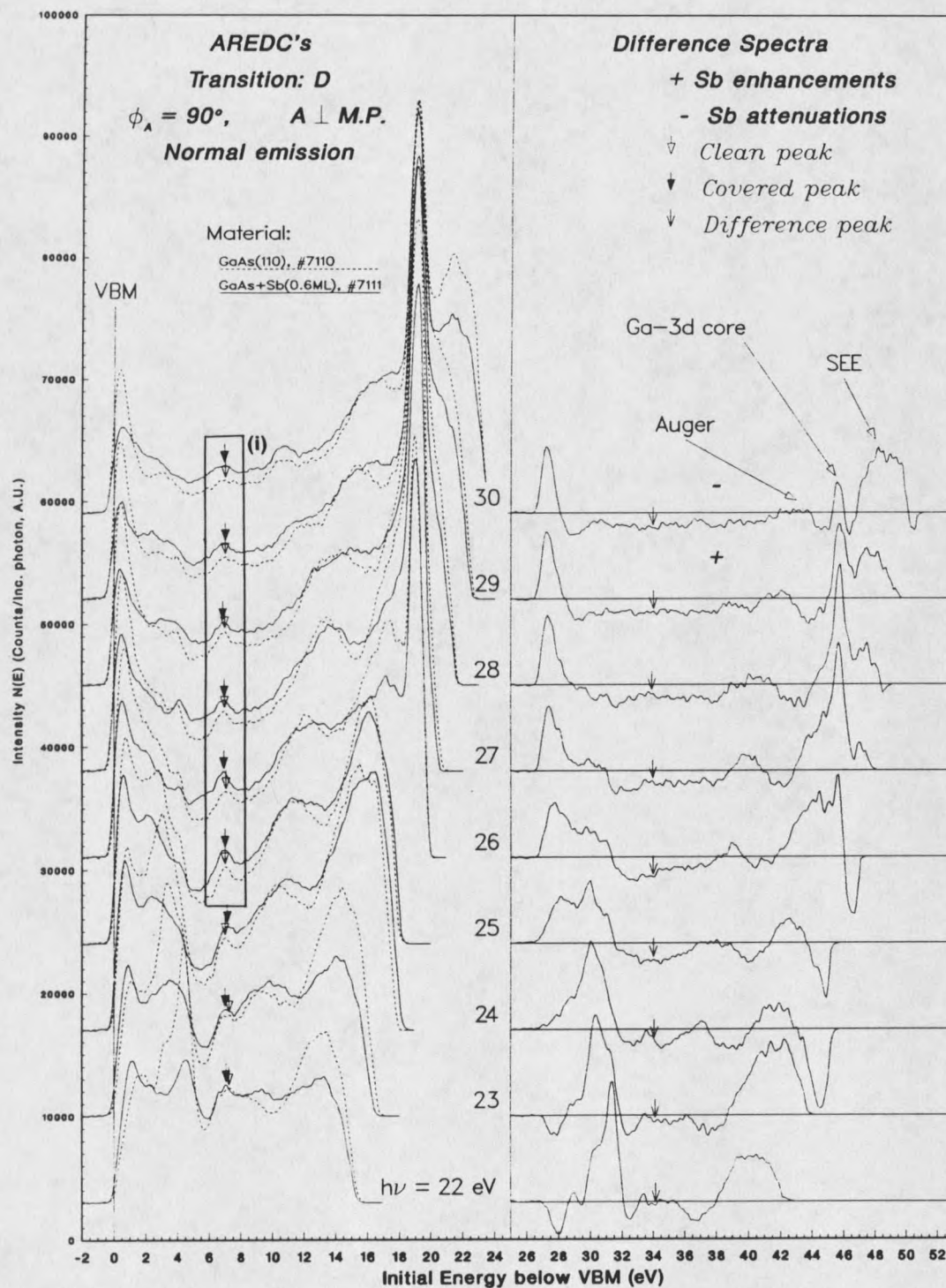


Figure 55. EDC difference spectra, transition D, pol. 90, $h\nu=22-30 \text{ eV}$. No significant amplitude modification or shifting occurs in this region.

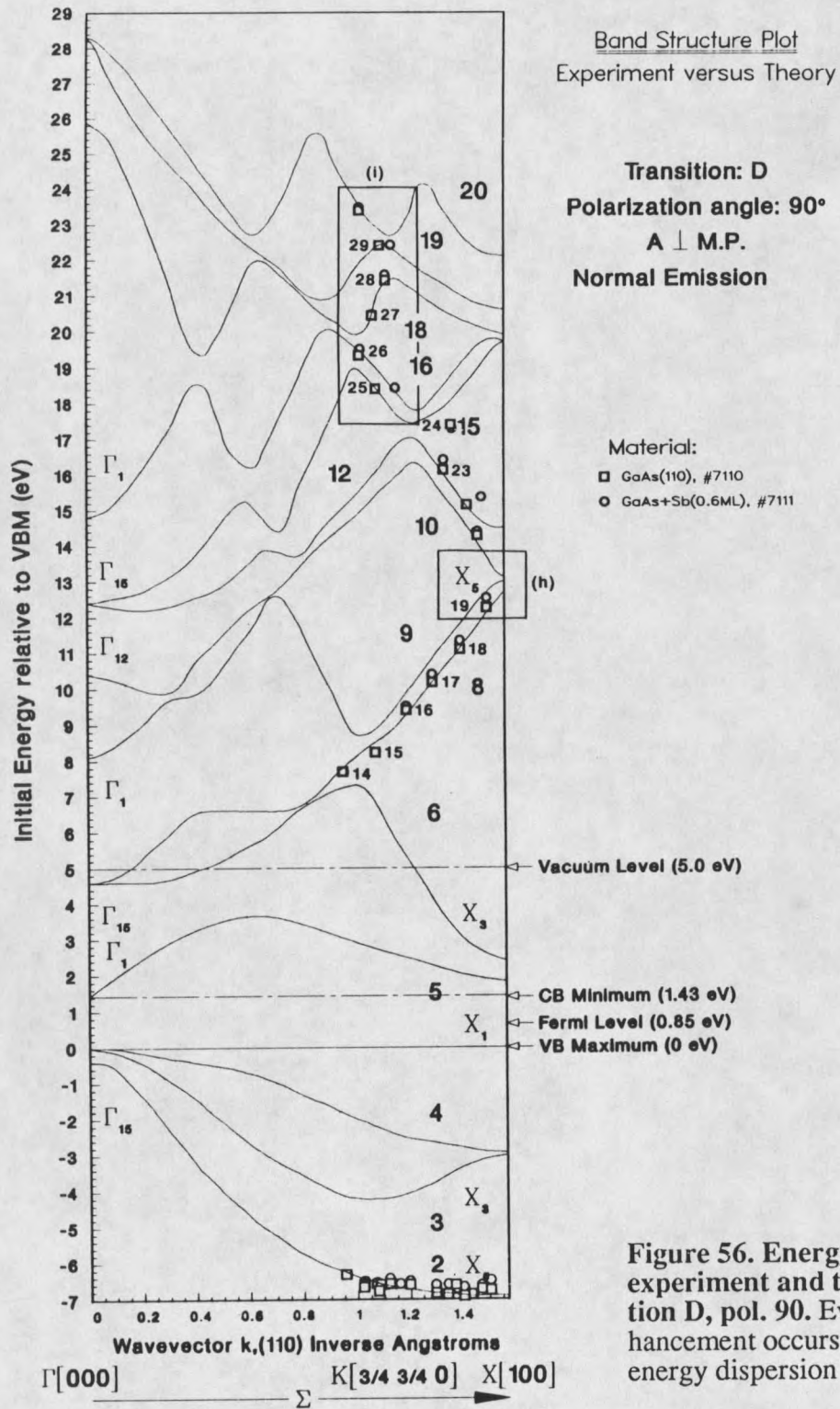


Figure 56. Energy bands of experiment and theory, transition D, pol. 90. Evanescent enhancement occurs in box (h). No energy dispersion in box (i).

For photon energies starting around 20 eV, the initial energies are very constant. This can be best seen in the structure plots of Figures 41, 73, and 91. After directly applying the bandmapping procedure, we obtain the results shown in box (i) of Figure 56. The vertical nature of the dispersion in the energy band diagram suggests that this transition is not a bulk band-like state, but rather could have surface resonance character. The antimony overlayer does not have a significant effect on either the energy position or peak amplitude of transition D. In the case of the germanium overlayer, Zurcher *et al.* (1982), report an enhancement in this region and suggest that the enhancement is a interface state. Band calculations do, in fact, place surface states in this region for the clean GaAs sample as well as the Sb and Ge overlayer systems.

The strongest effects resulting from the Sb overlayer are seen at $h\nu = 19$ and 20 eV [see box (h)] where the transitions are essentially at the X point of the Brillouin Zone. Here we see an amplitude enhancement due to the presence of the Sb overlayer. This is clearly shown in box (h) of Figure 54. To avoid possible confusion of closely lying peaks, the reader is reminded that the clean peak on the left-hand side of box (h) for $h\nu = 19$ and 20 eV is assigned to transition C which was previously discussed and marked in Figure 51.

Separation of transitions into sequences B, C, and D is based on trends seen in the final CB states, since all of these transitions originate from the same initial band, *i.e.*, VB 2. Together these three transitions account for almost the entire Σ -line ($0.2 \text{ \AA}^{-1}$ to $1.57 \text{ \AA}^{-1}$) along valence band 2. Apart from the unique behavior noted in box (i) of Figure 56, the various CBs fall along the FE-band and also along the "diamond" shaped region made up of CBs 9 and 10.

The antimony data as well as the germanium data (Zurcher *et al.* 1982) reveal a dispersionless transition called E, located near the valence band maximum for photon energies from 10 to 18 eV (Figures 57 and 58). The right-hand panel of difference curves indicate that the peak is uniformly attenuated by the addition of the antimony overlayer. Zurcher *et al.* observed a shifting of the structure in the GaAs+Ge data rather than an elimination of the peak. Figure 58 shows the peculiar nature of this state in region (j) on the energy band diagram. Rather than disperse along conduction band branches as do most of the other transitions we have examined, E "climbs across" the conduction bands from 10 to 16 eV, showing very little energy dispersion. This sort of dispersion behavior was just noted in the discussion of transition D. At a photon energy of about 17 eV, sequence E takes on dispersion characteristics of bulk band transitions and follows along the free electron (FE) band.

The sensitivity of this feature to the presence of a foreign atom (*i.e.*, germanium or antimony) coupled with its dispersionless nature from 10 to 18 eV, strongly suggests that feature E, in these circumstances, is a surface resonance of the atomically clean GaAs crystal, at least up until $h\nu = 18$ eV. At photon energies above 16 eV, the feature is a result of a VB 4 to free electron (FE) conduction band transition. Examination of the structure plots shows dispersion. It is very difficult to differentiate in the EDC spectra peaks E and A, since excitations from VBs 3 and 4 near the Γ -point are almost energy degenerate. The data for the other polarizations, supports this interpretation (see Figures 86 and 105).

The F sequence of peaks occurs at the low photon energy end of the suite of EDC spectra and is seen in Figure 59. The band assignments were made in a similar manner to the transitions discussed above and the results are displayed in Figure 60.

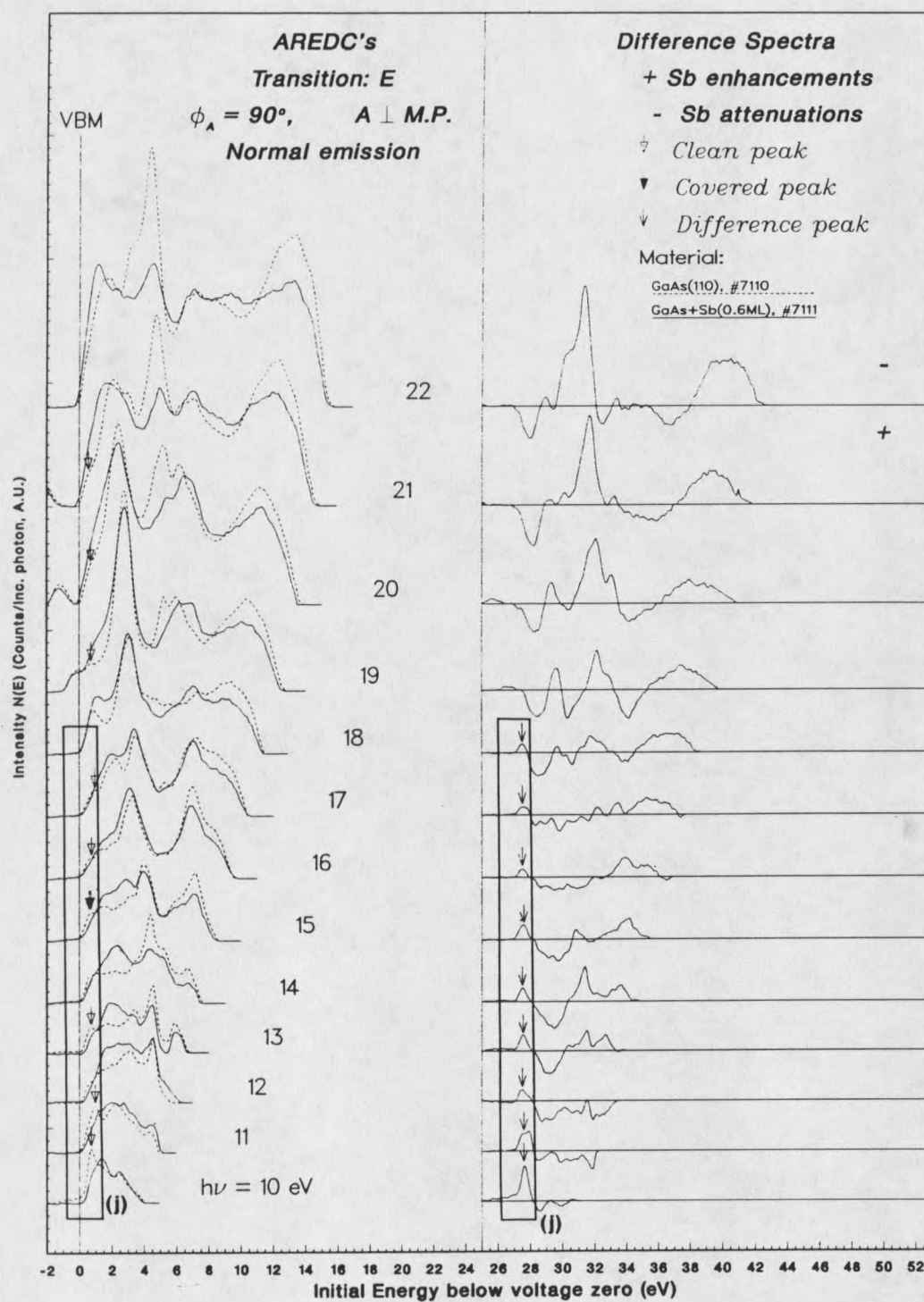


Figure 57. EDC difference spectra, transition E, pol. 90, $h\nu=10-22$ eV. This transition is dramatically attenuated by Sb overlayer. It is possibly a clean surface state.

Band Structure Plot

Experiment versus Theory

Transition: E
Polarization angle: 90°
A ⊥ M.P.
Normal Emission

Material:

- GaAs(110), #7110
- GaAs+Sb(0.6ML), #7111

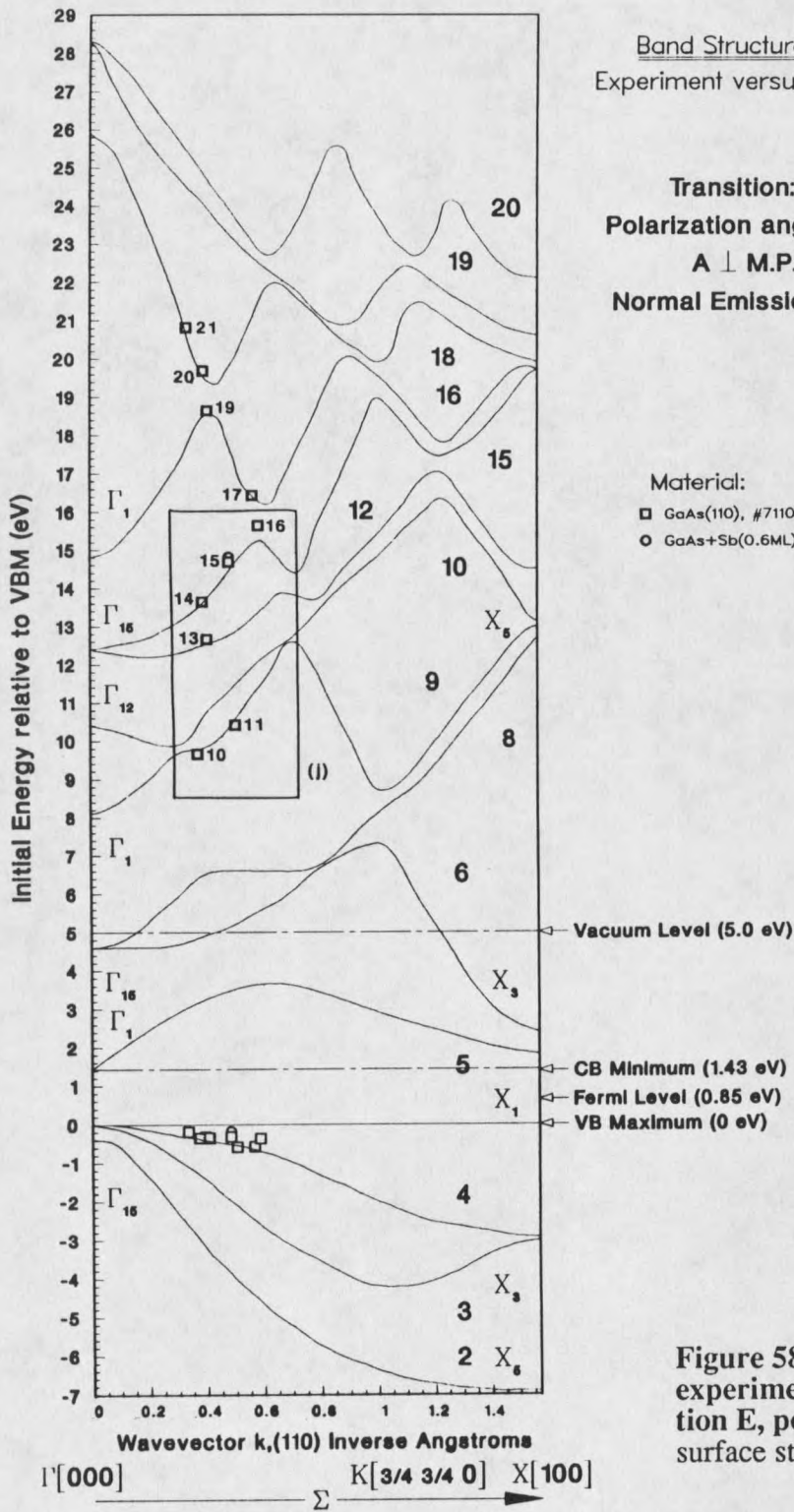


Figure 58. Energy bands of experiment and theory, transition E, pol. 90. This is a clean surface state below $h\nu = 16$ eV.

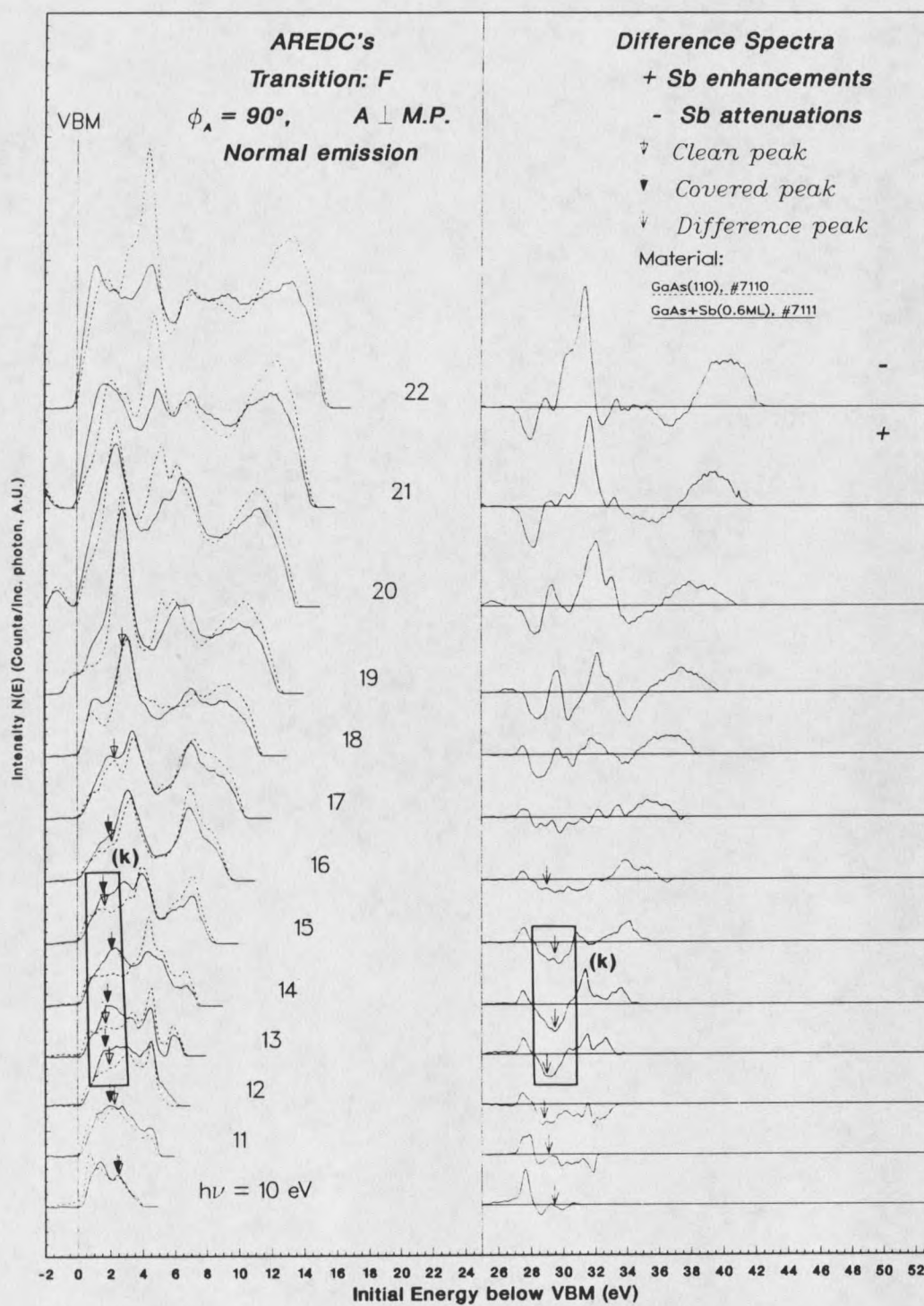


Figure 59. EDC difference spectra, transition F, pol. 90, $h\nu=10-22$ eV. Evanescent enhancement occurs within region (k) for hybridization gap between CBs 9 and 10.

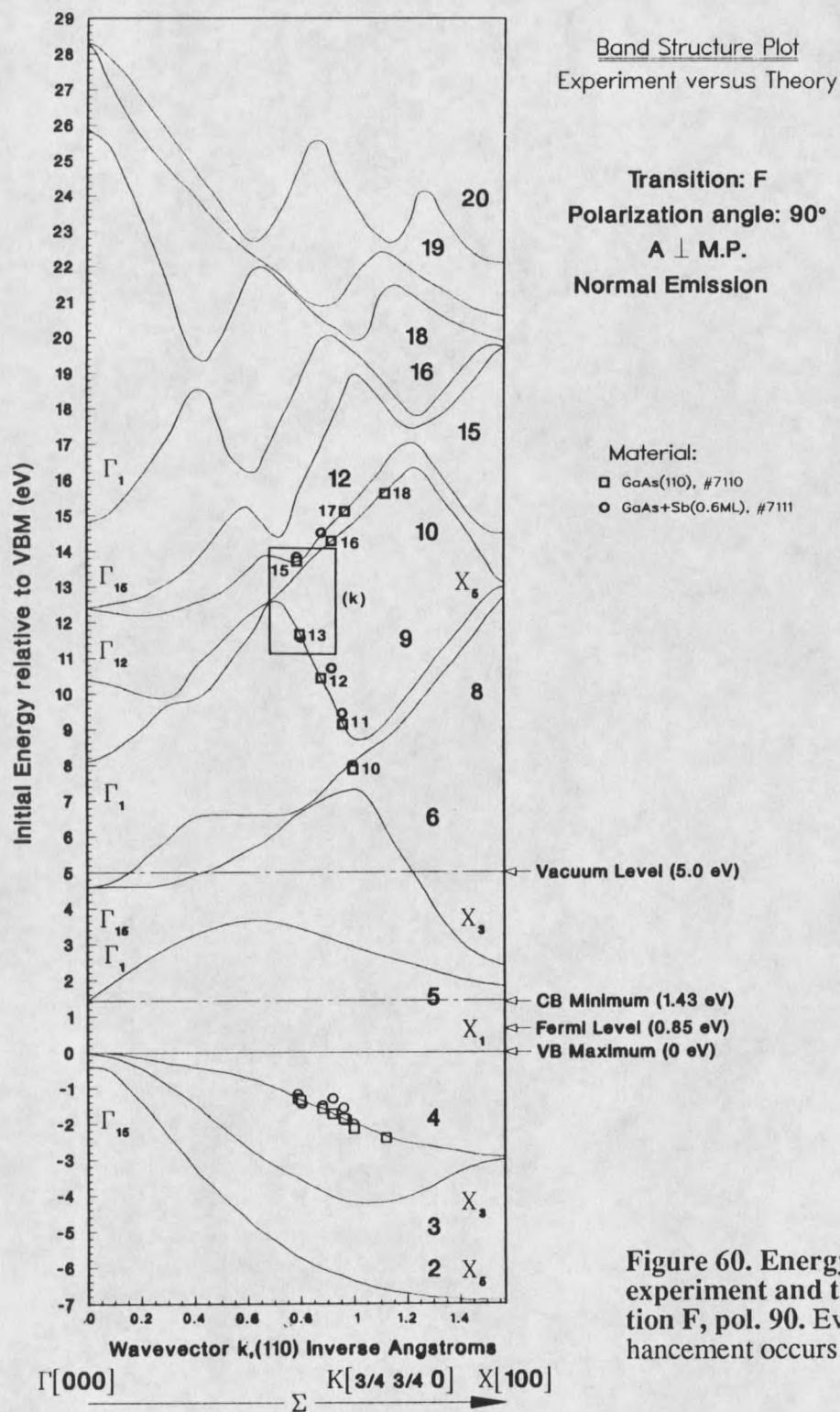


Figure 60. Energy bands of experiment and theory, transition F, pol. 90. Evanescent enhancement occurs in box (k).

Two distinct types of behavior are seen in this feature. First, the peaks for which $h\nu < 14$ eV correspond to transitions from VB 4 to the free electron CB, and would be associated with the high energy (*i.e.*, $h\nu > 16$ eV) transition regime of sequence E. Second, the peaks above a photon energy of 14 eV are connected with transitions from VB 4 to final states 10 and 12. This is similar to the transitions $2 \rightarrow 10,12$ as in transition sequence C. This conduction band dichotomy at $h\nu = 14$ eV exists for the other polarizations ($\phi_A = 0^\circ$ and $\phi_A = 180^\circ$) in Figures 90 and 110.

The complex character of peak sequence F seen in all the polarizations (Figures 60, 89, and 108) suggests that it could be a composite peak made up of several individual peak sequences. Even if it is possible to separate these components, rigorous curve fitting algorithms are required. However, without such extended efforts, we can still see the strong peak enhancement in all polarizations, in the vicinity of $h\nu = 14$ eV. This corresponds to box (k) shown in Figure 60.

It is interesting that the CB region contained in box (k) is the same region as in box (g) of Figure 53 for transition C. Transition C originated from VB 2, as opposed to sequence F which has initial states in VB 4. Both transitions are located near *K*-point of the Brillouin Zone. Here we have a situation analogous to the initial state effect seen in the transitions A and B which was discussed earlier in this section. Moreover, this situation occurs, not on the free electron band like in sequences A and B, but in the central hybridization gap of the FE-band [boxes (g) and (k)].

We have examined transitions from each of the VBs into the FE-band hybridization gap region at a momentum value of $0.7 \text{ \AA}^{-1}$ and initial energy 12 to 14 eV. These include transition C from VB 2, transition A from VB 3 and transition F from VB 4. The effects of the antimony overlayer are particularly strong in this region of the energy

band structure. We saw a characteristic amplitude attenuation in bulk band sequence C and a characteristic amplitude enhancement in bulk band transition F. Contrary to this, transition sequence A was unchanged by the antimony. Therefore it is not sufficient to have just the final conduction band state residing in a hybridization gap in order to predict the effect which an overlayer atoms will have on the bulk band transitions. The observations made with this dataset ($\phi_A = 90^\circ$), in conjunction with the other polarizations angles ($\phi_A = 0^\circ$ and $\phi_A = 180^\circ$), indicate that the nature of the initial state also plays an important role.

Two features in the EDC spectra (*e.g.*, Figure 44) occur at a constant kinetic energy. Hence when their initial energy is plotted against photon energy they move, by one eV increments, directly with the photon energy. Therefore, they are not interband transitions, but are due to structures in the secondary electron emission (SEE) and Auger emission related to the Ga-3d core hole, frequently labeled M_4VV .

The secondary electron emission (SEE) feature is easily seen in the direct EDCs and difference spectra from $h\nu = 16$ to 30 eV (see Figures 42 and 43). Electrons from this feature have a kinetic energy of 4 eV. This feature was reported in the GaAs+Ge study by Zurcher *et al.* (1982). As they show, the feature cannot be an Auger transition, since it occurs at photon energies below the core hole threshold for the Ga-3d core. It was attributed to a structure in the secondary electron emission resulting from a high density of empty states, which in turn is attributed to an empty surface state on the arsenic atom 8.9 eV above the valence band maximum (Zurcher *et al.* 1982). That structure is attenuated by the overlayer much more than the gallium Auger transition making it easily seen in the difference spectra. It is not polarization dependent and the sensitivity to antimony overlayers supports its surface-related nature.

The gallium Auger transition, which is a M_4VV sequence on the gallium atom, is a broad feature occurring with $E_k = 9$ eV. This results in an initial energy $E_i = -16.7$ eV in the EDC where $h\nu = 30$ eV. This transition is slightly attenuated by the antimony chemisorption, but the shape of the feature changes in a complicated fashion. It is best seen from $h\nu = 30$ eV down to 21 eV. Since the Auger mechanism involves the valence bands, it is not surprising that the Auger lineshape would change. This could be accounted for by charge transfer associated with the antimony bonding. This transition is not polarization sensitive as one would expect.

Comparison of Sb and Ge overlayers on GaAs(110)

In addition to the clean GaAs(110) data, Zurcher *et al.* (1982) performed PARUPS at normal emission on GaAs(110)+Ge(1/2-ML) and observed generally similar behavior as we did with GaAs(110)+Sb(0.6 ML).

We begin by looking at the case where $\phi_A = 90^\circ$ and $h\nu = 15$ eV shown in Figure 61. Here both the antimony (panel a) and the germanium (panel b) EDC spectra have been plotted with respect to the VBM. Both show the three prominent clean peaks E, A, and D. The smaller features, F and H are not well resolved in the germanium data. Similar changes are seen after overlayer formation in that the modification of peak D is the same for both the Sb and Ge overlayers, resulting in the new emission seen between 1 and 3 eV initial energy.

Data obtained at a photon energy of 18 eV with the same azimuthal polarization angle are also similar (Figure 62). Both systems show four clean features (E, A, B, and SEE).

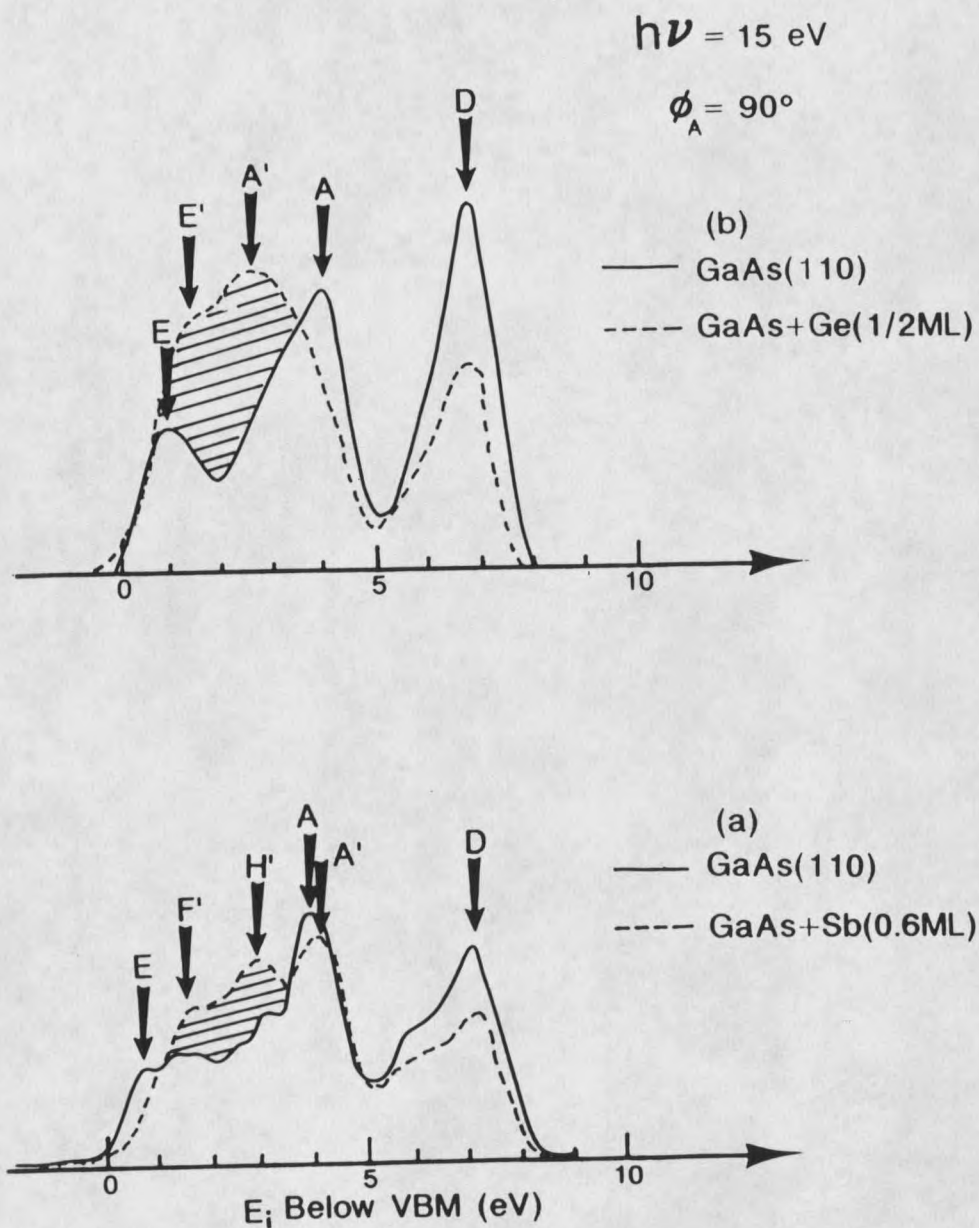


Figure 61. Sb and Ge overlayers on GaAs for polarization 90, $h\nu = 15 \text{ eV}$. GaAs+Ge was obtained by Zurcher *et al.* (1982). Much similarity between the effects of Ge and of Sb on clean features is noted.

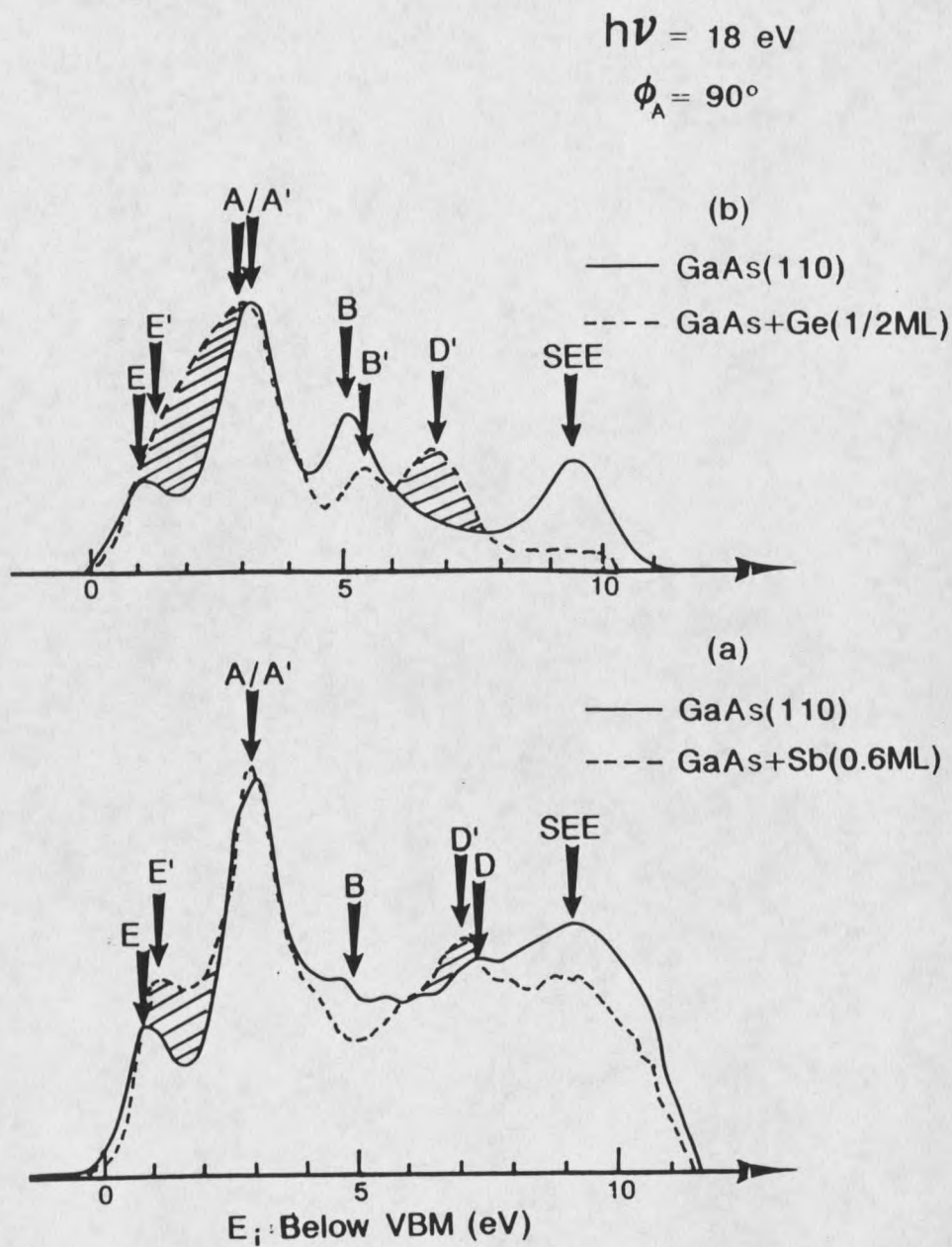


Figure 62. Sb and Ge overlayers on GaAs for polarization 90, $h\nu = 18 \text{ eV}$. GaAs+Ge was obtained by Zurcher *et al.* (1982). Here peak D', which Zurcher reports as an interface state is in close agreement with enhanced bulk feature D for GaAs+Sb.

However, B is not as well formed in the antimony data as in the germanium data and the clean peak D in germanium seems to be gone altogether. After overlayer formation, enhanced emission occurs between 1 and 3 eV and peak D' appears.

Figures 63 and 64 contain spectra at the same photon energies as we have just seen, but for a polarization where $A//MP$, *i.e.*, $\phi_A = 0^\circ$. When $h\nu = 15$ eV, the EDC spectra obtained are shown in Figure 63. Here four clean features occur in both systems. They are labeled as E, F, A, and D; peaks E and F are seen more clearly in the antimony data and this is probably due to the inherently higher resolution in the antimony data. Generally, clean peaks (solid curves) coincide, but complex enhancement occurs in the initial energy range from 0 to 4 eV for the overlayer samples. At larger initial energies, the two systems agree well. For germanium, peak E is shifted and enhanced to become E', whereas for the antimony covered sample, it is peak F which is shifted and enhanced, while peak E disappears.

Finally, Figure 64 shows the comparison for 18 eV and same polarization as seen in Figure 63. Once again, peak E is better formed and closer to the VBM for antimony than germanium, but the other clean peaks correlate quite well (*viz.*, A, B, and SEE). Relative amplitudes are also rather similar, except for the SEE peak. This discrepancy is due in part, to different model curves used for secondary electron background subtraction. After overlayer formation, new emission occurs towards the VBM in both Sb and Ge, but the new peak D' seen in Sb is not observed in Ge.

Overall, antimony and germanium induced changes in the GaAs EDC spectra are similar in character and magnitude. In other words, the similarities of the effects are more dominant than the differences.

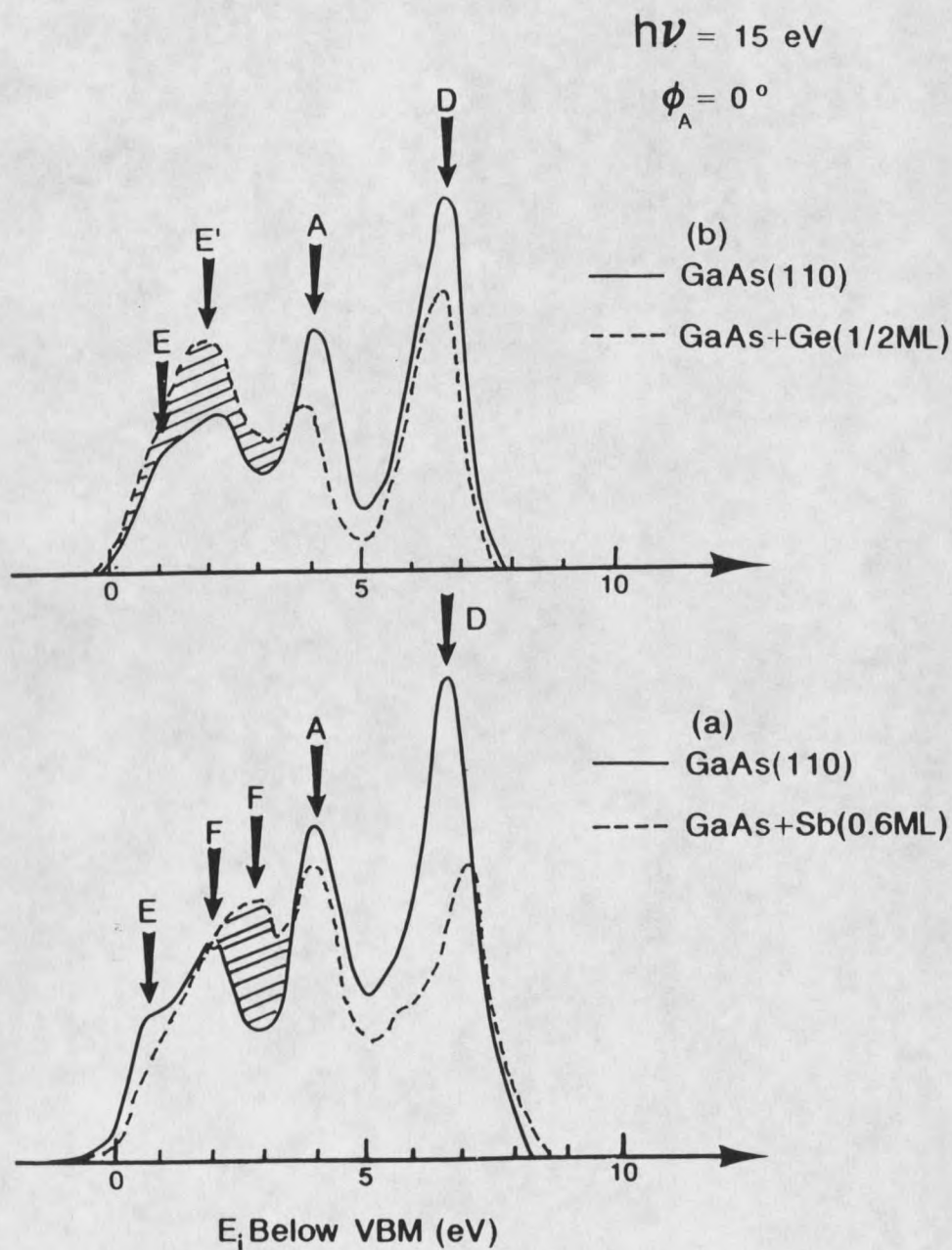


Figure 63. Sb and Ge overlayers on GaAs for polarization 0, $h\nu = 15 \text{ eV}$. GaAs+Ge was obtained by Zurcher *et al.* (1982). The overall effects of the Ge and the Sb are similar.

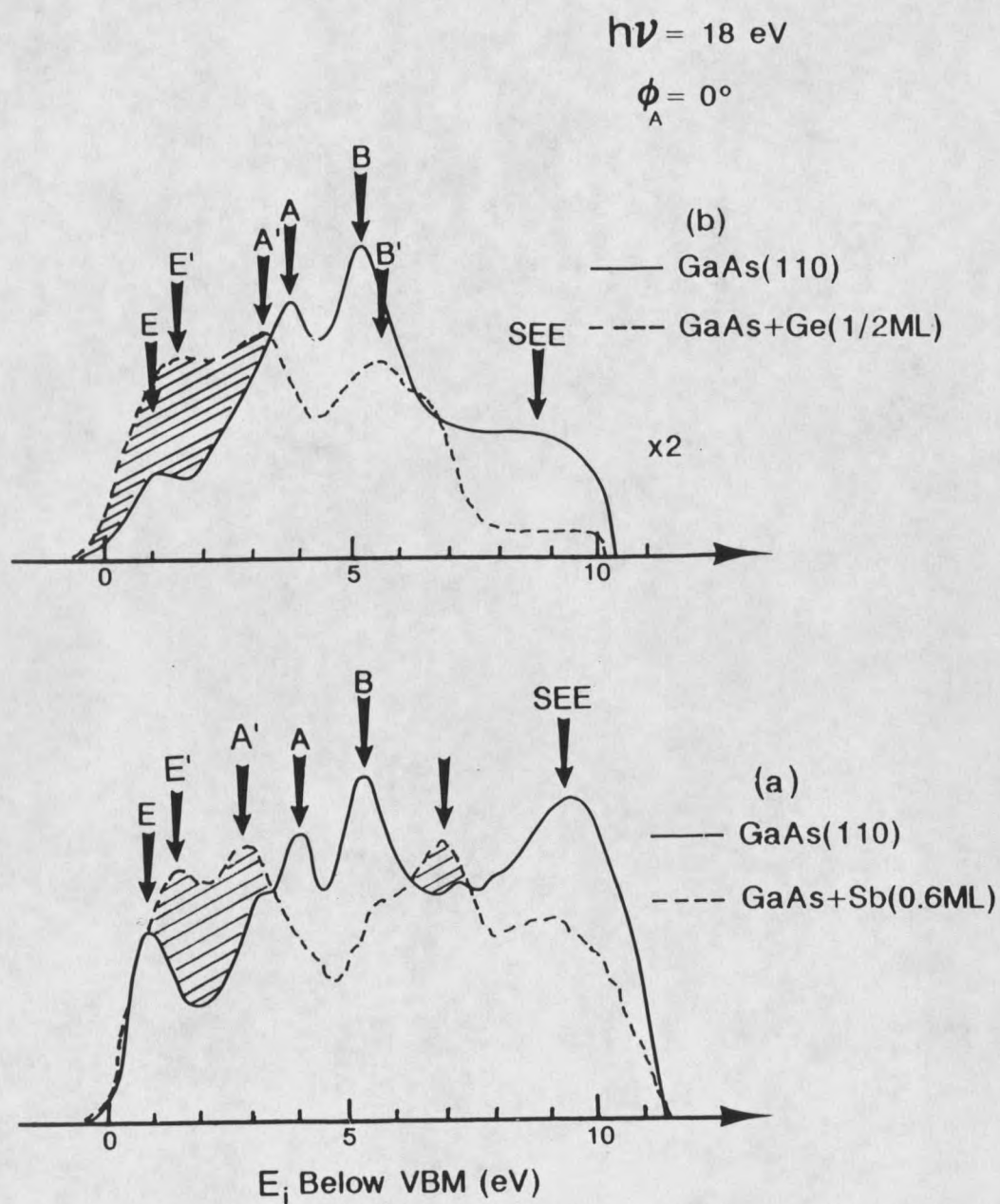


Figure 64. Sb and Ge overlayers on GaAs for polarization 0, $h\nu = 18 \text{ eV}$. GaAs+Ge was obtained by Zurcher *et al.* (1982). The effects of Ge and Sb are very similar, except for the new emission seen by peak D' in the Sb dataset.

This suggests that the substrate (*i.e.*, GaAs) plays a more important role in determining the emission which is observed than the particular type of overlayer atom (*i.e.*, germanium versus antimony).

Figures 46 and 61 through 64 show that the behavior of transition A for Sb is similar to that for Ge overlayers, except for case where $\phi_A = 90^\circ$ and $h\nu = 15$ eV (Figure 61). Here the Sb causes slight attenuations for A, whereas the Ge overlayer shifts the peak dramatically towards the VBM. It is this effect which is called the non-uniform band shift. Given this interpretation, we see how Ge causes a non-uniform band shift effect (Zurcher *et al.*), but Sb does not.

A comparison of the behavior of transition B for Sb and Ge overlayers is shown in Figures 61 and 63. Although there are some differences in peak character, the two systems exhibit generally similar behavior. The peak amplitude plots in Figure 50 demonstrate this common behavior as well. The non-uniform band shift for transition B in the GaAs+Ge study was found to be small ($\Delta E = -0.10$ eV).

High Energy Normal Emission EDCs

Figure 65 shows EDCs taken for $h\nu = 60$ eV for the GaAs(110), *as-cleaved* sample (solid curve) and the same sample with 1.6 ML of antimony on the surface (dashed curve). In order to investigate polarization effects, these data curves were taken for two azimuthal polarizations. Panel (a) shows the data for $\phi_A = 0^\circ$ where $A \parallel MP$, and panel (b) for polarization $\phi_A = 90^\circ$ where $A \perp MP$. The spectra for the covered sample were shifted by 300 meV to lower binding energy to account for Fermi level pinning at the surface.

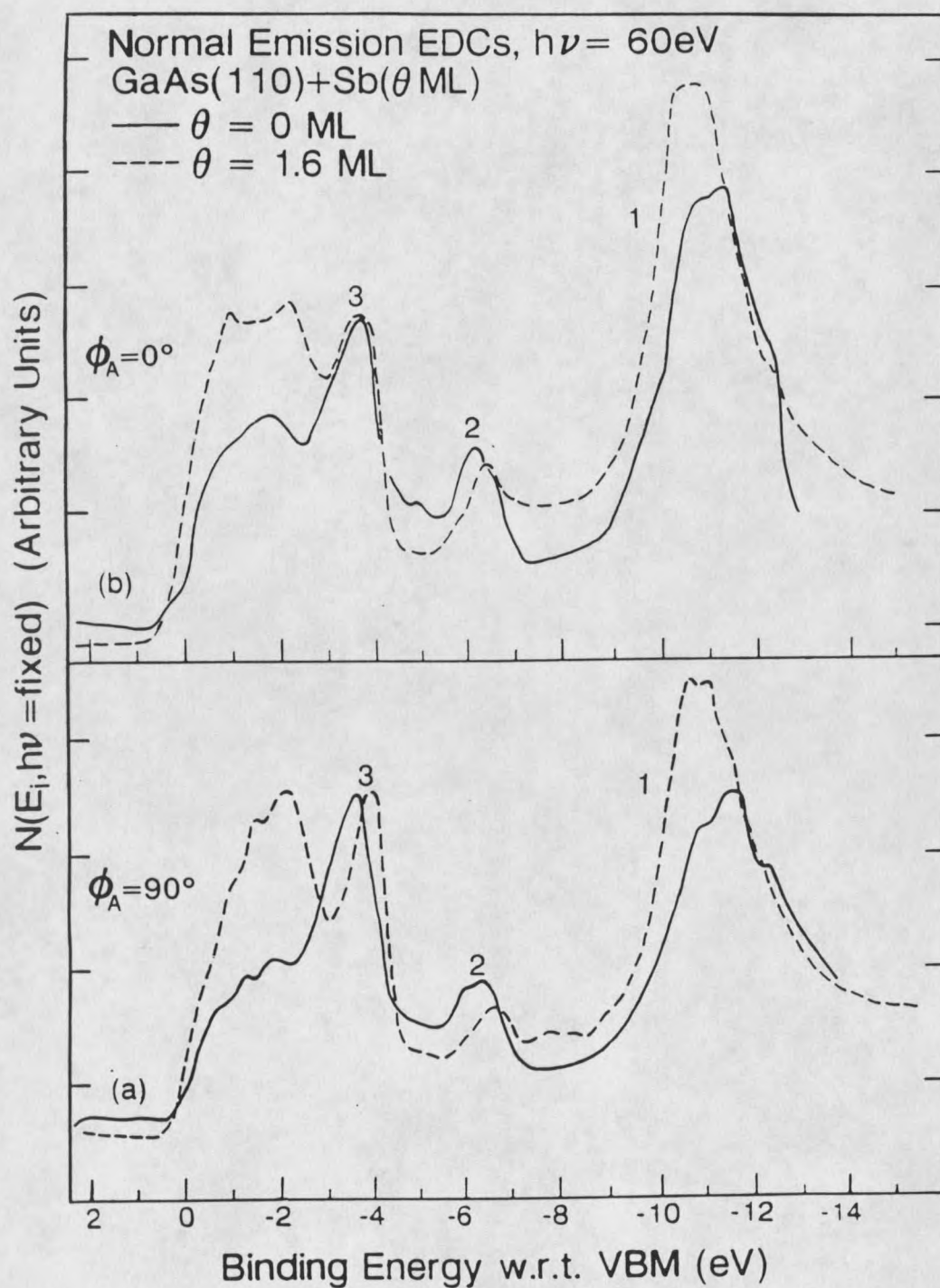


Figure 65. High energy normal emission EDC spectra.

Because of the higher final state energies compared to the case studies in the last section, the crystal potential is a smaller perturbation and consequently a nearly-free electron approximation can be used for the final state. The viability of the approach was demonstrated by Chiang *et al.* (1980) in their study of the normal emission photoemission for GaAs(110) from $25 \leq h\nu \leq 100$ eV. We will use their band assignments, since the peaks, labeled with their VB origins, are easily related to those seen by Chiang *et al.*

Peak 1 in Figure 65 originates from VB 1, which was not seen in the lower photon energy spectra since it has strong *s*-orbital character and consequently its photoabsorption cross section is weak at low photon energies $h\nu$. This feature is sharply enhanced by the antimony overlayer and shifted to lower binding energy by a large amount of -0.57 eV for $\phi_A = 0^\circ$ versus -0.39 eV for $\phi_A = 90^\circ$.

Peak 2 is emission from VB 2 to high-lying conduction band states. The energy shift here is opposite in direction to that of peak 1. The shift is smaller, but significant. It is +0.26 eV for $\phi_A = 0^\circ$ versus +0.45 eV for the $\phi_A = 90^\circ$ case.

Peak 3 associated with VB 3 also show shifts with the antimony coverage. The antimony-induced state near the VBM are apparent in these spectra where there is greater surface state sensitivity. The polarization effect implies that the upper state is odd and that the lower state has mixed symmetry since it is seen in both polarizations.

This data provides evidence that the non-uniform band shifting effect, as was reported in the GaAs+Ge interface system, also occurs in the GaAs+Sb interface system. This is because bands 1, 2, and 3 do not all shift by the same amount or even in the same direction. In order to examine these shifts in adequate detail, we need EDC spectra at several $h\nu$ values in order to change the $k_{\perp}$ parameter of the transitions.

Results

Several conclusions can be made based on the normal emission EDC:

(1) The EDC spectra obtained in this study have a sharper character than those previously reported which together with a more careful structure plot analysis result in a higher degree of mutual consistency between the data and the band calculations. Note that because the theoretical bands are used in the procedure, we cannot conclude that it is a strict check of the band theory.

(2) We report a new phenomenon, called the characteristic amplitude effect, whereby three-dimensional bulk band transitions are attenuated or enhanced in the EDC spectra by overlayer formation. The effect is also seen several times where the analysis places the final state in a hybridization gap. It occurs at all polarizations.

(3) Since transition A ($VB\ 3 \rightarrow FE$) and transition B ($VB\ 2 \rightarrow FE$) have common final states in the free electron (FE) band, we can say that the overlayer attenuation effect is an initial state effect. A similar effect was found for Ge overlayers on GaAs(110).

(4) Amplitude changes for the clean GaAs transitions (*e.g.*, A and B) were qualitatively similar for germanium overlayers and antimony overlayers on GaAs(110).

(5) In contrast to the observations by Zurcher *et al.* (1985) for ordered overlayers of germanium on GaAs(110), no significant non-uniform band shifting was found for ordered overlayers of antimony on GaAs(110) at low photon energies ($10 \leq h\nu \leq 30$ eV).

(6) Evidence for non-uniform band shifts were observed at higher photon energies (60 eV) where the surface contribution to the photoemission dominants. Overlayer-induced amplitude changes of bulk band features were also observed at higher photon energies.

There is no simple criterion for predicting whether the amplitude of a bulk transition will increase (*e.g.*, characteristic enhancement), decrease (*e.g.*, characteristic attenuation), or remain unchanged by the addition of the Sb overlayer. We also note that this phenomena seems to be more related to the nature of overlayer effects on the substrate (*e.g.*, GaAs) rather than the particular type overlayer atom (*i.e.*, Sb versus Ge).

In order to relate these empirical observations to the characteristic amplitude effect, it would be important to (1) investigate the effect in other ordered and non-ordered overlayer systems and (2) to carry out theoretical calculations to predict the effect. Experimentally, it would be interesting to know if other overlayers (*e.g.*, Au, Bi or Al) have the same effect on GaAs or related III-V compound semiconductors (*e.g.*, GaSb or InAs). Theoretically, knowing the atomic structure of the surface region (Duke *et al.* 1982) may make it possible to mathematically relate changes in surface potential to the coefficients governing the admixture of evanescent and bulk wavefunctions which contribute to the photoemission signal. A calculation of this kind would probably need to incorporate a wavefunction matching approach for the interfacial region.

In the case of the enhancement (*e.g.*, transition F), it is not possible to determine if it is due to modification of the initial state or the final state. If it is a final state dominated effect, we can understand how the overlayer modifies the matching conditions between the excited Bloch wave in the crystal and the time-reversed LEED

wave function in the vacuum. The disparity of overlayer-induced effects for transition A and B, led us to the conclusion that the effect is initial state in nature, making the overlayer modification difficult to understand.

Constant Final Energy Spectroscopic (CFS) Study

Since the final state energy is not fixed in the EDC mode of photoemission, the analysis of phenomena (*e.g.*, identification of surface states) occurring at single values of $k_{\parallel}$ is complicated. The kinetic energy of the photoelectrons changes across an EDC spectra because the analyzer's kinetic energy window is scanned. Some effects are dependent on the photoelectron's kinetic energy, *e.g.*, the escape depth and the parallel component of the momentum, $k_{\parallel}$ of the photoelectrons. Changes in the former effect are usually negligible, however the $k_{\parallel}$ variations are large in a single EDC. Hence to study the electronic structure at a specific place in the surface Brillouin Zone requires putting together the analysis of many EDC spectra. However, in the case of the CFS, the final state energy and hence the photoelectron's kinetic energy is constant, $CFS \sim N(h\nu; E_f = \text{fixed})$ (see Table 1). Most importantly, the fixed kinetic energy means that all the electrons which comprise the CFS came from a single location in the surface Brillouin Zone. This enhances the capabilities of photoemission for studying surface state effects in the presence of bulk states.

Experimental Considerations

The angle-resolved CFS experiment used the Seya monochromator which prohibited measurement of core level spectra for sample diagnostics. However, having verified

the consistency between overlayer thickness determined from the core level spectra versus the quartz-crystal oscillator (QCO) measurements, the QCO-derived thicknesses were reliably used (see Chapter 5).

The sample was a *p*-type GaAs crystal (Zn-doped, $N = 3.5 \times 10^{18}/\text{cm}^3$). In order not to introduce data collection artifacts into the experiment, the sample was never moved during the measurements. As such, new cleavings and Sb overlayer preparations were done for each polarization ($A \perp MP$ and $A \parallel MP$). At each polarization, photoemission was measured at two SBZ points, *viz.*, $\bar{X}'(Ga)$ and $\bar{M}(Ga)$.

Data Processing

The most important processing applied to the ARCFS spectra was removal of the light curve signature. A light curve signature is imparted into the data from the optical response characteristics of the monochromator and is measured with a tungsten mesh photodiode. The synchrotron radiation passes through this mesh prior to striking the crystal sample so that as the CFS data $N(h\nu; E_f = \text{fixed})$ is recorded, a corresponding tungsten mesh light curve $I_{w,i}(h\nu)$ is also collected.

In order to remove the effects of the light curve from the raw CFS spectra, the spectra were divided by the spectral light curve. However, the tungsten mesh photocurrent is not a perfect measure of the photon flux (*i.e.*, it does not have a flat spectral response) and must also be corrected. Its departure from an ideal photodetector response is most prominent at low (10 eV) and high (30 eV) photon energies. A more ideal photodetector is thought to be sodium salicylate fluorescence $I_{ss}(h\nu)$ from a freshly prepared film, however I_{ss} cannot be continuously acquired with the CFS spectra.

Consequently, the sodium salicylate signal I_{ss} was periodically measured in order to correct the I_w curve. These curves along with the correction factor for the tungsten light curve are displayed in Figure 66.

A correction factor, $C(h\nu) = I_w/I_{ss}$ is obtained which indicates how the tungsten mesh signal deviates from the ideal response. To account for the time dependence of the synchrotron radiation flux, the individual light curves, $I_{w,i}(h\nu)$ taken concurrently with the CFS spectra are compared to a master curve $I_w(h\nu)$. This was done by cross-correlating the two curves and finding a least squares line with slope m . The slope m is the ratio of the light intensity of the individual light curve to the master tungsten mesh light curve. Figure 67 shows an example of the normalization as applied to a particular CFS spectra which is given by

$$N_{norm}(h\nu; E_f = \text{fixed}) = \frac{N_{raw}}{I_{ss} m} \quad (51)$$

Data and Analysis

Photoemission at two symmetry points were measured with the CFS technique, $\bar{X}'(Ga)$ which is on the mirror plane (MP) in the direction of the Ga dangling bond (*i.e.*, $\phi_A = 0^\circ$) and $\bar{M}(Ga)$ which is at the corner of the surface Brillouin Zone (SBZ), also in the Ga dangling bond direction. For each SBZ point, two polarization conditions, $A//MP$ and $A \perp MP$ were used, which allowed determination of state symmetries in the mirror plane case. The four datasets are shown in Figures 68-71; the clean spectra are dashed and the covered spectra are solid. The final state energy, referenced to the VBM, is annotated to the left of each curve.

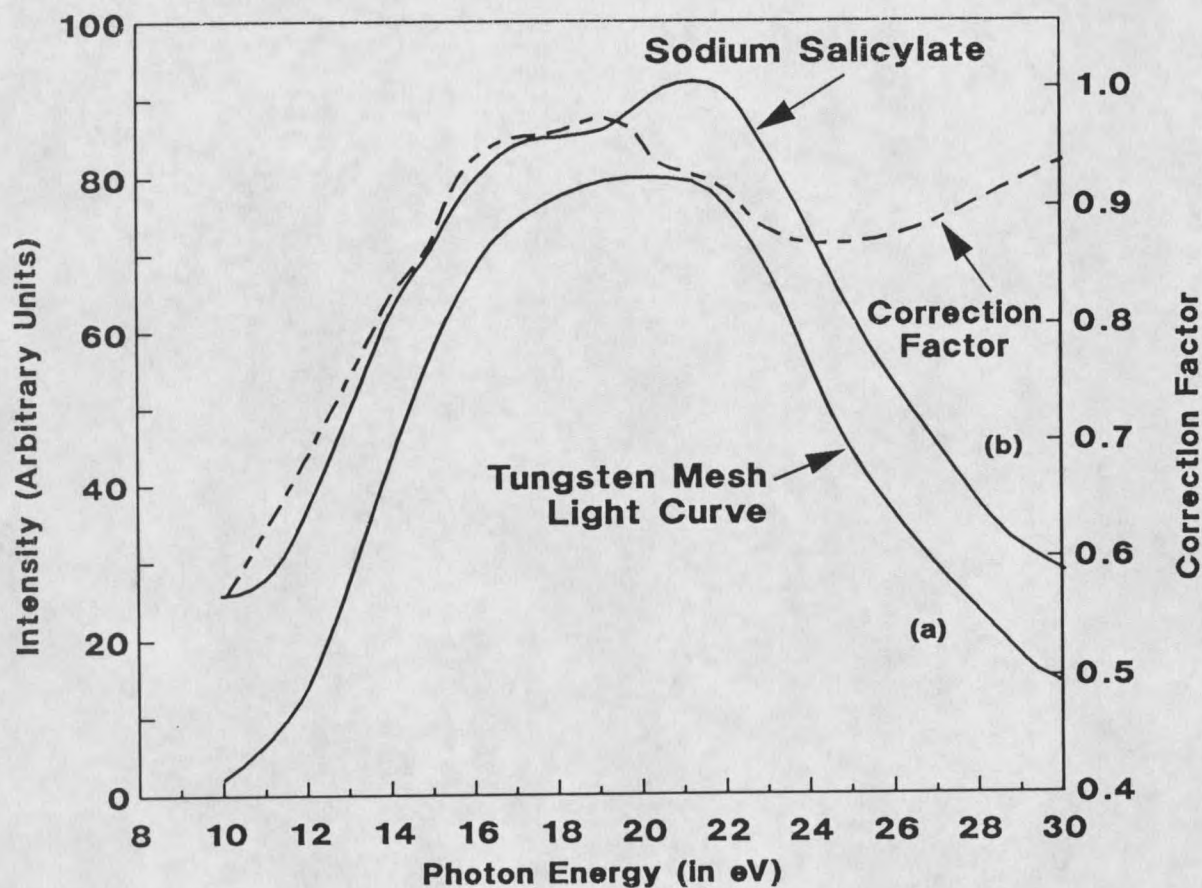


Figure 66. Stainless Steel Seya light curves. The differences between tungsten mesh photocurrent (a) and sodium salicylate photocurrent (b) are contained in the correction factor C. Ideal tungsten mesh response occurs when $C=1$.

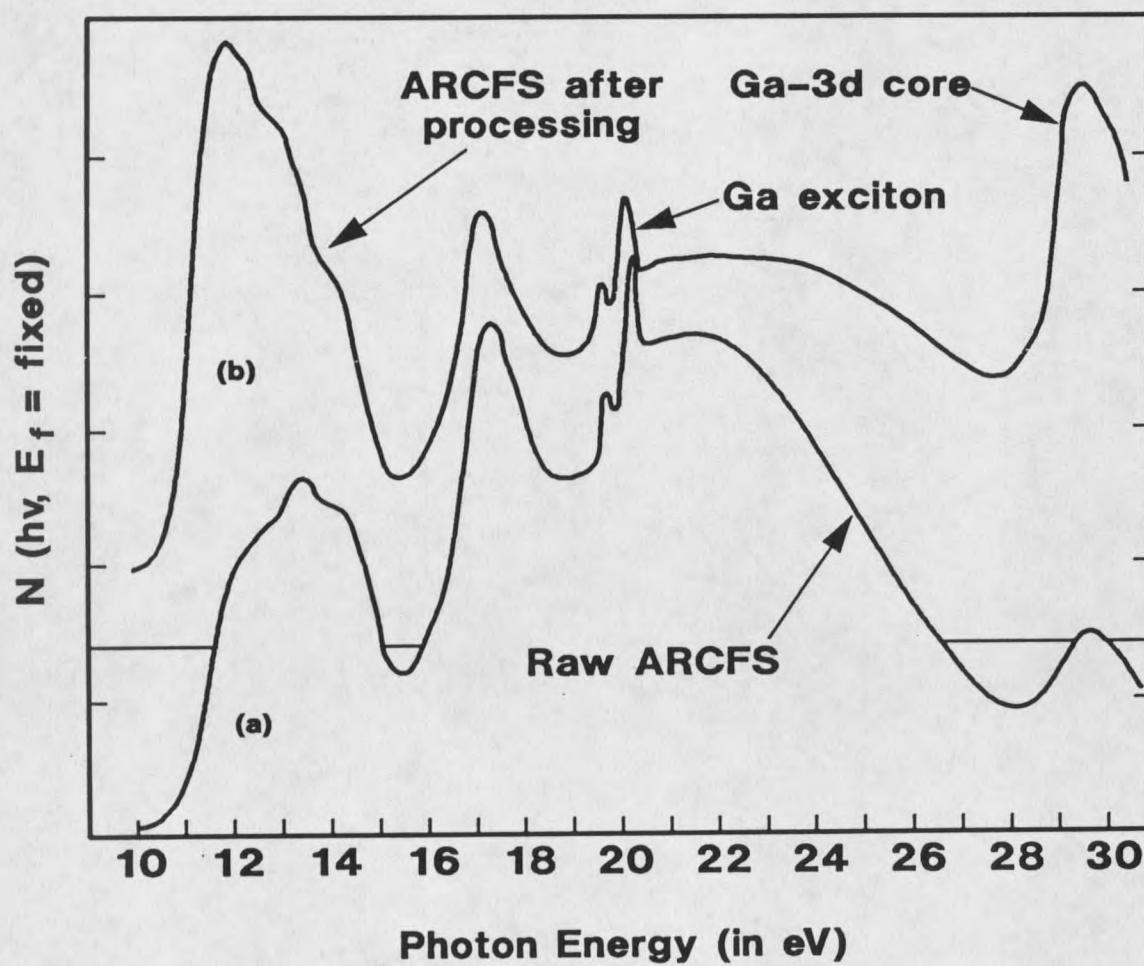


Figure 67. Light curve corrections applied to CFS data. Curve (a) is the angle-resolved CFS before processing. Application of Equation 51 produces curve (b).

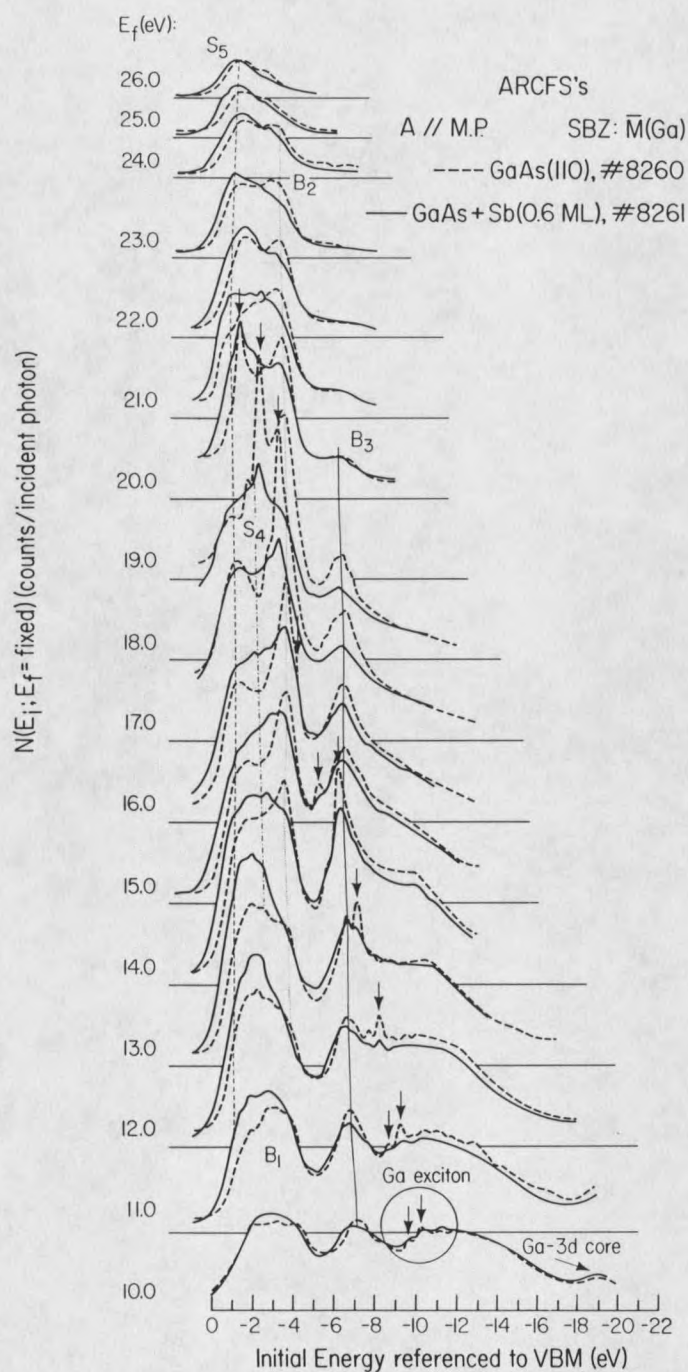


Figure 68. ARCFS spectra at $\bar{M}(\text{Ga})$ and pol. 0 for GaAs(110)+Sb(0.6 ML).

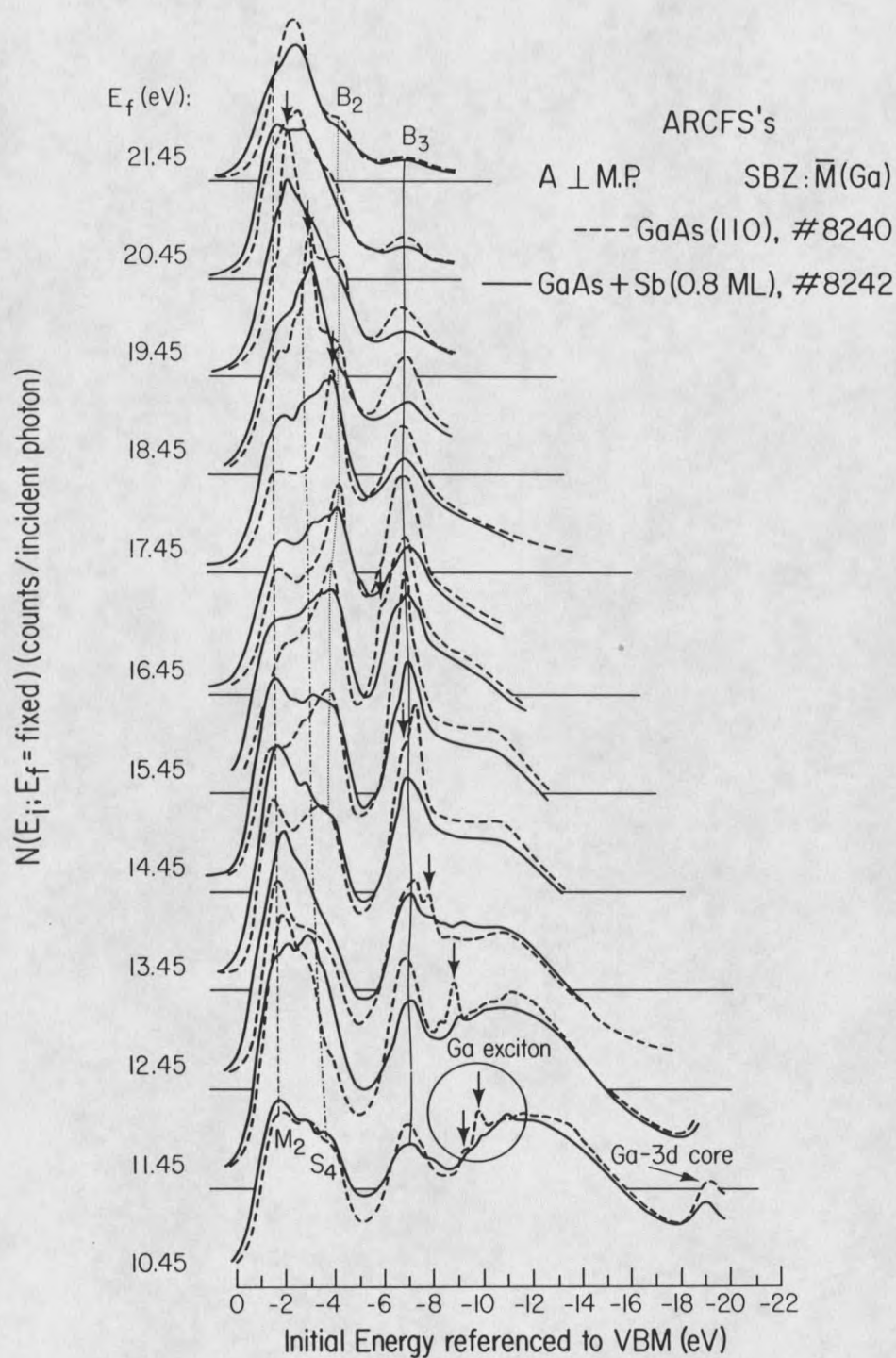


Figure 69. ARCFS spectra at $\bar{M}(Ga)$ and pol. 90 for GaAs(110)+Sb(0.8 ML).

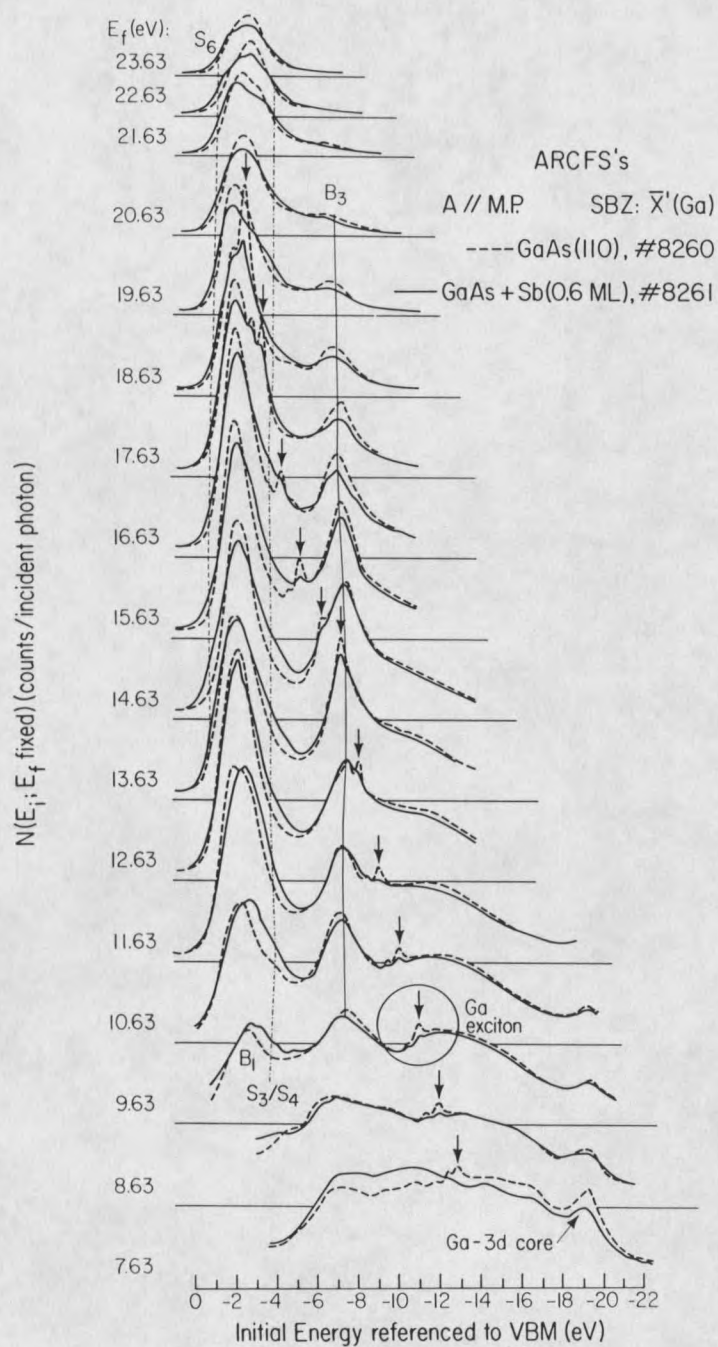


Figure 70. ARCFS spectra at $\bar{X}'(\text{Ga})$ and pol. 0 for GaAs(110)+Sb(0.6 ML).

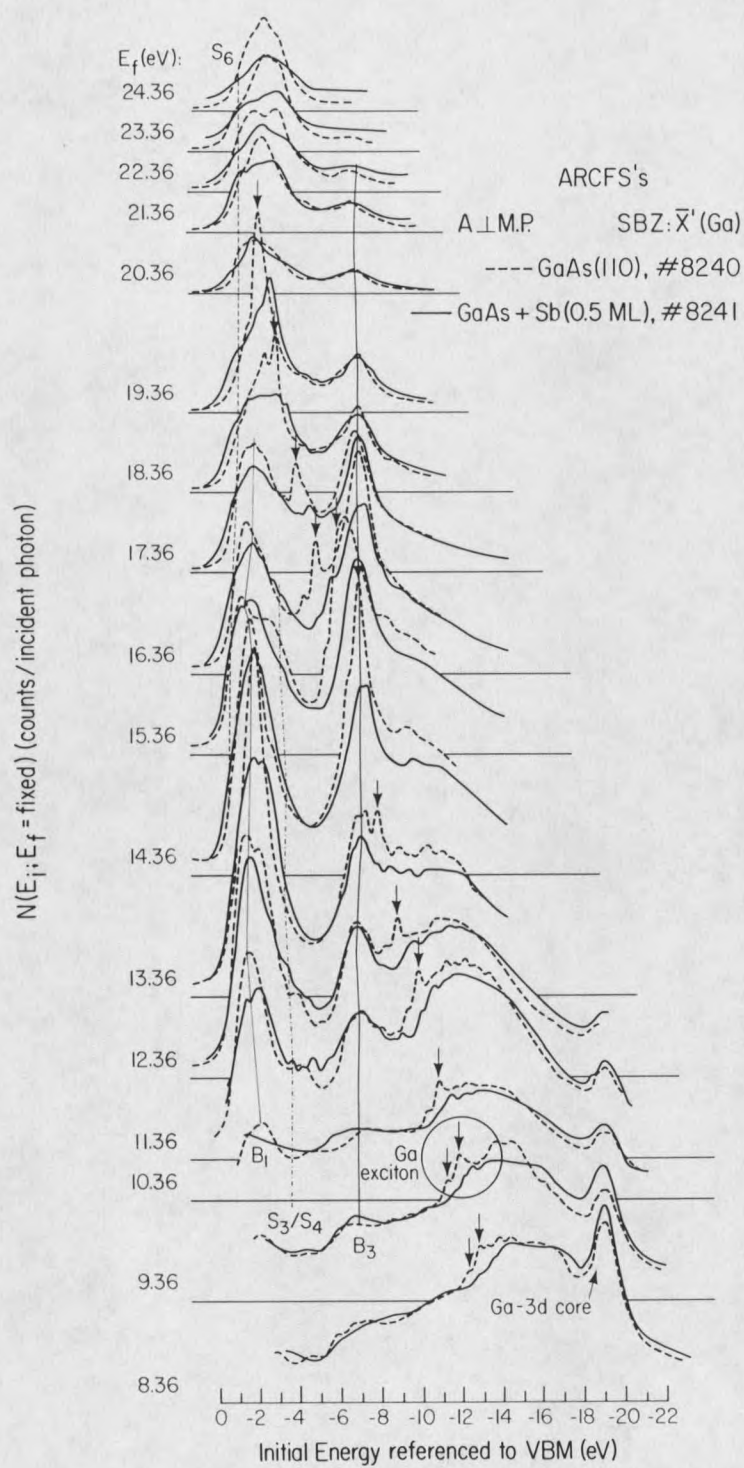


Figure 71. ARCFS spectra at $\bar{X}'(Ga)$ and pol. 90 for GaAs(110)+Sb(0.5 ML).

The data are plotted against initial energy E_i , referenced to the VBM which was determined from previous measured values of the Ga-3d core. The energy alignment of the clean and covered spectra was made by matching the Ga-3d core peaks ($E_i = 18.8\text{eV}$). The advantage of plotting the curves against E_i is that transition sequences which do not show energy dispersion are quite likely to be surface-related states. Conversely, those which move about in energy as the final energy is changed have a $k_{\perp}$ property and hence are bulk-related states.

A distinctive feature of the CFS data is the Ga core threshold exciton, which always emerges at the same photon energies (*viz.*, 19.9 eV and 20.2 eV). The exciton's energy position shifts by the same amount as the final energy and is noted by arrows in the figures. Since the exciton involves the Ga dangling bond, its pronounced surface sensitivity is clearly seen in the figures. Direct emission from the Ga-3d core is noted with an arrow.

Results

Figure 72 shows the theoretical band structure for GaAs(110) + Sb(1 ML), p(1x1) from the calculations of Mailhoit *et al.* (1985). In order to emphasize the surface states, the initial energy (referenced to VBM) is plotted against the parallel component of momentum $k_{\parallel}$ suppressing any $k_{\perp}$ dependence. Normal emission Γ occurs at either side of the diagram followed in order by the $\bar{X}$, $\bar{M}$, and $\bar{X}'$ symmetry points. These points correspond to the points by the same name in Figures 10 and 11. The shaded areas represent the bulk bands which have been projected onto the two-dimensional SBZ.

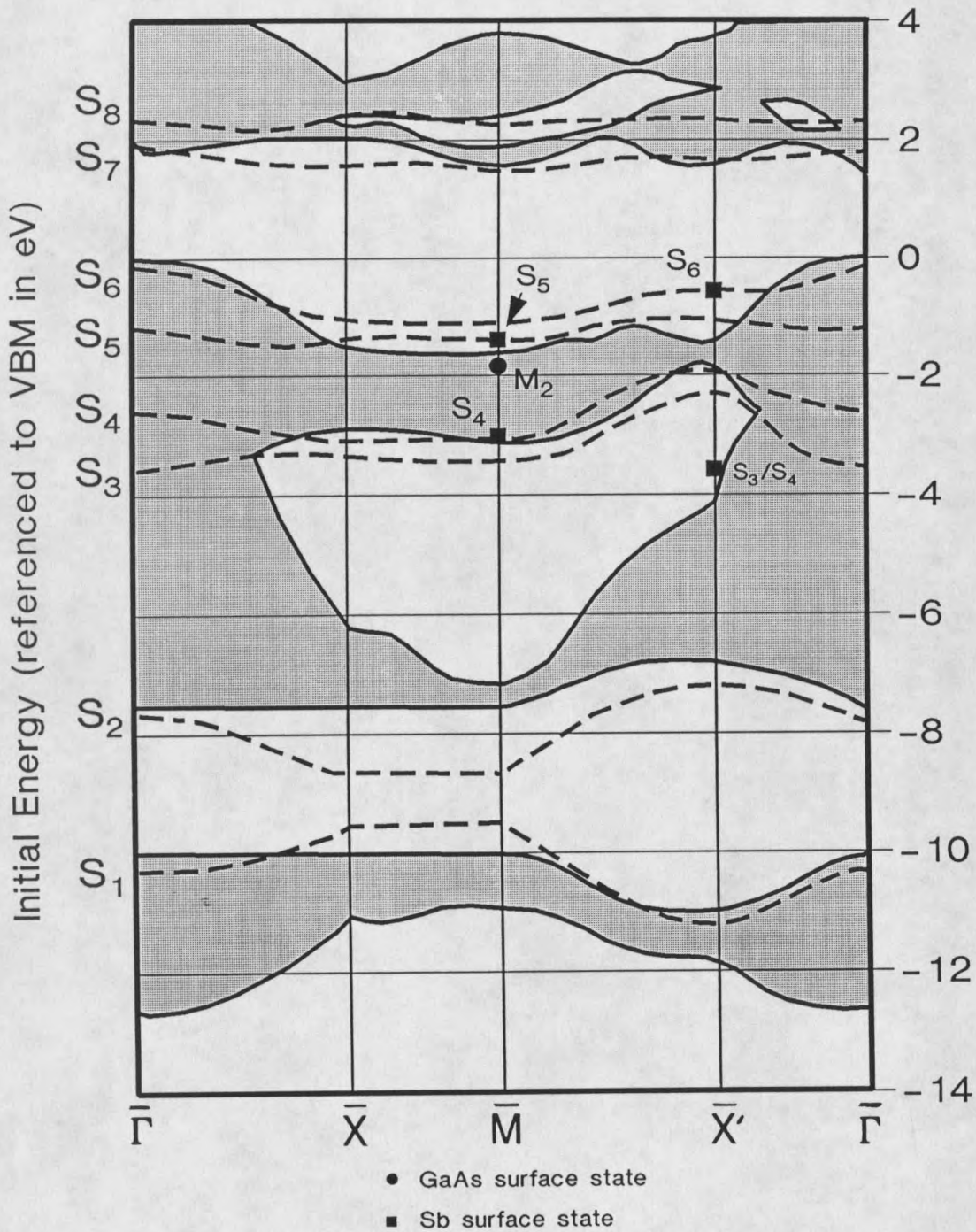


Figure 72. Surface states located on theoretical energy band diagram.

The upper valence bands start at the VBM and go downwards to around -7.8 eV. In the center of the diagram, is the characteristic "stomach" region within the VBs where bulk band states are not allowed to exist. The forbidden energy gap which exists between -8 and -10 eV is called the heteropolar gap because it exists only in heteropolar semiconductors such as GaAs (Harrison 1980). The lower VBs of GaAs begin at about -10 eV and are around 2 eV wide depending on the location in momentum space. At the top of the diagram, we see the first two eV of the conduction bands.

The overall shape of the CFS spectra is governed by the emission from the bulk band electronic structure. For example, at the $\bar{M}$ -point, the bulk band structure is divided into a zone (shaded) near the VBM which is ~2 eV wide and a narrow neck at about -7 eV which is ~0.5 eV wide.

The corresponding CFS spectra are shown in Figures 68 and 69. In these spectra, there is bulk band emission in all spectra from about -2 to -4 eV caused by the states in the upper valence band zone and from around -6.5 to -7.5 eV caused by the narrow valence band neck at deeper energy. A region devoid of emission centered around -5 eV in both Figures 68 and 69 is due to the wide stomach region shown in Figure 72. Similar behavior is seen for photoemission from the $\bar{X}'$ -point (see Figures 70 and 71), although the widths of the zones change according to what is seen in Figure 72.

Apart from the Ga exciton and direct Ga-3d core emission, the features in the angle-resolved CFS spectra which are not accounted for by the bulk band emission can be attributed to surface-related features. These surface-related peak sequences fall into two main groups; (1) GaAs substrate surface states, and (2) GaAs+Sb interface-related states. Both the substrate and interface surface states are dispersionless; however the former exist in the clean sample, while the latter appear in the interface sample. These

states are summarized in the following table where the transition labeling is consistent with previous work wherever possible. The first three states (S_4 , S_5 , and M_2) occur at the $\bar{M}$ -point, whereas the last two (S_3/S_4 and S_6) are present at the $\bar{X}'$ -point. The initial state energy, referenced to the VBM, as determined from the CFS spectra is noted in Table 8.

Table 8. Surface-related states at $\bar{M}(Ga)$ and $\bar{X}'(Ga)$.

Name	SBZ	$E_i(eV)$	$A//MP$	$A\perp MP$	Type of state
S_4	$\bar{M}$	-3.0	Strong	Strong	GaAs+Sb interface (c,d)
S_5	$\bar{M}$	-1.3	Moderate	Weak	GaAs+Sb interface (b-e)
M_2	$\bar{M}$	-1.8	Absent	Strong	GaAs substrate (a)
S_3/S_4	$\bar{X}'$	-3.8	Weak	Weak	GaAs+Sb interface (c-e)
S_6	$\bar{X}'$	-0.5	Weak	Weak	GaAs+Sb interface (b-e)

a Williams *et al.* (1978)

b Skeath (1982) experimentally observed only S_5 near VBM.

c Bertoni *et al.* (1983)

d Mailhoit *et al.* (1985)

e Mårtensson *et al.* (1986)

The relative amplitude strengths at each polarization ($A\perp MP$ and $A//MP$) are noted in columns four and five in the table. The type of state, according to the above classification, is contained in the last column of Table 8. We will discuss these states in this order.

At the $\bar{M}$ symmetry point, the overall bimodal shape of the angle-resolved CFS spectra is due to the bulk band electronic structure. With the addition of the Sb overlayer, the CFS emission near the VBM is enhanced, while the emission occurring at higher initial energy around -7 eV is attenuated. This is seen as the enhanced regions in Figures 68 ($A//MP$) and 69 ($A\perp MP$). It is apparent from the theory that the enhancement near the VBM is associated with the Sb overlayer. According to the theory, eight

antimony-derived surface states, S_1 through S_8 , exist (Mailhoit *et al.* 1985 and Bertoni *et al.* 1983) and are shown as dashed lines in Figure 72 (see Chapter 4 for details). Apart from the deeper s -like states (S_1 and S_2) which tend not to emit at these photon energies, the occupied Sb surface states (S_3 , S_4 , S_5 , and S_6) occur on either side of the bulk valence band zone which lies above the stomach region. In crossing the SBZ region from $\bar{X} \rightarrow \bar{M} \rightarrow \bar{X}'$, these Sb levels exist as surface states, however near the $\bar{\Gamma}$ -point they become mixed with the bulk bands and therefore exist as surface resonances, which explains why they were not easily seen at normal emission. When the GaAs(110)+Sb interface is formed and these Sb states are created, we expect to see enhanced photoemission occurring in the region near the VBM and as we pointed out, this is observed in Figures 68 and 69. To go beyond this general conclusion and assign individual surface states to particular features in the CFS spectra will require closer inspection of the curves, beginning with Figure 68.

Three features (B_1 , B_2 and B_3) in Figure 68 ($\bar{M}(Ga)$ and $A // MP$) show significant energy dispersion, and therefore are identified as bulk band transitions. Transition B_1 disperses from about -3.5 to -1 eV as the final state energy increases from ~ 11 to ~ 21 eV, respectively. Transition B_2 monotonically disperses a total of about 0.5 eV from around -3.3 to -3.8 eV. It is seen best at the higher final state energies. Emission from the VB zone below the stomach region is attributed to transition B_3 , which also monotonically disperses from -6.3 to -7 eV.

Transition B_3 can be assigned an initial state of VB 2, even without knowing the exact band structure at the $\bar{M}$ -point. This assignment can be made by extrapolating the normal emission band structure (*e.g.*, Figure 49) from $\bar{\Gamma}$ to $\bar{M}$ based on the behavior seen in Figure 72. In Figure 49, we recall that VBs 2, 3, and 4 converge towards the VBM as the wavevector approaches zero. This results in an energy band overlap of VBs 3/4 and

VB 2 of about 4 eV, which is the energy different between the VBM and the Σ_1^{min} -point. We can now imagine the SBZ point moving away from Γ towards $\bar{M}$ according to Figure 72. When this occurs the band overlap mentioned above will disappear, as the left-hand side of VB 2 moves downwards in energy, and an energy gap (stomach) is formed. Therefore, VB 2 at $\bar{M}$ becomes a very flat band situated around an initial energy of -7 eV, which corresponds to the narrow region at the $\bar{M}$ -point seen in Figure 72. As we saw in the normal emission experiment, excitations from VB 2 were associated with transitions B, C, and D. These transitions, especially transition B, showed the characteristic amplitude effect. This effect was defined as overlayer-induced amplitude changes in bulk band transitions. It is clear from Figures 68 and 69 that this effect is also manifest at the $\bar{M}$ symmetry point in transition B_3 . In addition, it is observed in transition B_2 which is from VBs 3 or 4.

Two surface-related states (S_4 and S_5) are observed at $\bar{M}$ which are associated with the interface system GaAs(110)+Sb. Both of these Sb-induced surface states have been calculated by Bertoni *et al.* (1983), see Table 4, and Mailhoit *et al.* (1985), see Table 5. The energy location of the states is shown in Figure 72 for the Mailhoit *et al.* calculation, although Bertoni *et al.* obtains essentially the same results. One of the states S_5 , has been experimentally seen often (Skeath 1982 and Mårtensson *et al.* 1986), but the other state S_4 is newly reported here. All are true surface states, since they lie at the edge of the valence band region and are not degenerate with the bulk structure.

The S_4 state is most clearly seen in Figure 69 for $A_{\perp}MP$. Here it has an initial energy of about -3 eV and shows no dispersion. It occurs in a region where substrate related features are absent, making it easy to see (*e.g.*, $E_f = 11.45$ to 14.45 eV). In the other polarization, *viz.*, $A_{\parallel}MP$, it is not as well formed, but does still fill in the valley between the substrate features for $E_f = 15$ to 18 eV. This state has been plotted on the theoretical

energy band diagram of Figure 72 and agrees much better with the calculations than the state which Mårtensson *et al.* (1986) reports, suggesting that Mårtensson *et al.* are really seeing another state, possibly associated with a clean surface state.

The S_5 state occurs closer to the VBM than S_4 and has a moderate to weak amplitude at the $\bar{M}$ -point for $A // MP$. Consistent with other photoemission data which has been obtained on S_5 , this state does not occur as a well-formed peak, but rather as extra emission at the VBM. It is most clearly seen for $A // MP$ (Figure 68) when $E_f = 19, 20$, and 21 eV. At the final state energies of $E_f = 15$ through 19 eV, there is interference with the B_1 bulk band transition, preventing us from seeing it clearly. For a final energy of 11 eV the bulk band interference is absent and the S_5 enhancement is seen again. It is weak at the other polarization, *i.e.*, $A \perp MP$, suggesting that it may have polarization dependence. However, since the $\bar{M}$ -point is off the MP, parity cannot be assigned on this basis. The state S_5 has also been plotted in Figure 72, the theoretical energy band diagram, and agrees well with the calculations.

An additional dispersionless peak sequence M_2 with $E_i = -1.8$ eV is clearly seen at the $\bar{M}$ -point for the polarization condition where $A \perp MP$ (Figure 69). However, it is absent in the opposite polarization, *i.e.*, $A // MP$. It is noted in Figure 72 as a solid circle within the bulk band zone. The polarization behavior agrees with Williams *et al.* (1978), who did a photoemission survey of the main SBZ symmetry points for contamination-sensitive PARUPS features on GaAs(110). For the GaAs+Sb sample, M_2 is enhanced significantly by the overlayer formation, especially for final state energies $E_f = 11.45$ to 18.45 eV. Enhancement of this feature could be the reason for the difficulty in seeing S_5 at $A \perp MP$. Since it shows no energy dispersion but does have high surface sensitivity to the adsorption of foreign atoms, it is classified as a substrate surface state (see Table 8).

At the $\bar{X}'$ symmetry point, the upper VB zone of the bulk band electronic structure narrows significantly so that the four Sb associated states and the bulk bands are unmixed. The forbidden energy gap (stomach) is narrower than was seen at $\bar{M}$, however the width of the lower VB zone below the stomach region is considerably larger than what exists at $\bar{M}$. As we saw in the case of the $\bar{M}$ -point; the overall shape of the CFS is governed by the bulk band structure. This is evident in the ARCFS spectra in Figure 70, where a single bulk peak called B_1 exists and corresponds to emission from the narrow bulk band states around -1.7 eV. Because peak B_1 disperses several hundred meVs, it is classified as a bulk band feature. Unlike at the $\bar{M}$ point, bulk band state B_2 does not exist at the $\bar{X}'$. Instead, the emission from the lower VB zone generates a broad distribution around -7 eV. The most pronounced feature of this distribution was called B_3 at the $\bar{M}$ symmetry point. At the $\bar{X}'$ -point, it is present at both polarization conditions, *i.e.*, $A \perp MP$ (Figure 70) and $A \parallel MP$ (Figure 71). Note that the amplitude effects on B_3 caused by the Sb overlayer are not as large as they are at the $\bar{M}$ symmetry point. This suggests that the characteristic amplitude effect could have $k_{\parallel}$ dependence, but a rigorous structure plot analysis like we did for normal emission would be required to substantiate this further.

Antimony-related states are also seen at the $\bar{X}'$ point, but in the case of the deeper state, we will not be able to discriminate between S_3 and S_4 , so it will be henceforth referred to S_3/S_4 . These states are displayed on the theoretical energy band diagram of Figure 72.

Either side of the peak sequence B_1 in Figures 70 and 71 show Sb overlayer-related enhancements, although they are much weaker than the corresponding effects seen in Figures 68 and 69. The S_3/S_4 states is around -3.8 eV and the S_6 states is at an initial energy of approximately -0.5 eV. The existence of this Sb-induced emission can be understood by studying the theoretical energy band diagram in Figure 72. Theoretically,

we see that there are Sb-related states S_3 through S_6 predicted to exist on either side of the narrow bulk band region in the upper VB zone. This arrangement of bulk and surface states is consistent with experimental observation, since Figures 70 and 71 show Sb induced emission around -1 eV and -4 eV. However, there is some disagreement, since not only is the bulk feature B_1 wider than Figure 72 suggests, but the S_3/S_4 states are deeper in energy than the theory predicts.

CHAPTER 8

SUMMARY

The goal of this research work has been along two main directions; the design and development of enhanced angle-resolved photoemission capabilities for the M.S.U. research group at the University of Wisconsin's Synchrotron Radiation Center (see Chapter 5), and the application of this experimental system to the investigation of the electronic properties of semiconductor interface systems.

The particular system chosen for study was the ordered overlayer -semiconductor system, $GaAs(110) + Sb(\theta ML), p(1 \times 1)$ where $\theta = 1/2 - 2ML$. The reasons for choosing this system included previous studies (Chapter 4) which indicated that this system had several properties of an ideal interface system including epitaxy, abruptness, and chemical stability (Skeath 1981). In addition, theoretical calculations (Bertoni *et al.* and Mailhoit *et al.*) of the interface electronic properties had been performed (see Chapter 1).

Enhanced angle-resolved photoemission capabilities were achieved by building a compact plane mirror analyzer (PMA) which could be angularly positioned anywhere within 4π steradians at a constant radius from the analysis point of the sample. This alleviated the polar and azimuthal coupling problems which were inherent with the previously constructed angle-resolved CMA (Knapp and Lapeyre 1982). These enhancements would allow independent selection of polarization conditions and analysis angles so that the user could easily measure points in the surface BZ of the sample with well controlled and flexible geometry. To accomplish this goal for independent selection of θ_A

and ϕ_A , a precision twin-axis goniometer was designed and built. For temperature dependent experiments, a small, reliable heated sample holder was built. Other spectroscopic methods which were added to the systems were LEED, Auger, XPS, and ELS.

The experimental examination of the GaAs(110)+Sb interface system was contained in two efforts. The first (Chapter 6) dealt with measurement of valence band effects on the core levels and was composed of two experiments:

(1) By detailed linefitting of the high-resolution Sb-4d core spectra it was shown that two Lorentzian doublets are needed to achieve a good match with the data. From this it was inferred that two inequivalent Sb atoms exist on the surface. The line which is shifted to deeper binding energy is assigned to the Sb-As site and the other line which is moved to shallower binding energy is associated with the Sb-Ga site. The energy splitting between the lines was 0.38 eV. The As-3d line show both surface and bulk components for the clean sample, but after Sb deposition, only a single line is seen. This supports the model where the surface reconstruction of the (110) surface is restored to the bulk atomic arrangement after Sb deposition.

(2) Examination of the Sb-4d core level versus Sb overlayer thickness and preparation was performed by measuring the enhanced emission associated with core hole decay. It was determined that this excitation from both spin-orbit components of Sb-4d core to an empty Sb-derived surface state was nonexcitonic and Auger in nature. This was judged from the linewidth and CIS spectra. Furthermore, the energy location of this state S'_1 was calculated to be 1.18 eV. But the exact value would depend on the relative contribution from the two energetically different Sb surface sites. Photoemission yield spectra demonstrated that the effect could be seen in the integrated photocurrent

and had polarization isotropy, like the As core hole decay, but unlike the Ga core exciton. Coverage dependent electron energy loss spectra (ELS) manifested the same effects which showed that core hole decay phenomenon are independent of the process which generates the core state.

A second effort was directed towards a systematic search for overlayer-induced interface states (Chapter 7). This was done at the Γ point via the normal emission EDC mode of photoemission and at the $\bar{M}(Ga)$ and $\bar{X}'(Ga)$ points in the SBZ for two orthogonal polarization conditions.

(1) A high degree of consistency was obtained between theoretical energy band calculations and experimentally observed transitions. This was because of the sharper character present in the spectra than previously reported coupled with a more careful structure plot analysis. The method which was adopted and whose implementation was refined is the structure plot method of Williams *et al.* (1986). Six major transition sequences were analyzed (A-F) for three orthogonal light polarization conditions. Initial and final band assignments were made for all the peaks analyzed and located on the theoretical energy band diagram. Detailed examination of effects of the Sb on peak energy location and amplitude were made. At low photon energies ($10\text{eV} \leq h\nu \leq 30\text{eV}$) no anomalous peak shifting (*i.e.*, non-uniform band shifting) was observed in contradistinction to the GaAs+Ge overlayer system (Zurcher *et al.* 1982).

Amplitude changes in bulk band features induced by the Sb overlayer were closely studied. Transition A showed minimal amplitude attenuation by the Sb, while B was dramatically affected. Furthermore, these two transitions originate from different initial states (VB 3 versus VB 2), but share common final states (*i.e.*, FE or free electron band). This band structure relationship indicates that the mechanism which causes the

overlayer-induced amplitude changes in bulk-related emission features, which we have termed the characteristic amplitude effect, is dependent on the initial state of the transition.

One possible explanation of these characteristic changes in bulk band amplitudes involves the conduction band hybridization gaps (HG) in the electronic structure. One particular hybridization gap of interest occurs at $k_{\perp} \sim 0.7 \text{ \AA}^{-1}$ and $E_{\perp} \sim 12 - 14 \text{ eV}$, and is common to the final states of these transitions studied. Transition A at $h\nu \sim 16 \text{ eV}$, transition B at $h\nu \sim 18 - 19 \text{ eV}$, and transition F at $h\nu \sim 13 - 15 \text{ eV}$. Each of these transitions have a different initial state and each show a qualitatively different amplitude effect. Transition A, from VB 3, is unchanged by the Sb overlayer, transition B, from VB 2, is attenuated, and transition F, from VB 4, is enhanced by the Sb. Although the characteristic amplitude effect is also observed when the final states are not in hybridization gaps, this example underscores the importance of the initial state of the photoabsorption process in predicting how the effect will be shown and that enhancement can also occur.

Because the characteristic amplitude effect is observed in GaAs+Ge (Zurcher *et al.* 1982) to the same degree as it is in GaAs+Sb, we suggest it is ordered overlayers on the substrate (*e.g.*, GaAs) which plays a more important role in the process than does the type of ordered overlayer atom (*i.e.*, Sb versus Ge).

Evidence for non-uniform band shifting was observed at higher photon energies around 60 eV where the photoemission probe is more surface sensitive. Overlayer-induced amplitude changes of bulk band features were also observed at higher photon energies.

(4) Angle-resolved CFS spectra were collected at the $\bar{X}'$ and the $\bar{M}$ symmetry points for two polarizations, *viz.*, $A \perp MP$ and $A \parallel MP$. This approach involved scanning the photon energy while holding $k_{\parallel}$ fixed, and was useful in order to separate bulk band and surface state features.

Two Sb-derived states, S_4 and S_5 , were detected at the $\bar{M}$ -point. Two others, S_3/S_4 and S_6 , were also found at the $\bar{X}'$ -point. Their initial energies agree well with theoretical calculations (see Figure 72). The S_3/S_4 state at $\bar{X}'$ is about 1 eV lower than the calculations predict it to be. However, S_4 at $\bar{M}$ is in much closer agreement with the theory than any previous reports. A substrate surface state M_2 is observed near the VBM for the $\bar{M}$ -point and is in agreement with other workers who have studied the clean GaAs surface (Williams *et al.* 1978).

Future work would involve analyzing the ARCFS data in a similar manner to the structure plot method used in the normal emission EDC work. The bulk band structure is being calculated at the $\bar{X}'(Ga)$ and $\bar{M}(Ga)$ symmetry points in the SBZ by Calandra's group. These calculations are used to establish the theoretical structure plots which are cross-correlated with the experimental structure plots to determine the component of momentum perpendicular to the sample surface. After this cross-correlation, initial and final band assignments can be made and the bulk band states located on the energy band diagram. Doing this has several advantages:

- (1) Surface-related states can be separated from the bulk band states based on the way these states plot on the energy level diagram (*i.e.*, dispersion).
- (2) Detailed study of the energy shifts induced by the overlayer can be undertaken. Any anomalous energy shifting, such as non-uniform band shifting can possibly be inferred.

(3) Characteristic amplitude attenuations and enhancements can be characterized and possibly related to the location of hybridization gaps as in the case of normal emission.

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APPENDICES

APPENDIX A

NORMAL EMISSION EDC DATA
POLARIZATION ANGLE 0

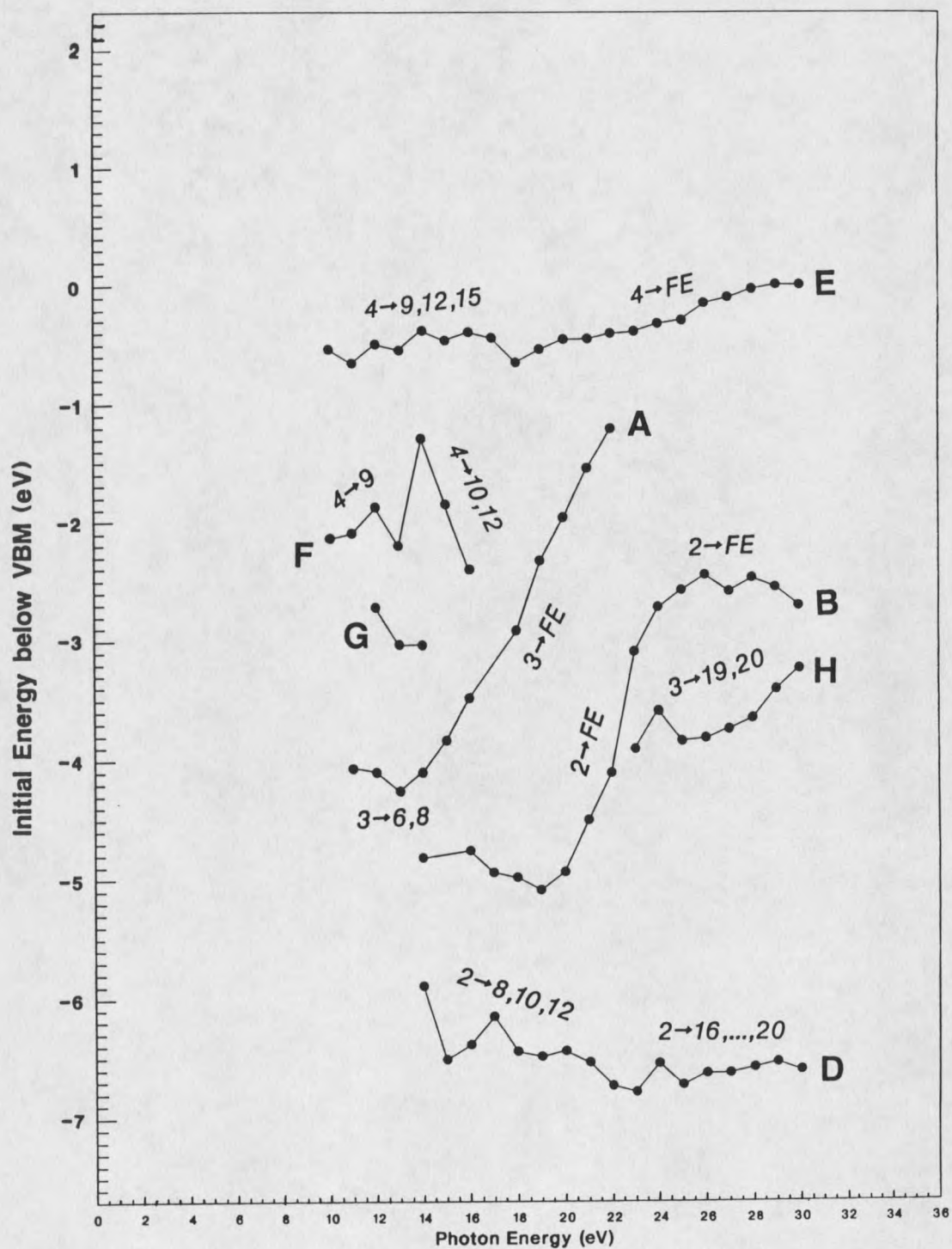


Figure 73. Experimental structure plot for GaAs(110), pol. 0.

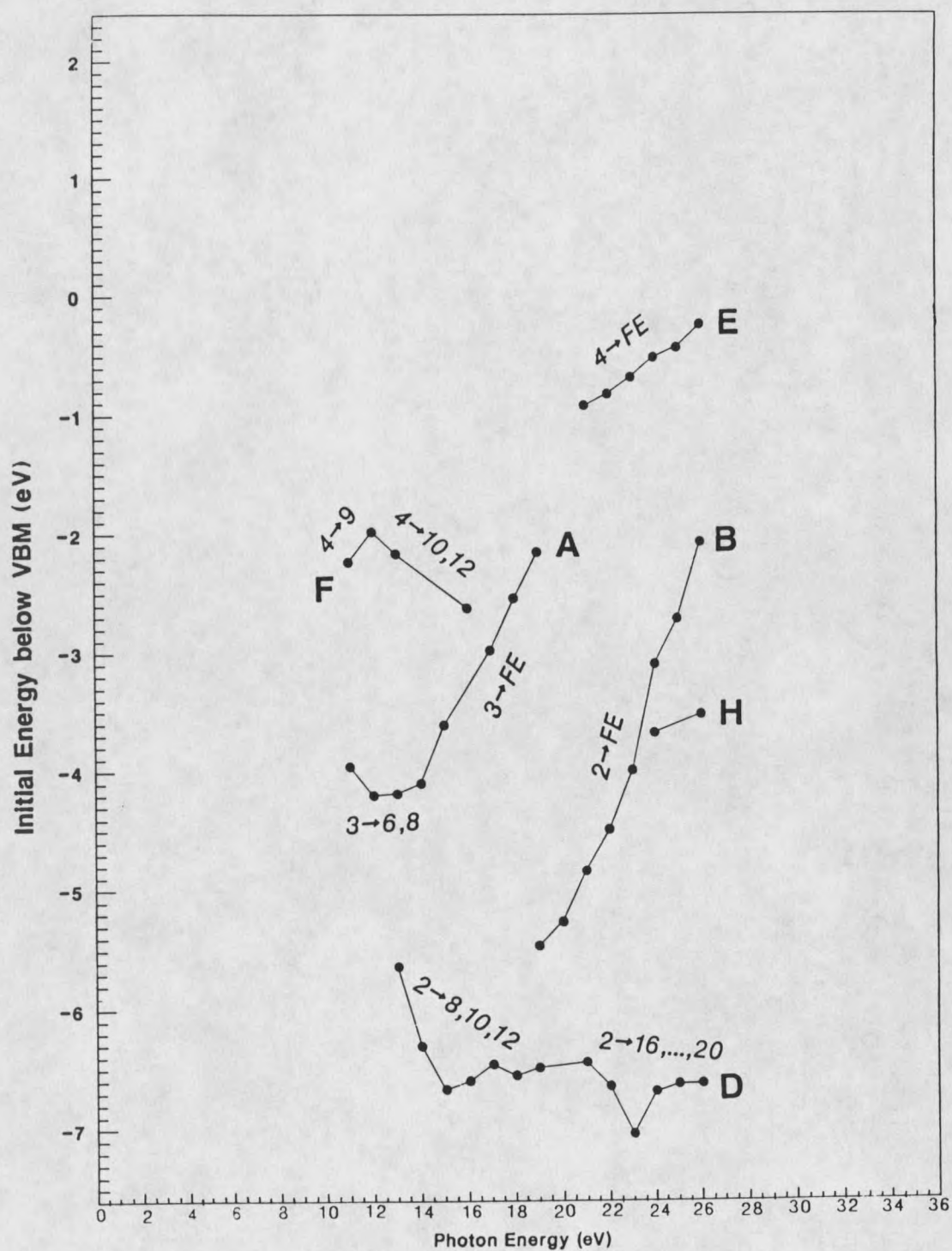


Figure 74. Experimental structure plot for GaAs(110)+Sb(0.6ML) for pol. 0.

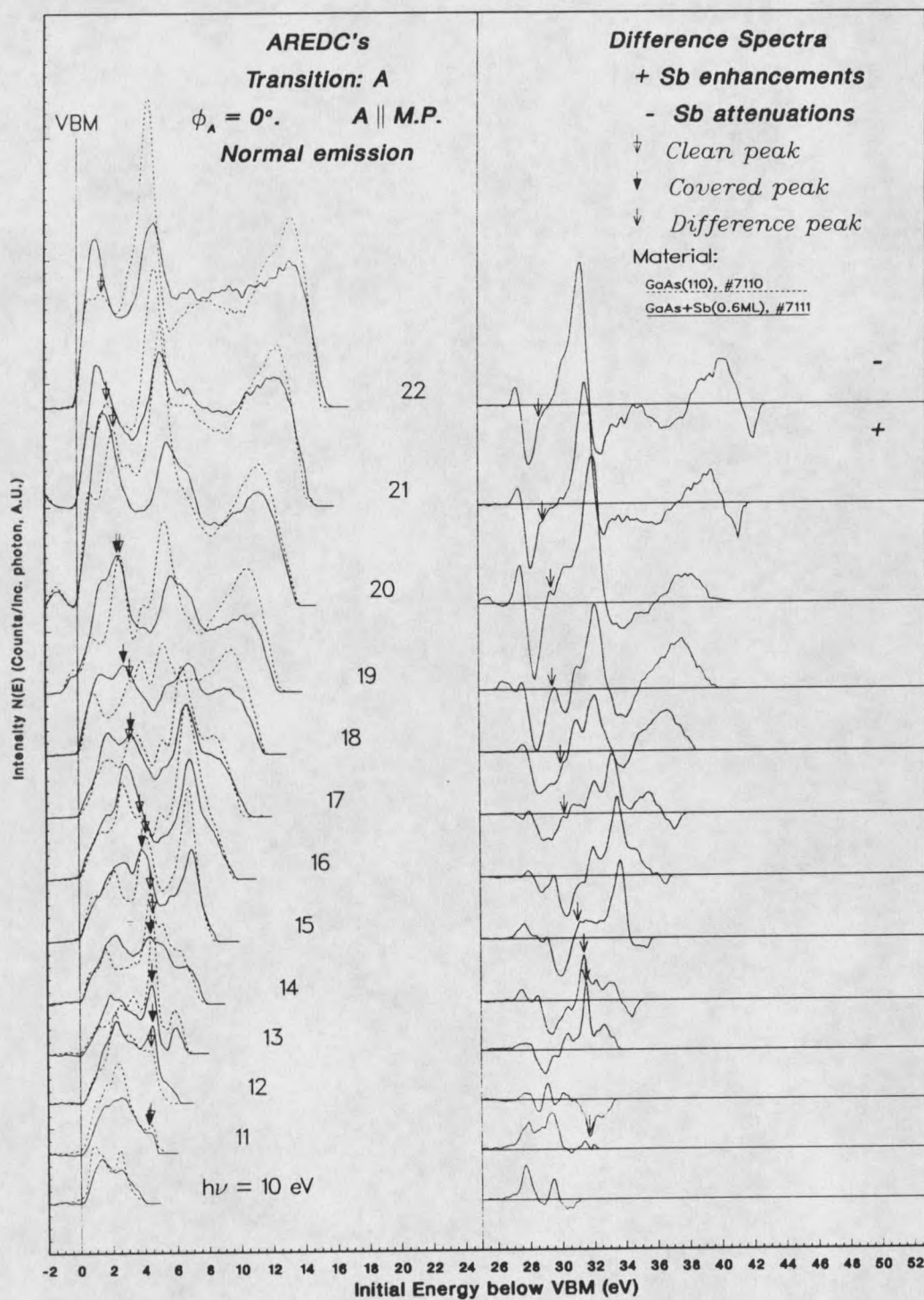


Figure 75. EDC difference spectra, transition A, pol. 0, $h\nu=10-22$ eV.

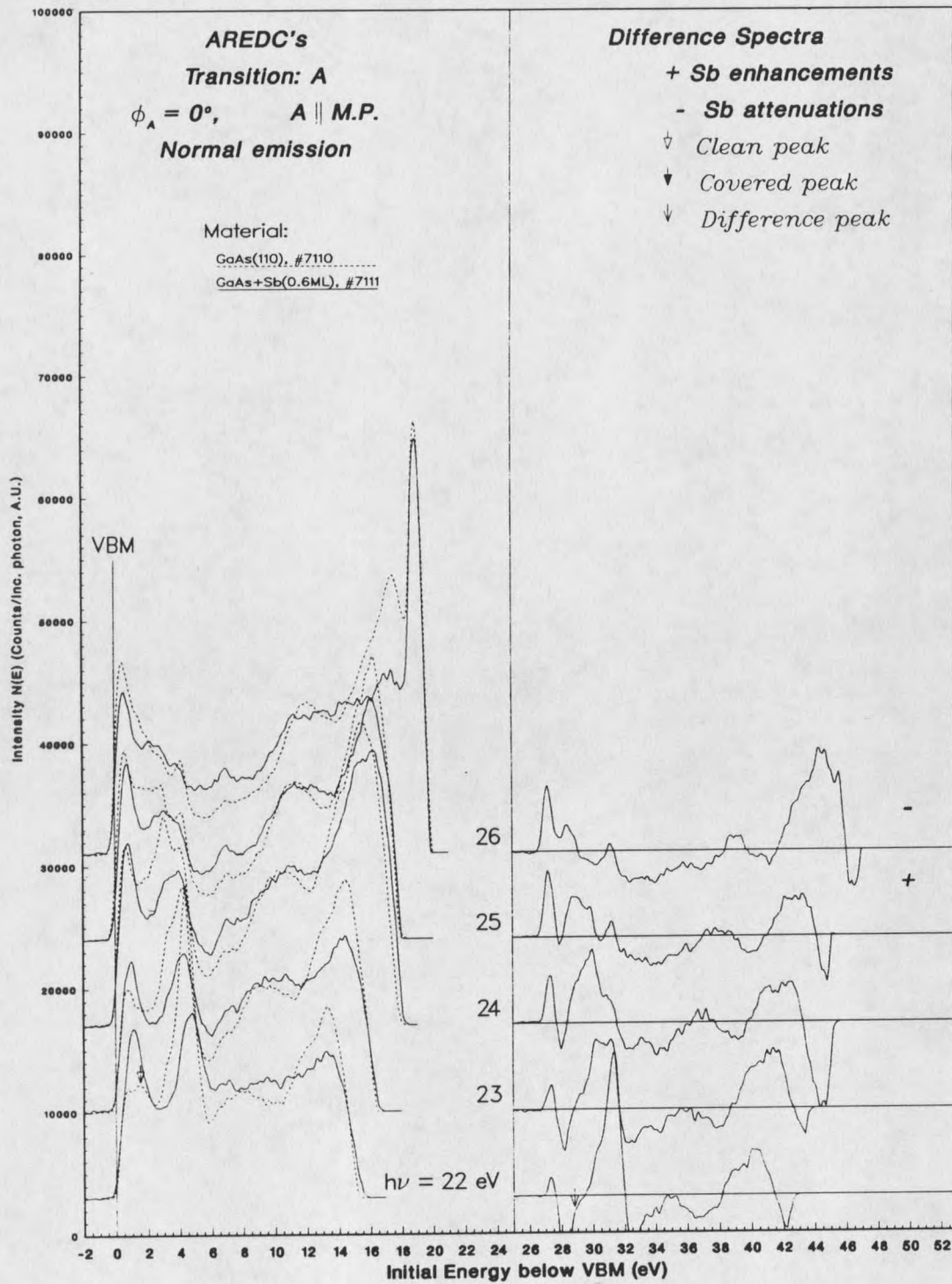


Figure 76. EDC difference spectra, transition A, pol. 0, $h\nu=22-26 \text{ eV}$.

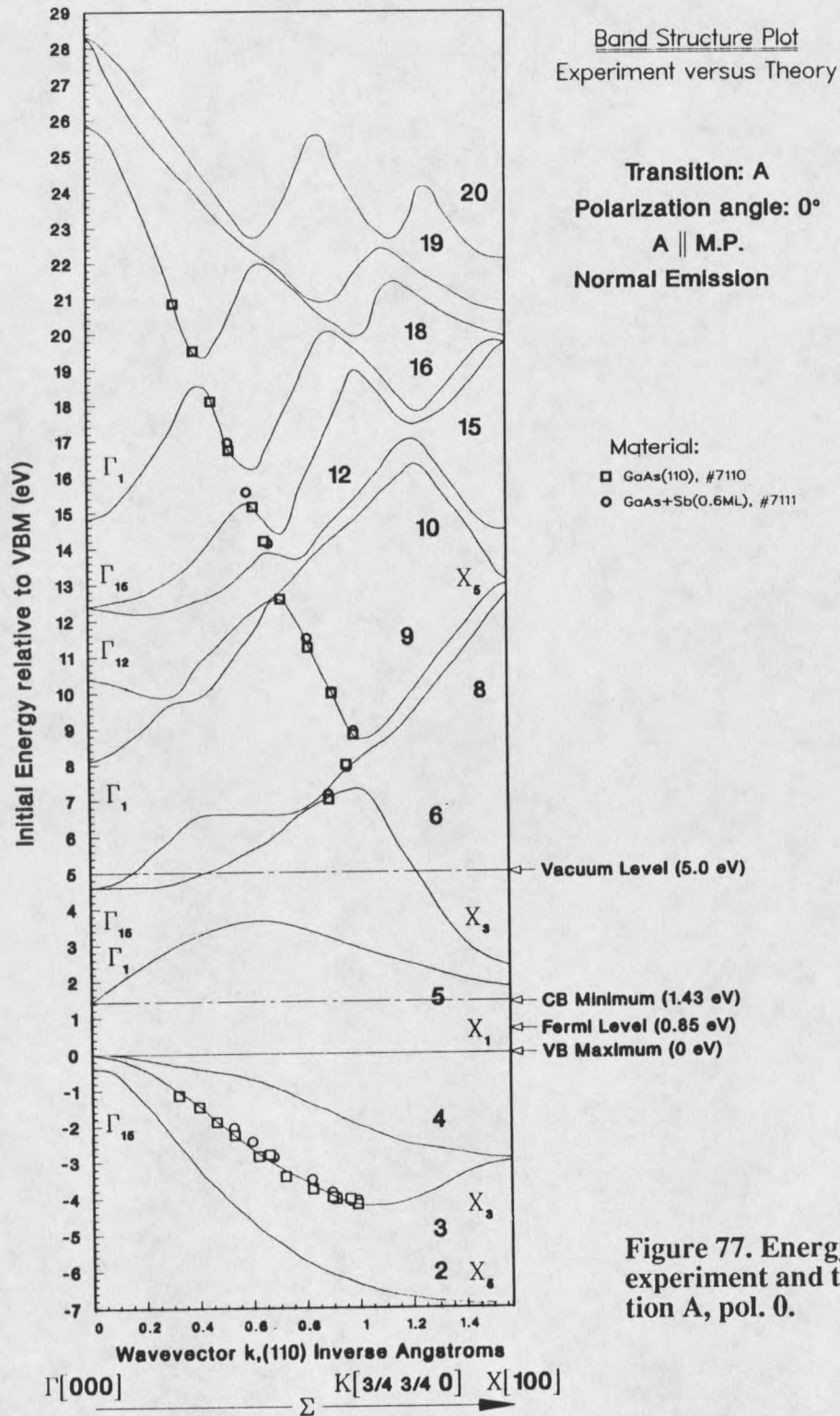


Figure 77. Energy bands of experiment and theory, transition A, pol. 0.

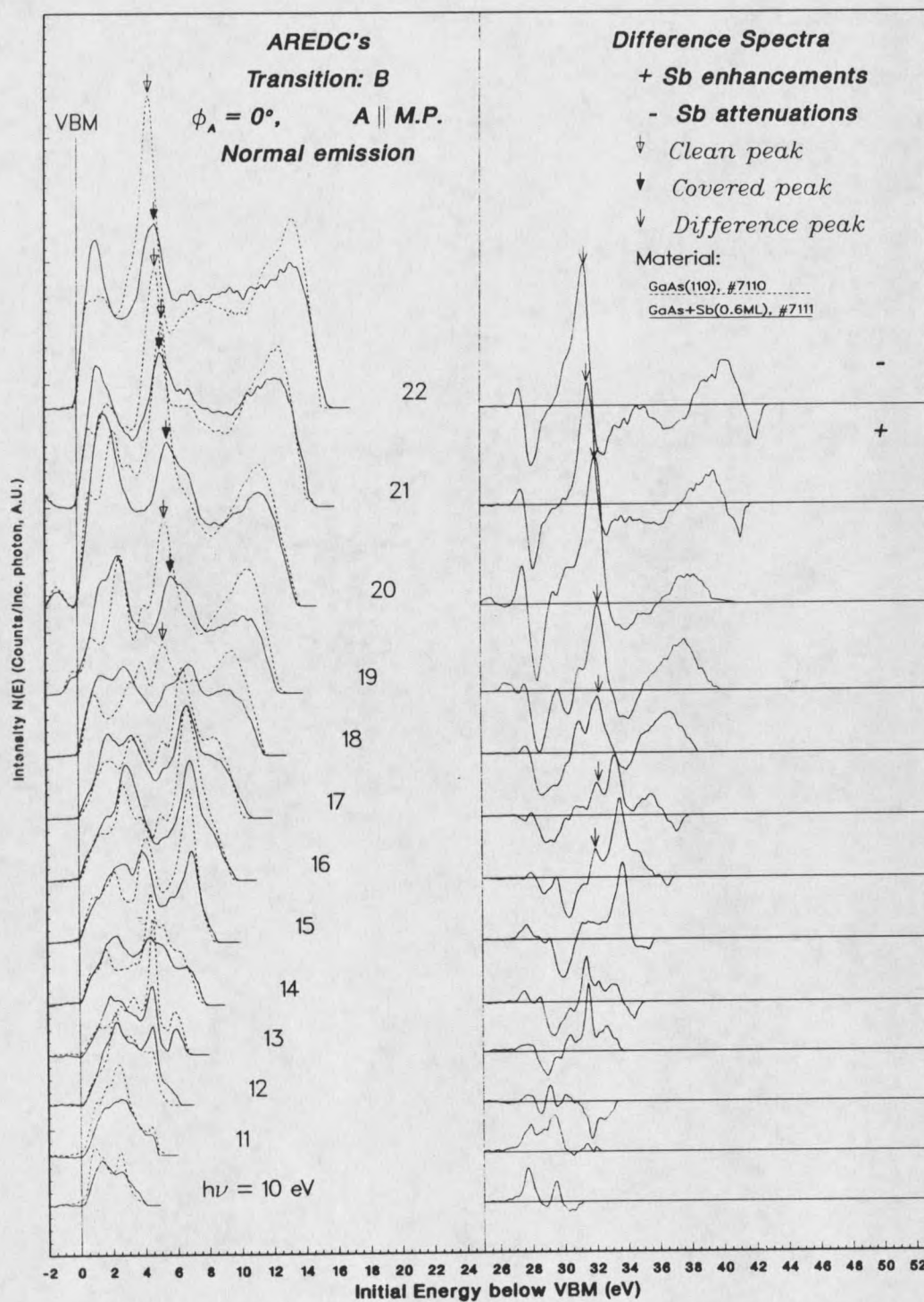


Figure 78. EDC difference spectra, transition B, pol. 0, $h\nu=10-22$ eV.

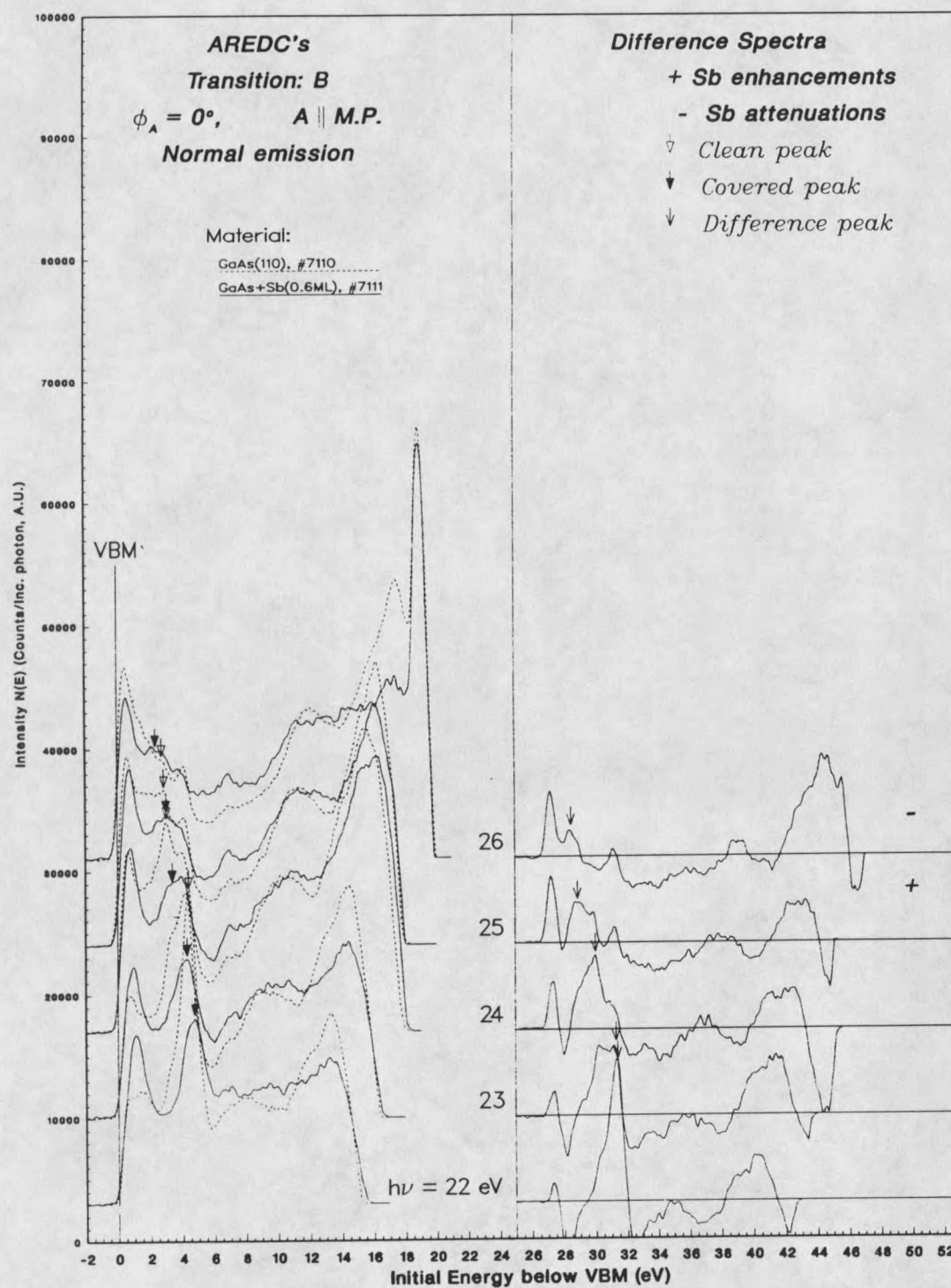


Figure 79. EDC difference spectra, transition B, pol. 0, $h\nu=22-26$ eV.

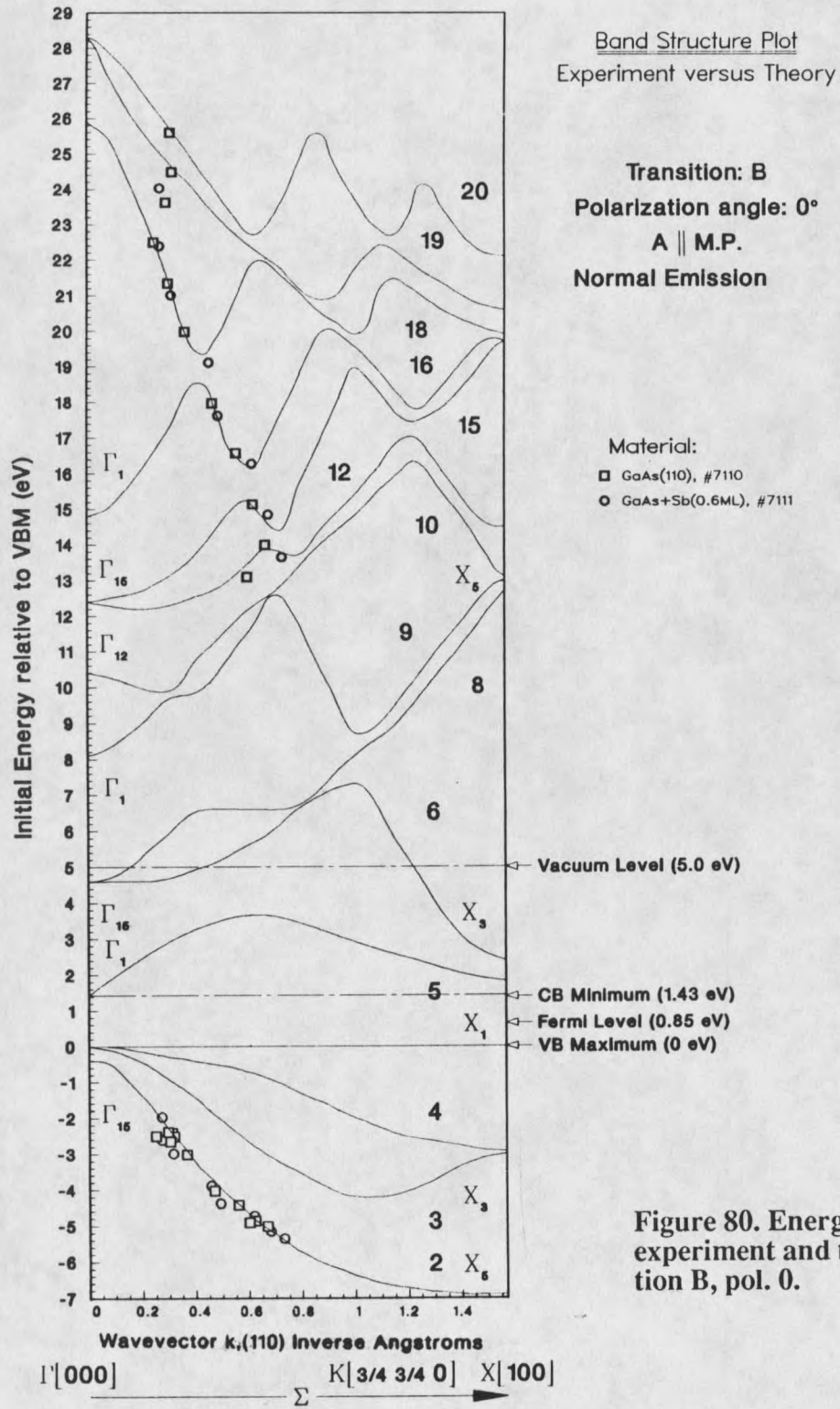


Figure 80. Energy bands of experiment and theory, transition B, pol. 0.

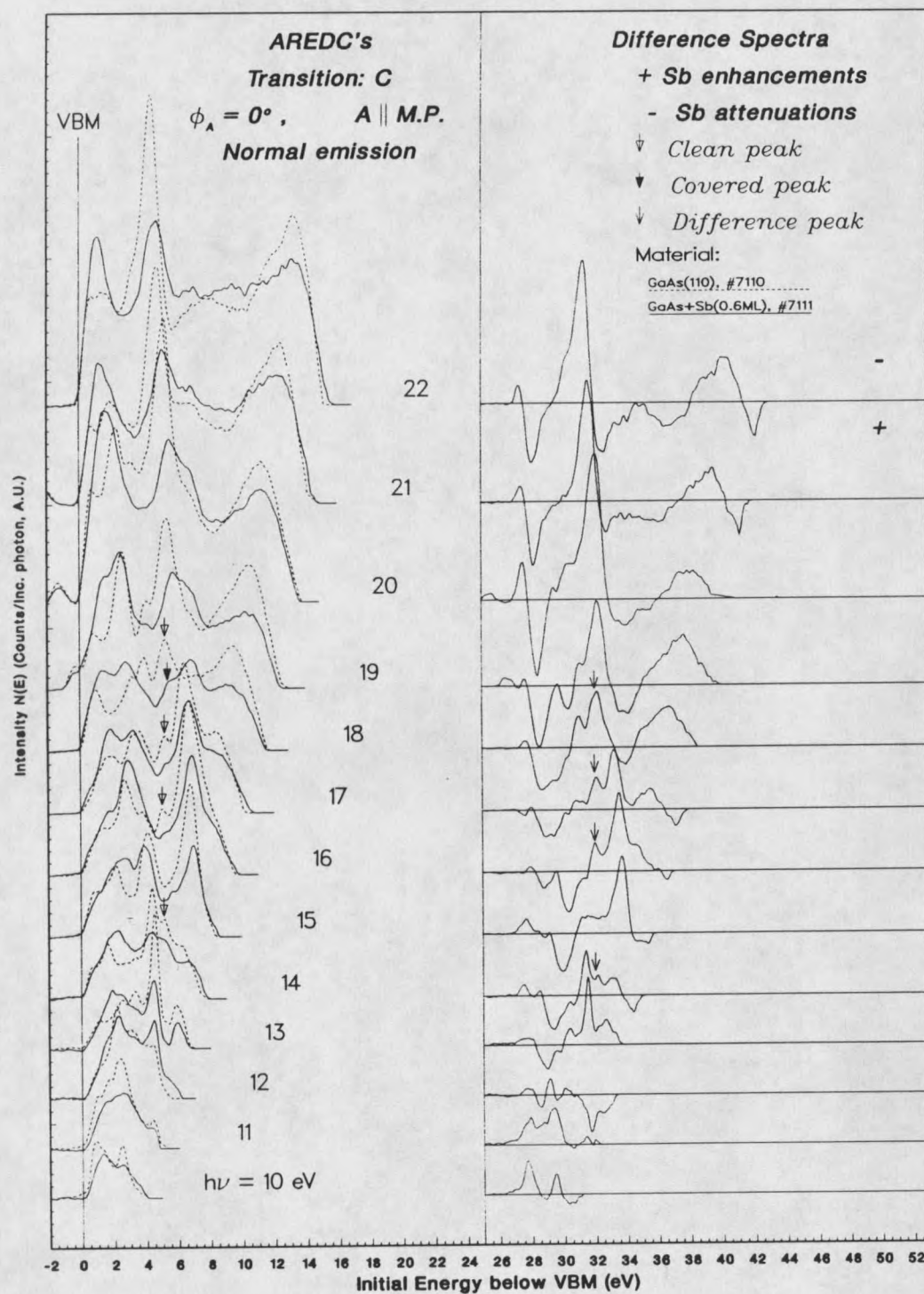


Figure 81. EDC difference spectra, transition C, pol. 0, $h\nu=10-22 \text{ eV}$.

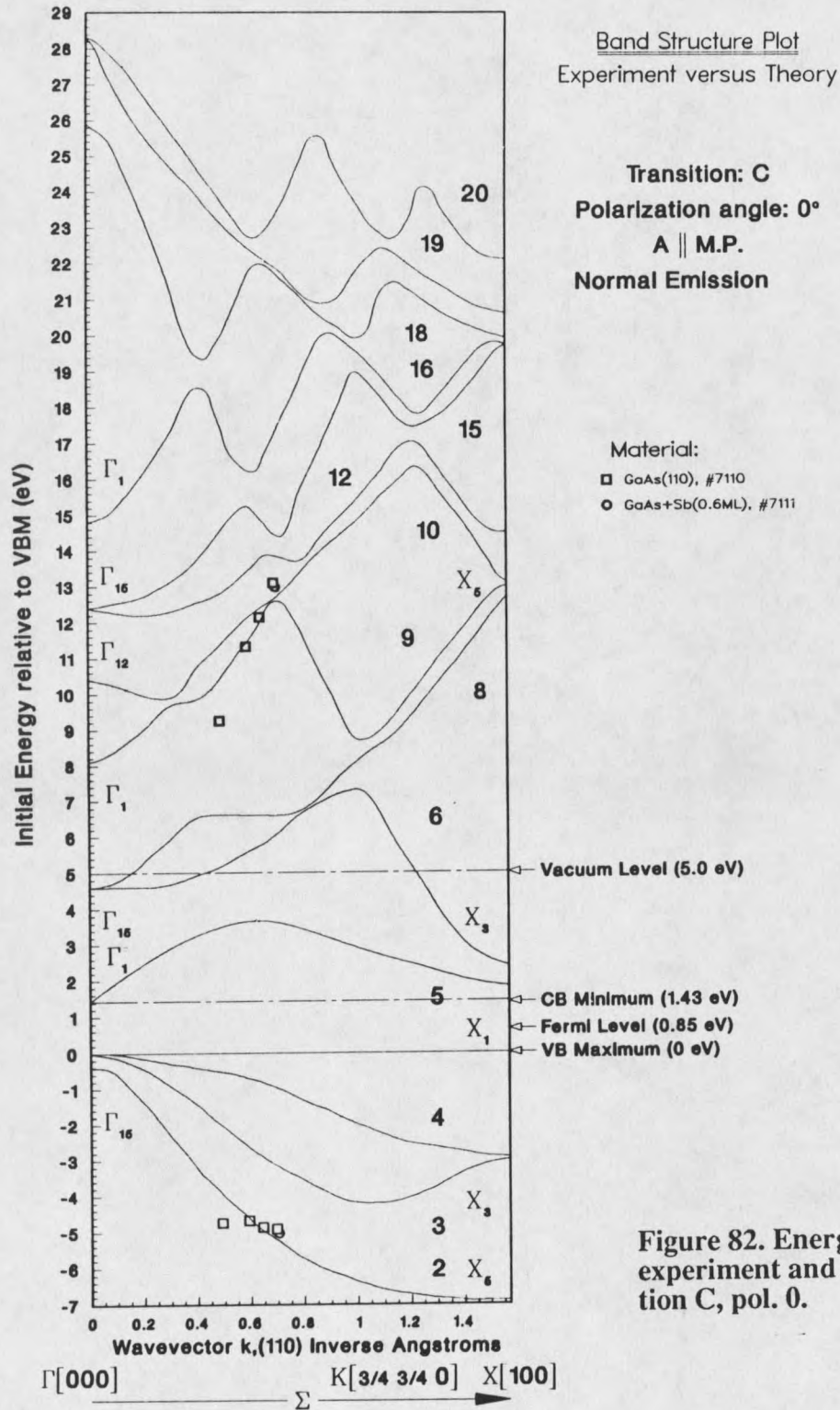


Figure 82. Energy bands of experiment and theory, transition C, pol. 0.

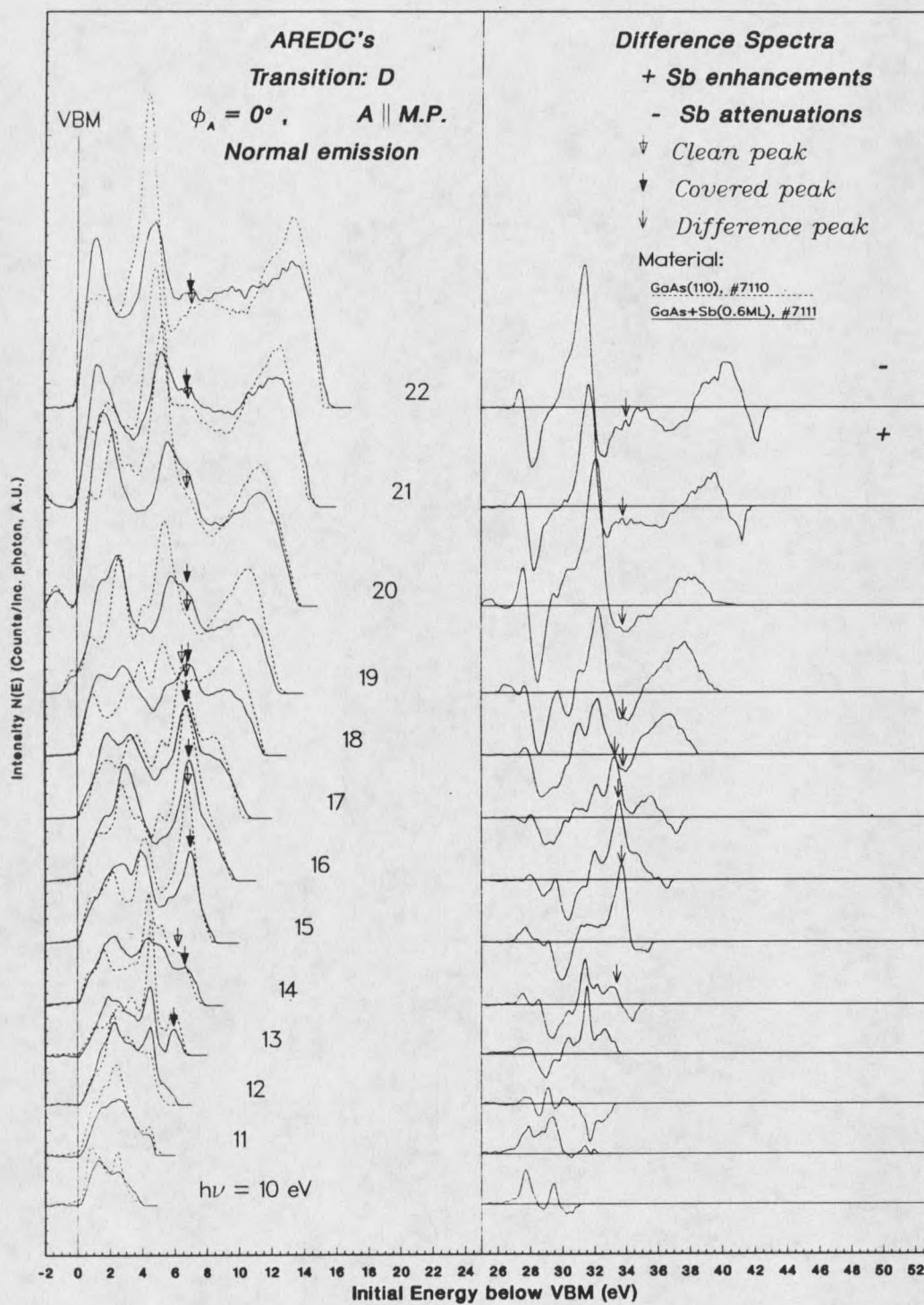


Figure 83. EDC difference spectra, transition D, pol. 0, $h\nu=10-22$ eV.

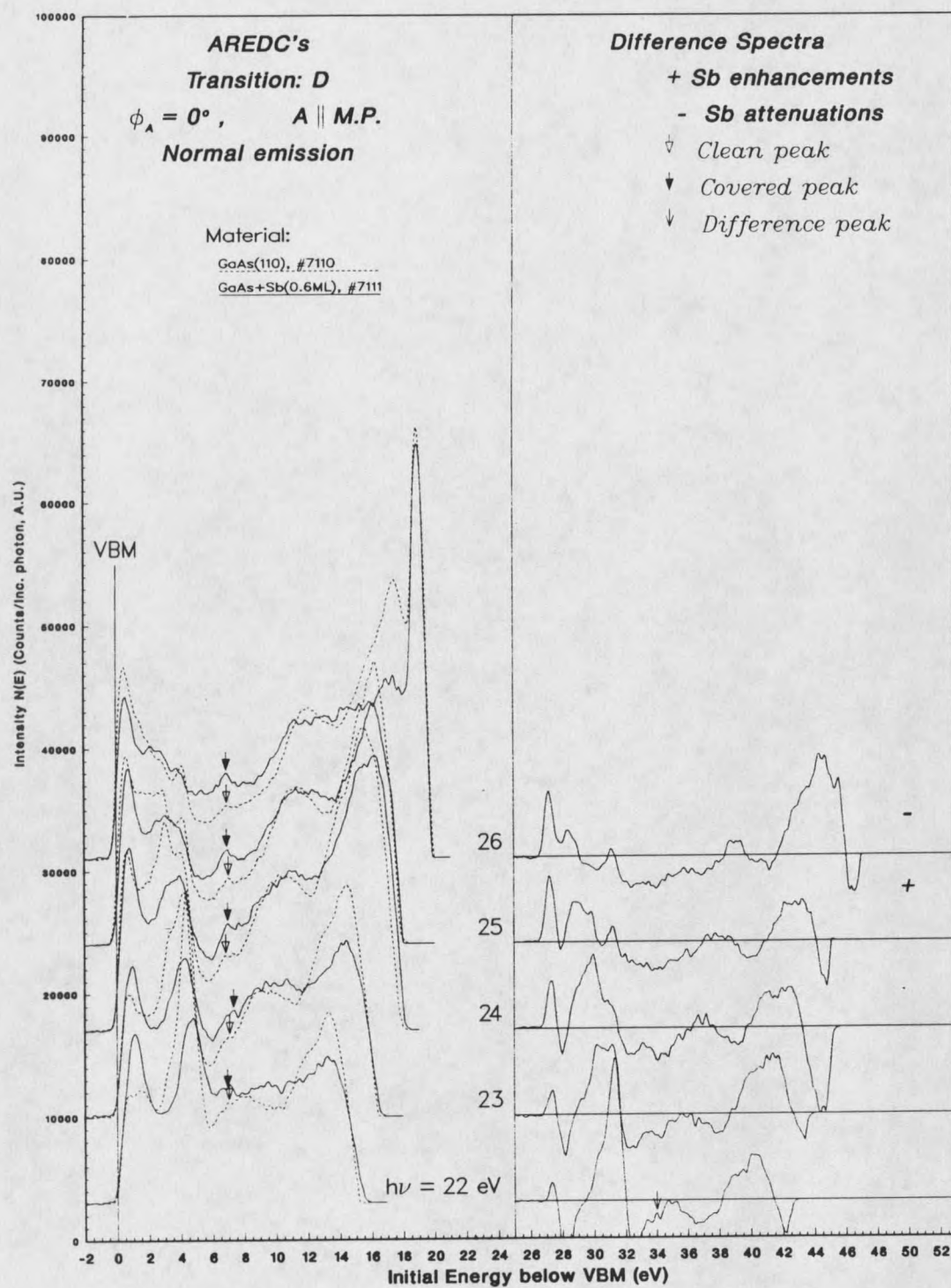


Figure 84. EDC difference spectra, transition D, pol. 0, $h\nu=22-30$ eV.

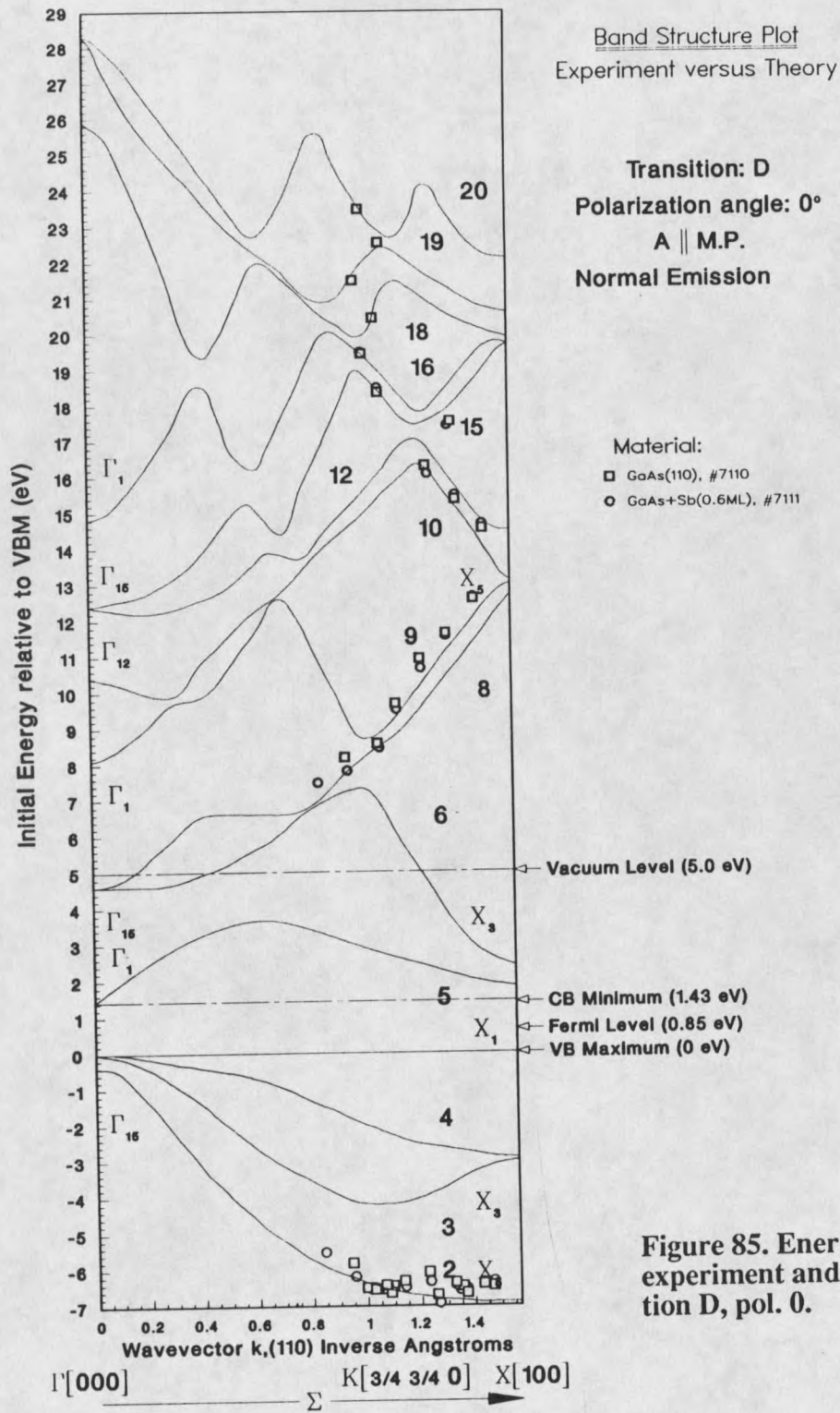


Figure 85. Energy bands of experiment and theory, transition D, pol. 0.

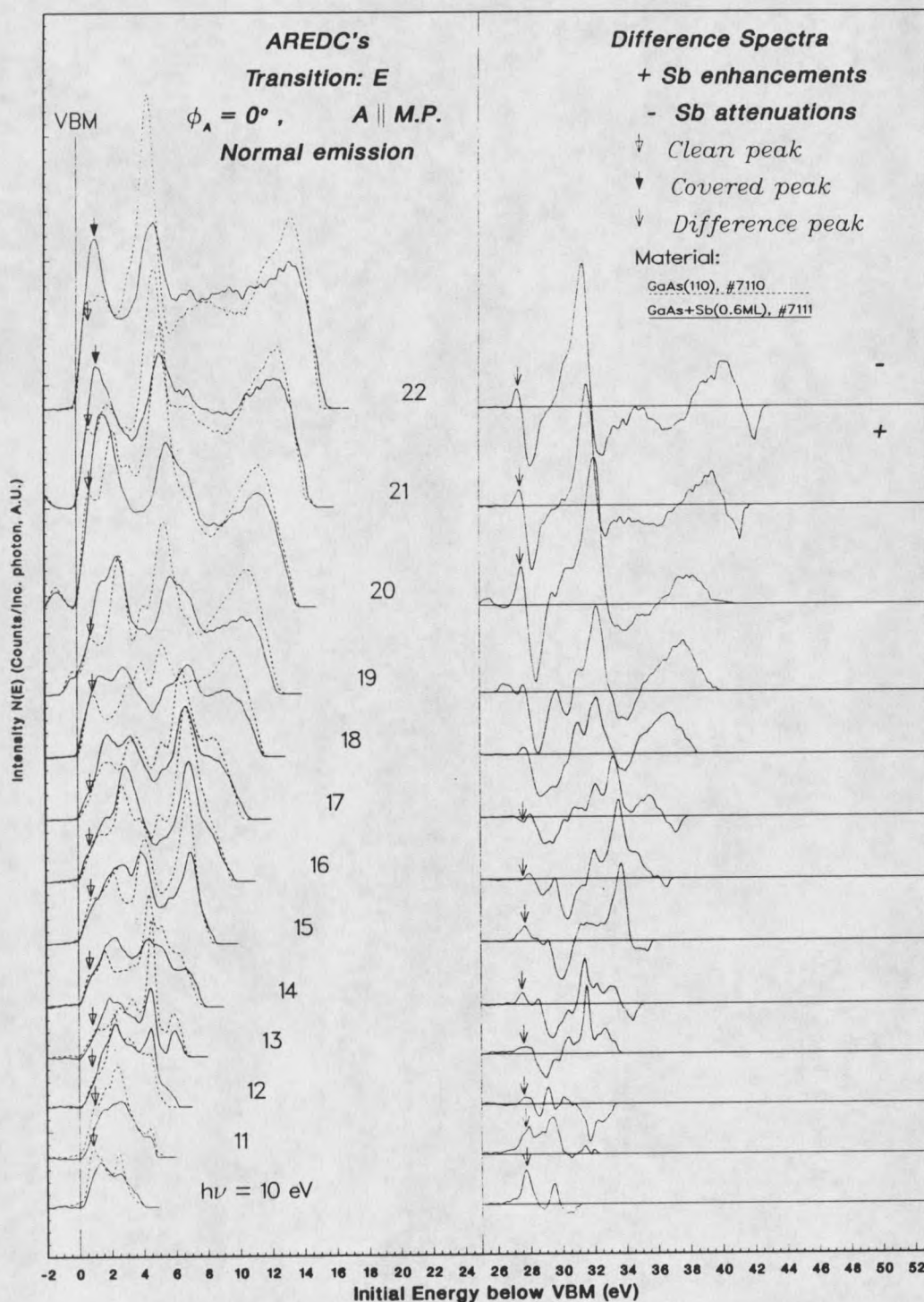


Figure 86. EDC difference spectra, transition E, pol. 0, $h\nu=10-22 \text{ eV}$.

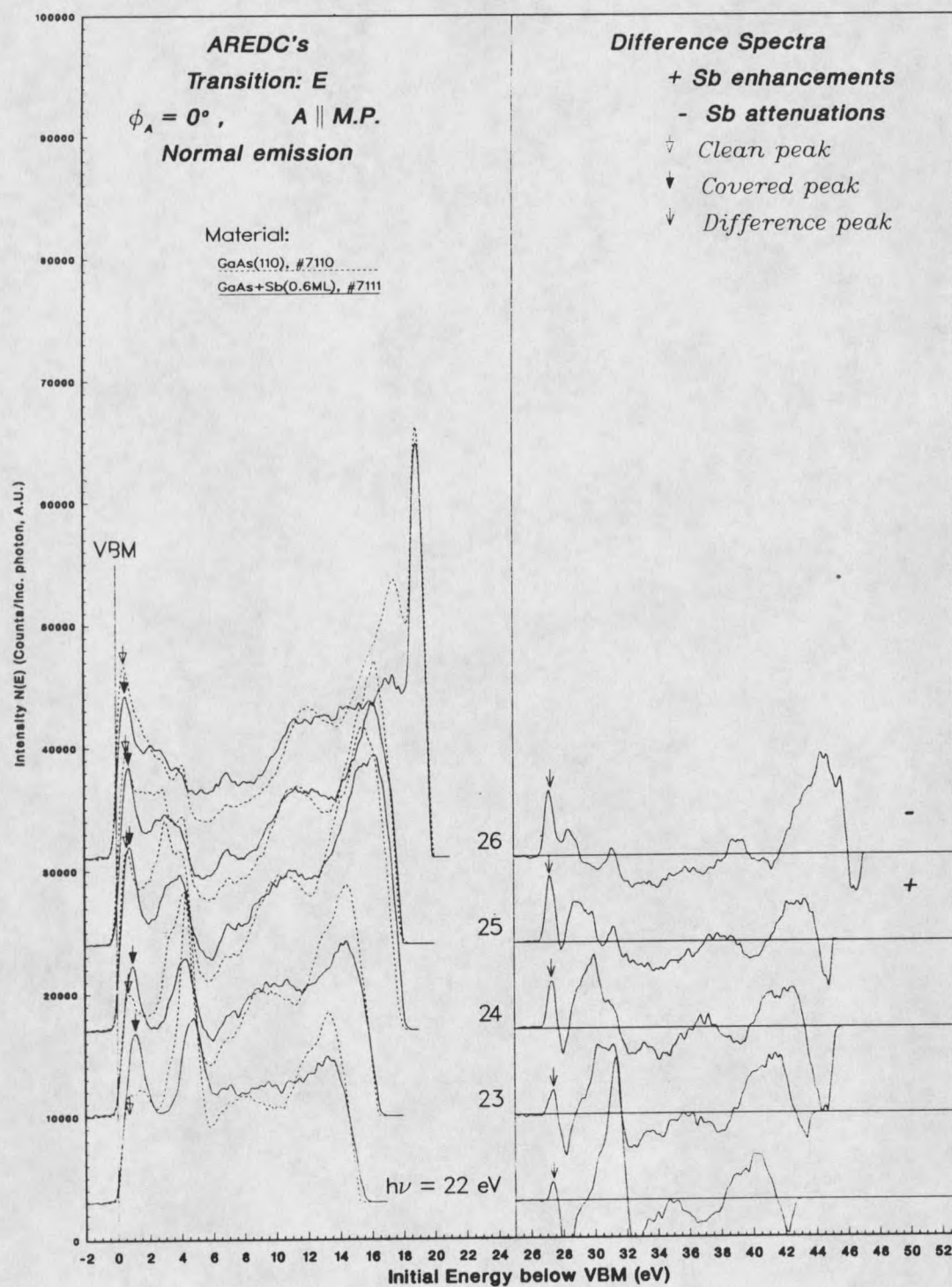
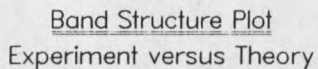


Figure 87. EDC difference spectra, transition E, pol. 0, $h\nu=22-26$ eV.



Transition: E
Polarization angle: 0°
A || M.P.
Normal Emission

Material:

- GaAs(110), #7110
- GaAs+Sb(0.6ML), #7111

- Vacuum Level (5.0 eV)

- CB Minimum (1.43 eV)

- Fermi Level (0.85 eV)

- VB Maximum (0 eV)

Figure 88. Energy bands of experiment and theory, transition E, pol. 0.

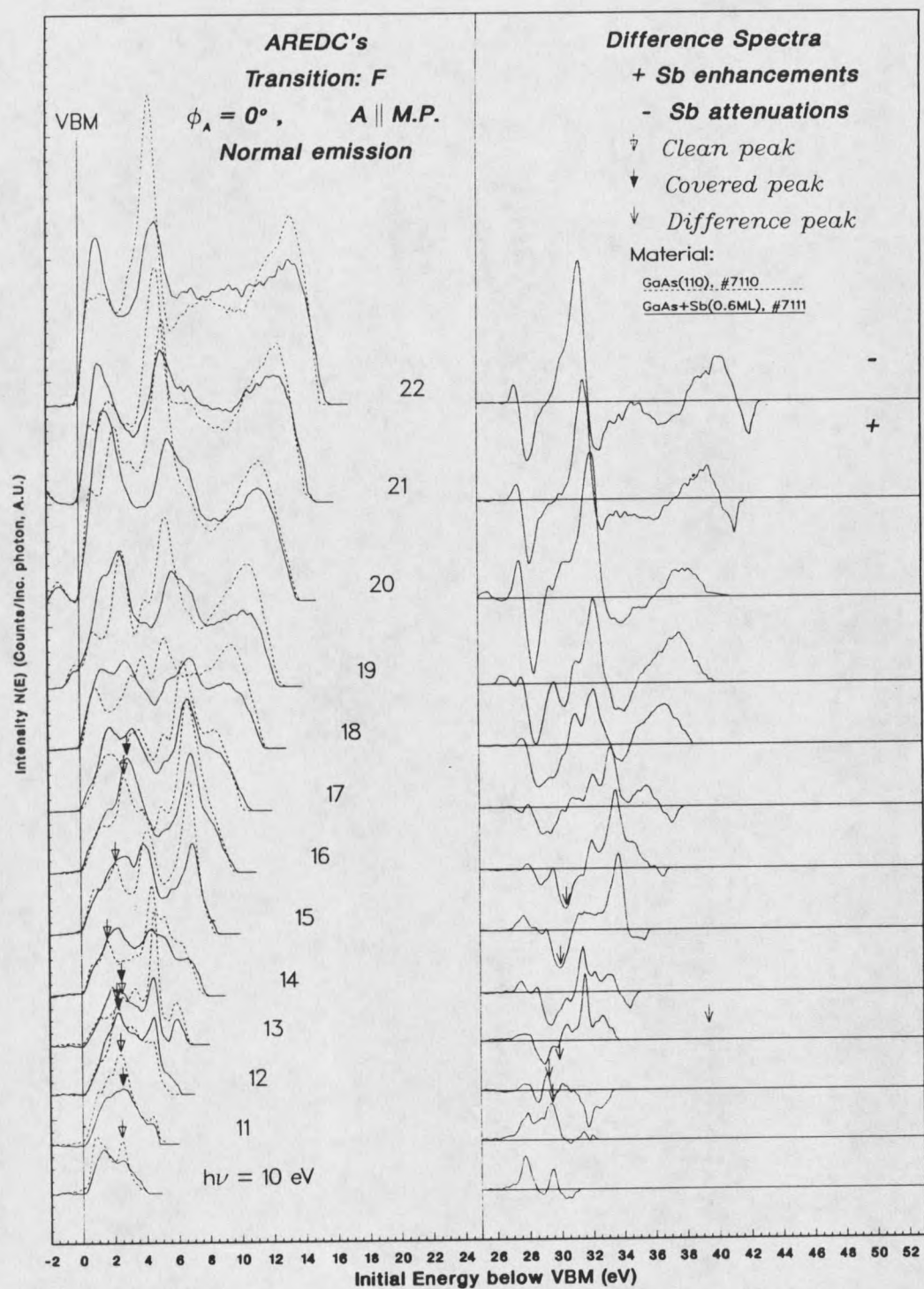


Figure 89. EDC difference spectra, transition F, pol. 0, $h\nu=10-22$ eV.

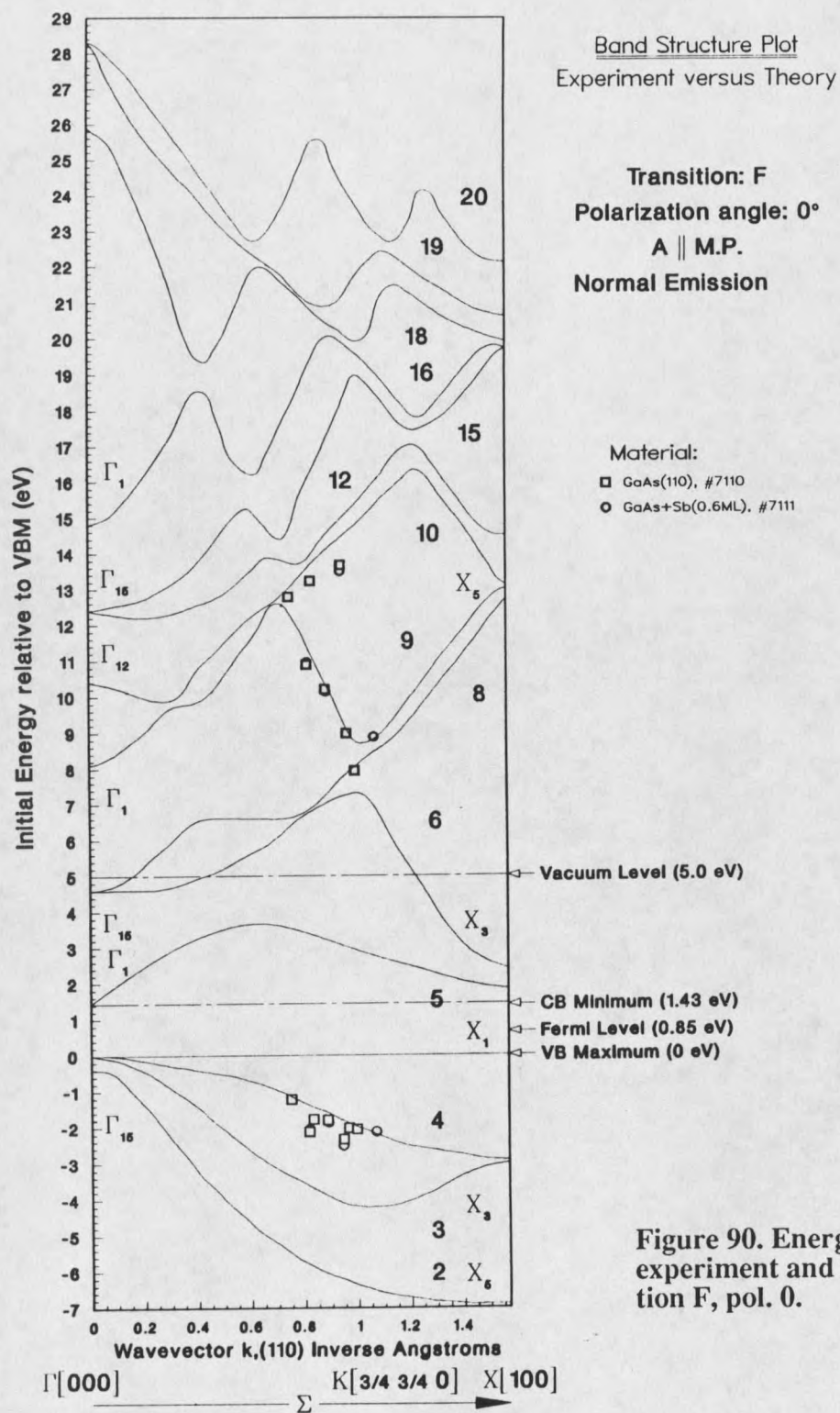


Figure 90. Energy bands of experiment and theory, transition F, pol. 0.

APPENDIX B

NORMAL EMISSION EDC DATA
POLARIZATION ANGLE 180

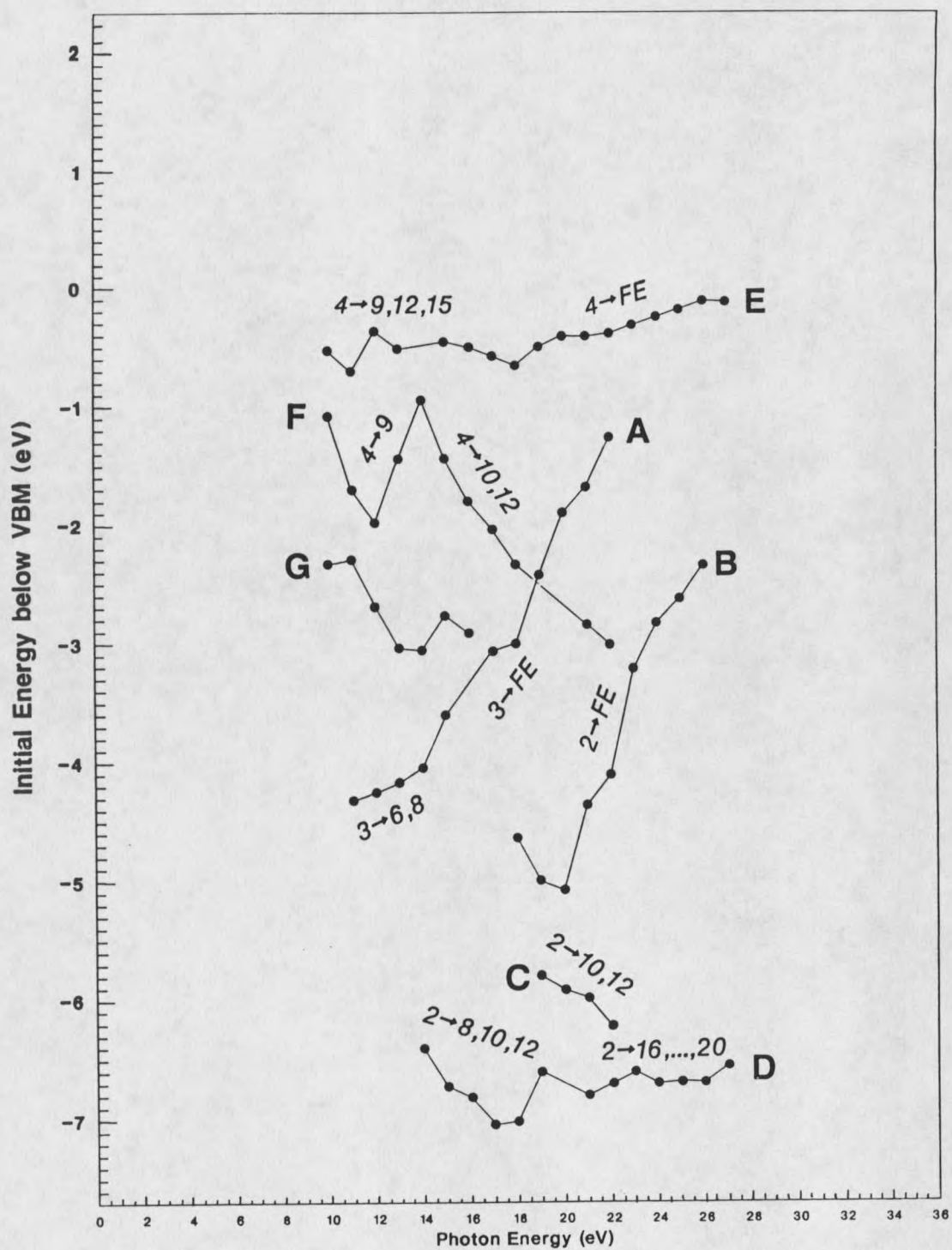


Figure 91. Experimental structure plot for GaAs(110), pol. 180.

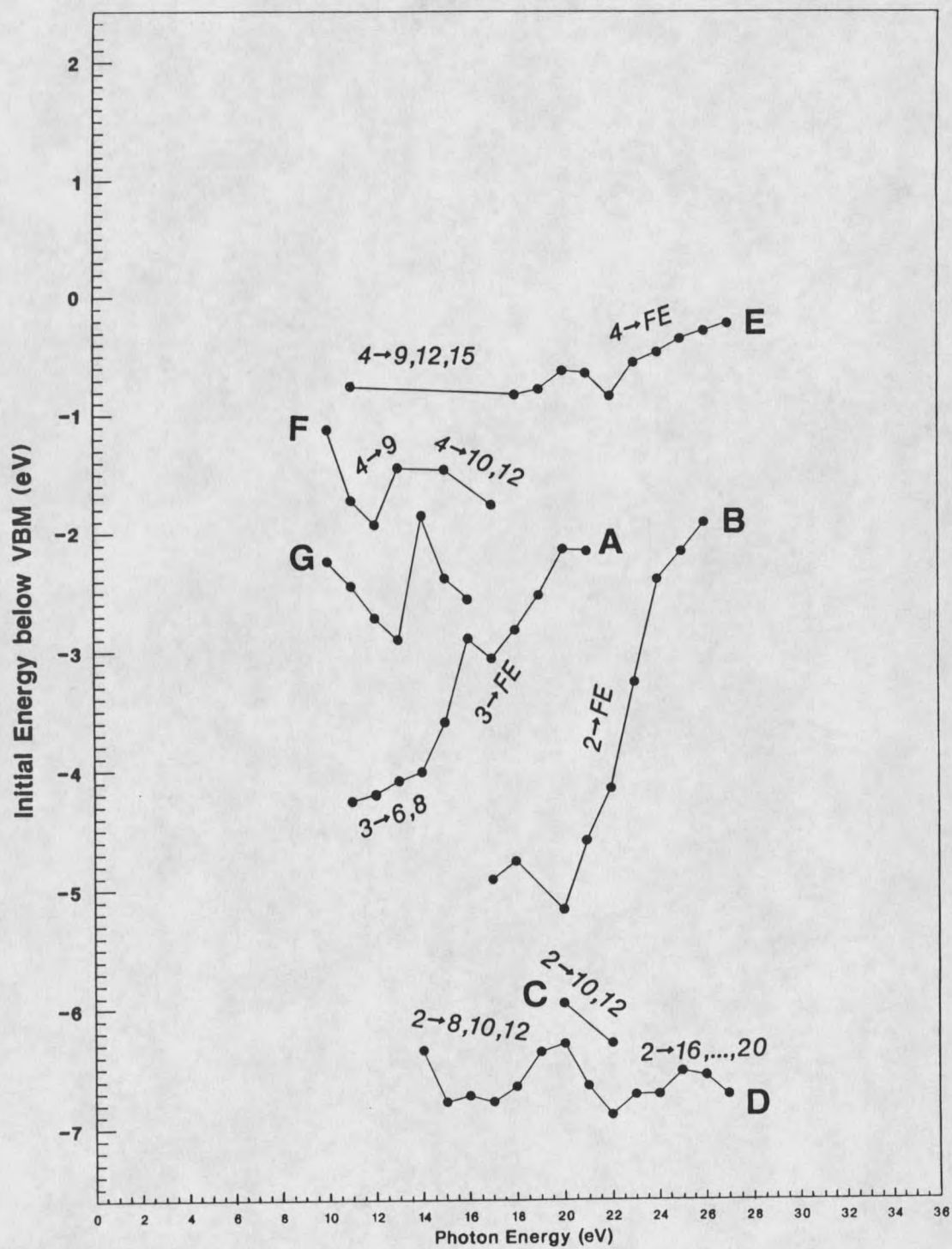


Figure 92. Experimental structure plot for GaAs(110)+Sb(0.6ML), pol. 180.

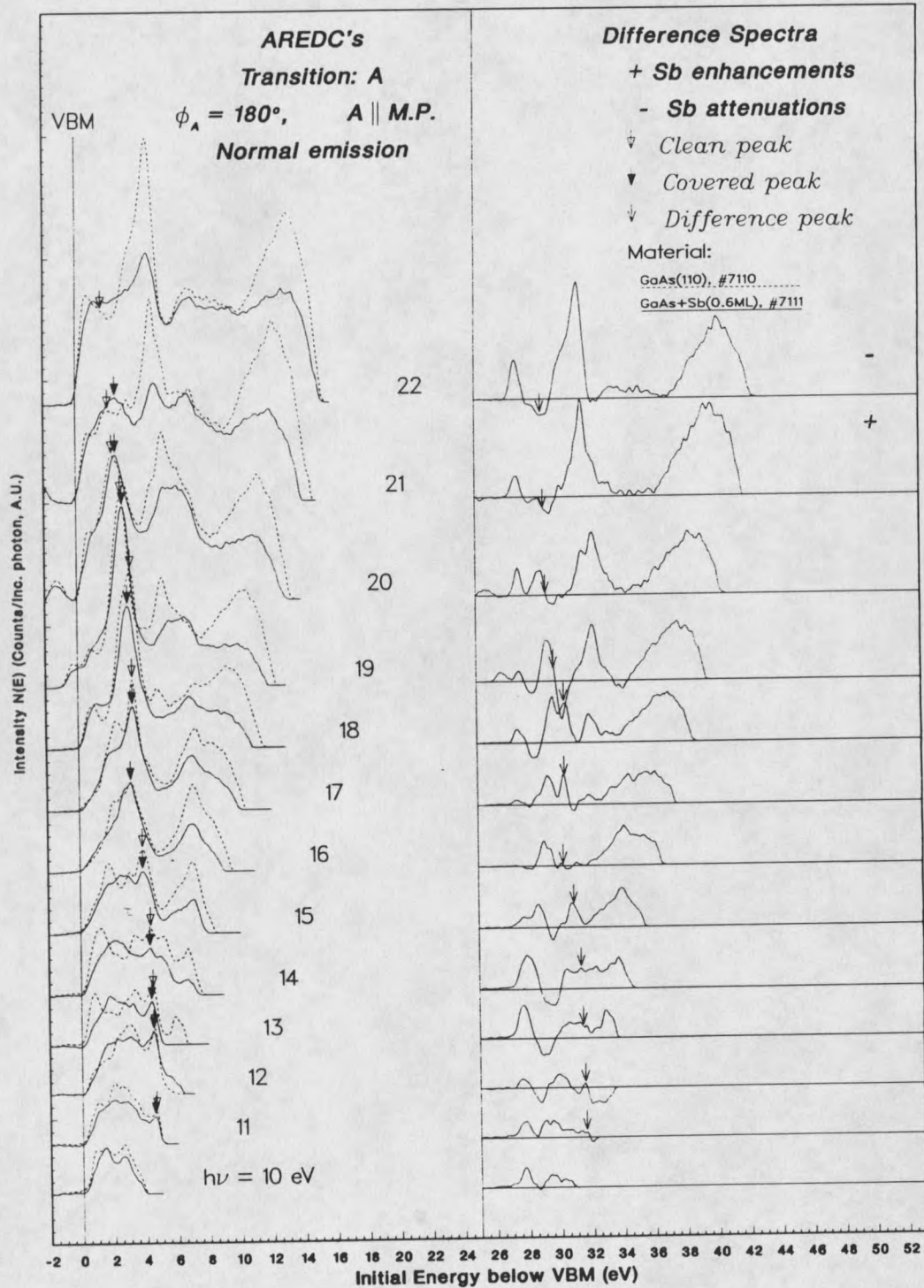


Figure 93. EDC difference spectra, transition A, pol. 180, $h\nu=10-22 \text{ eV}$.

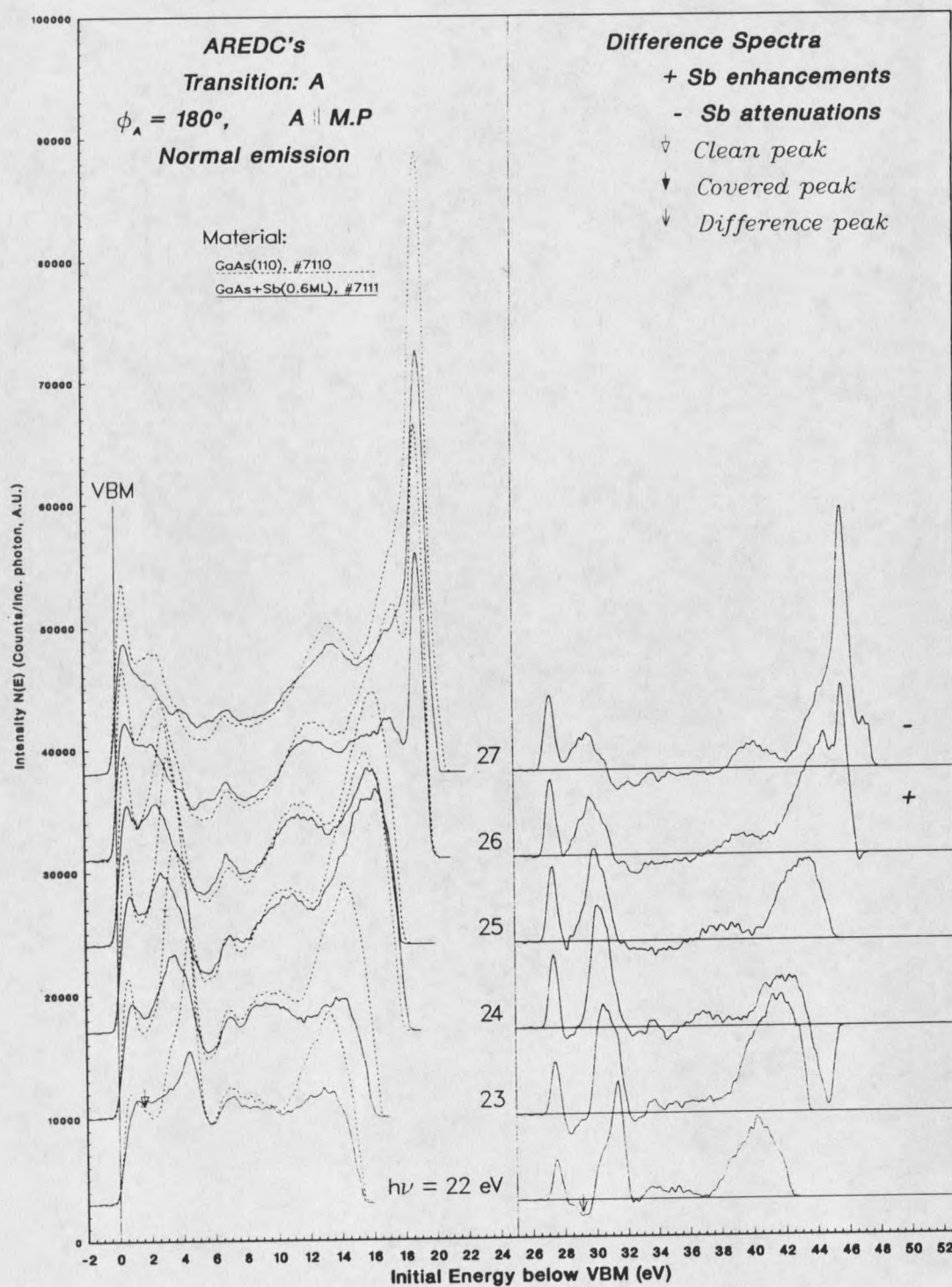


Figure 94. EDC difference spectra, transition A, pol. 180, $h\nu=22-30 \text{ eV}$.

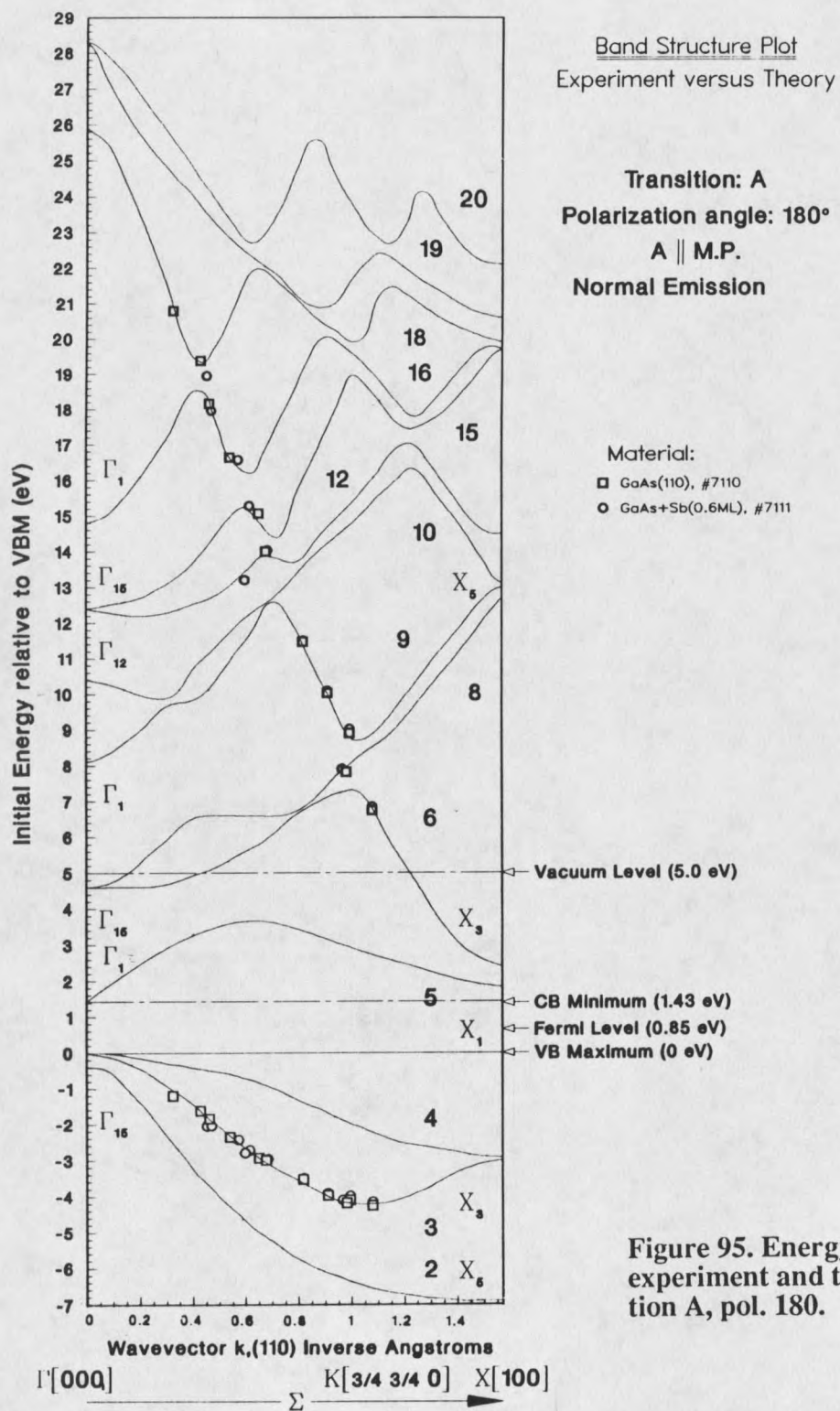


Figure 95. Energy bands of experiment and theory, transition A, pol. 180.

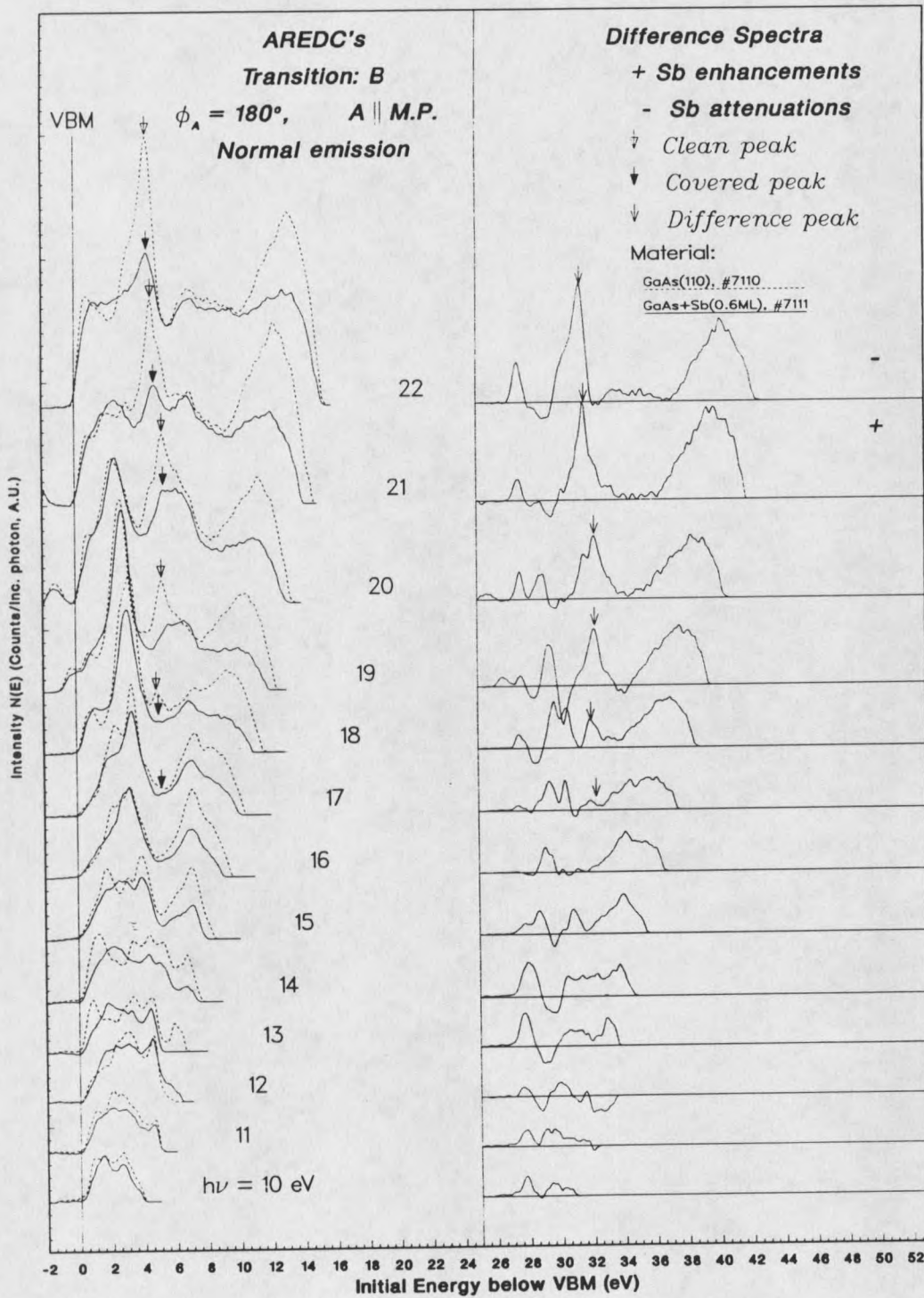


Figure 96. EDC difference spectra, transition B, pol. 180, $h\nu=10-22$ eV.

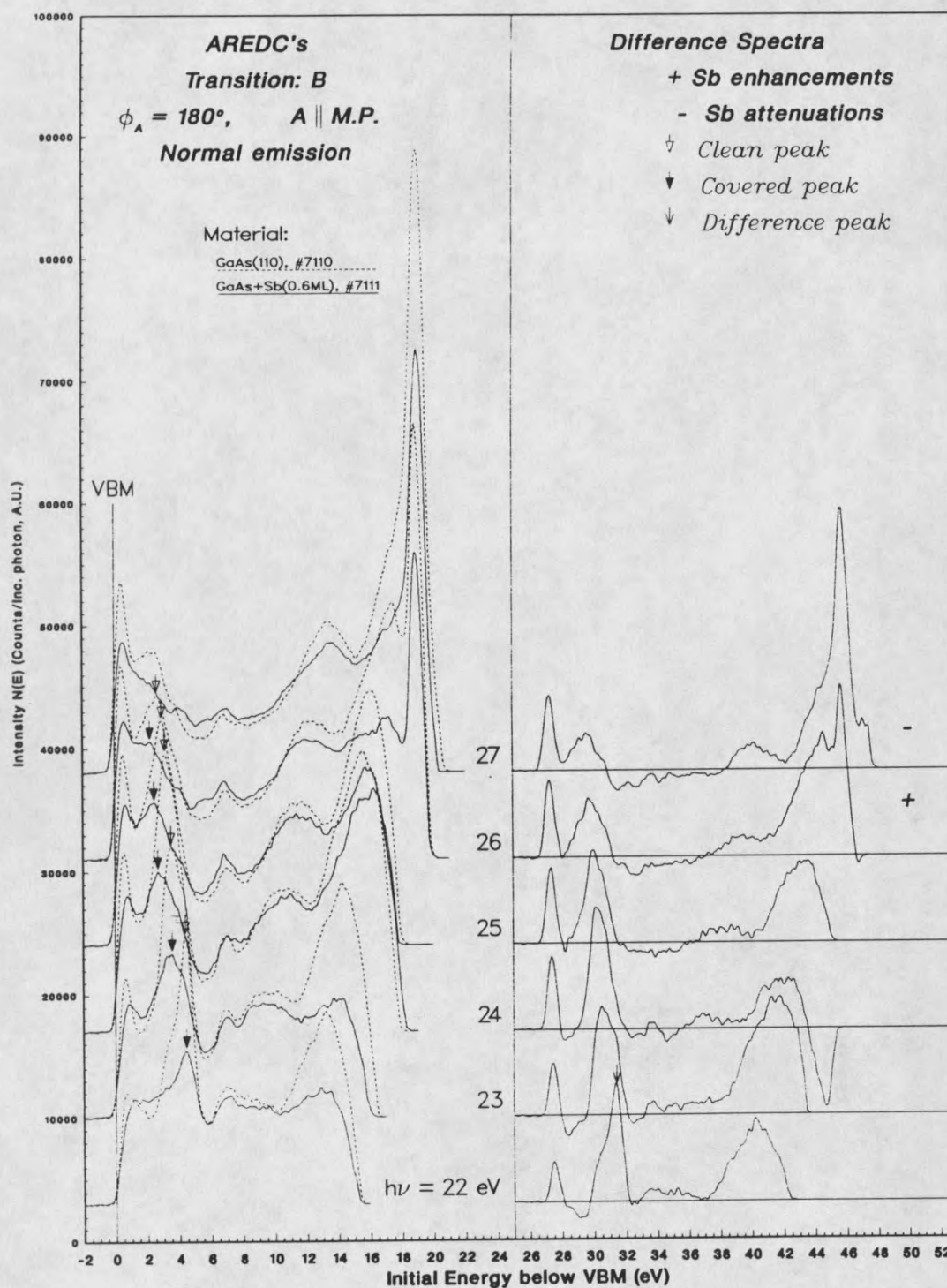


Figure 97. EDC difference spectra, transition B, pol. 180, $h\nu=22-30 \text{ eV}$.

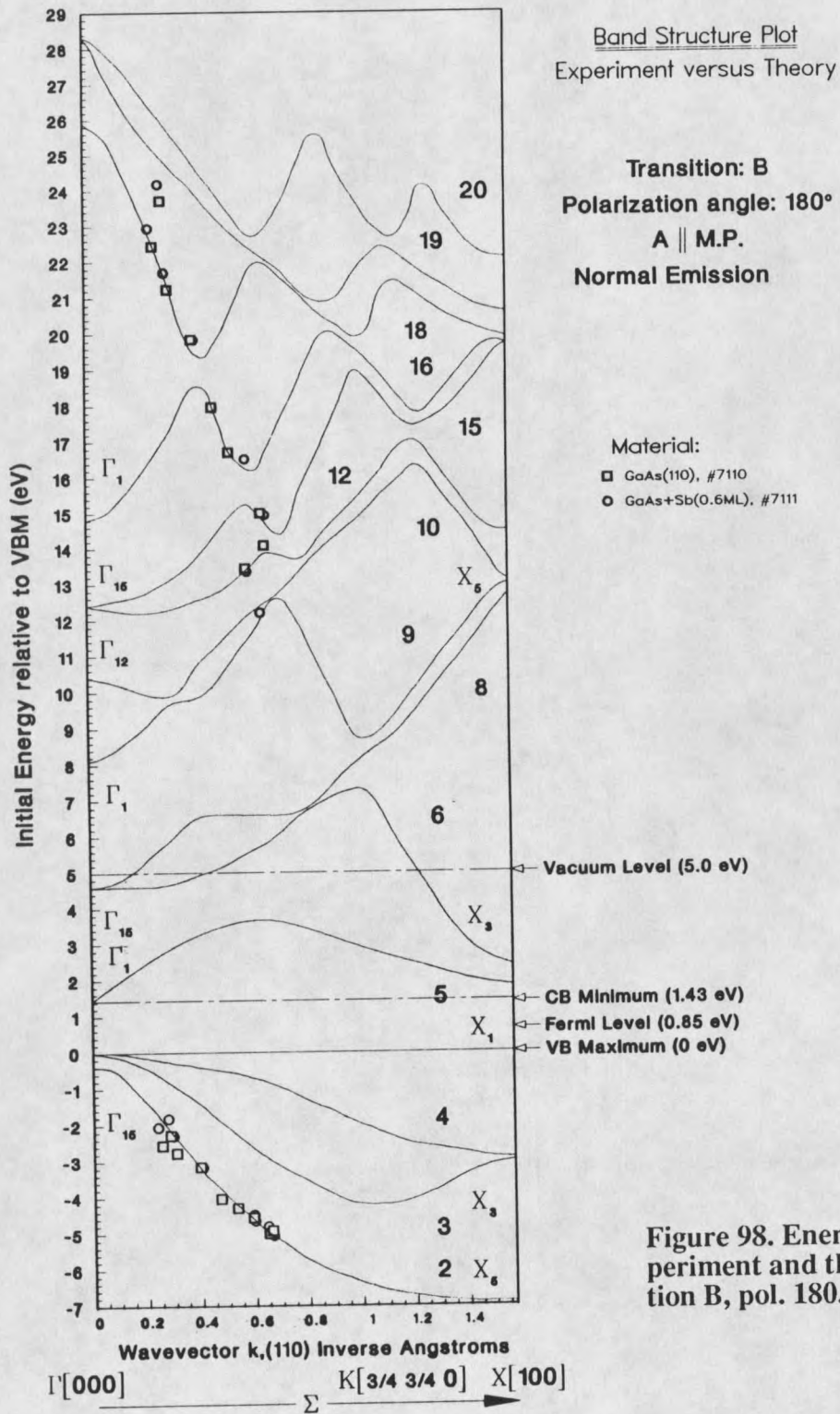


Figure 98. Energy bands experiment and theory, transition B, pol. 180.

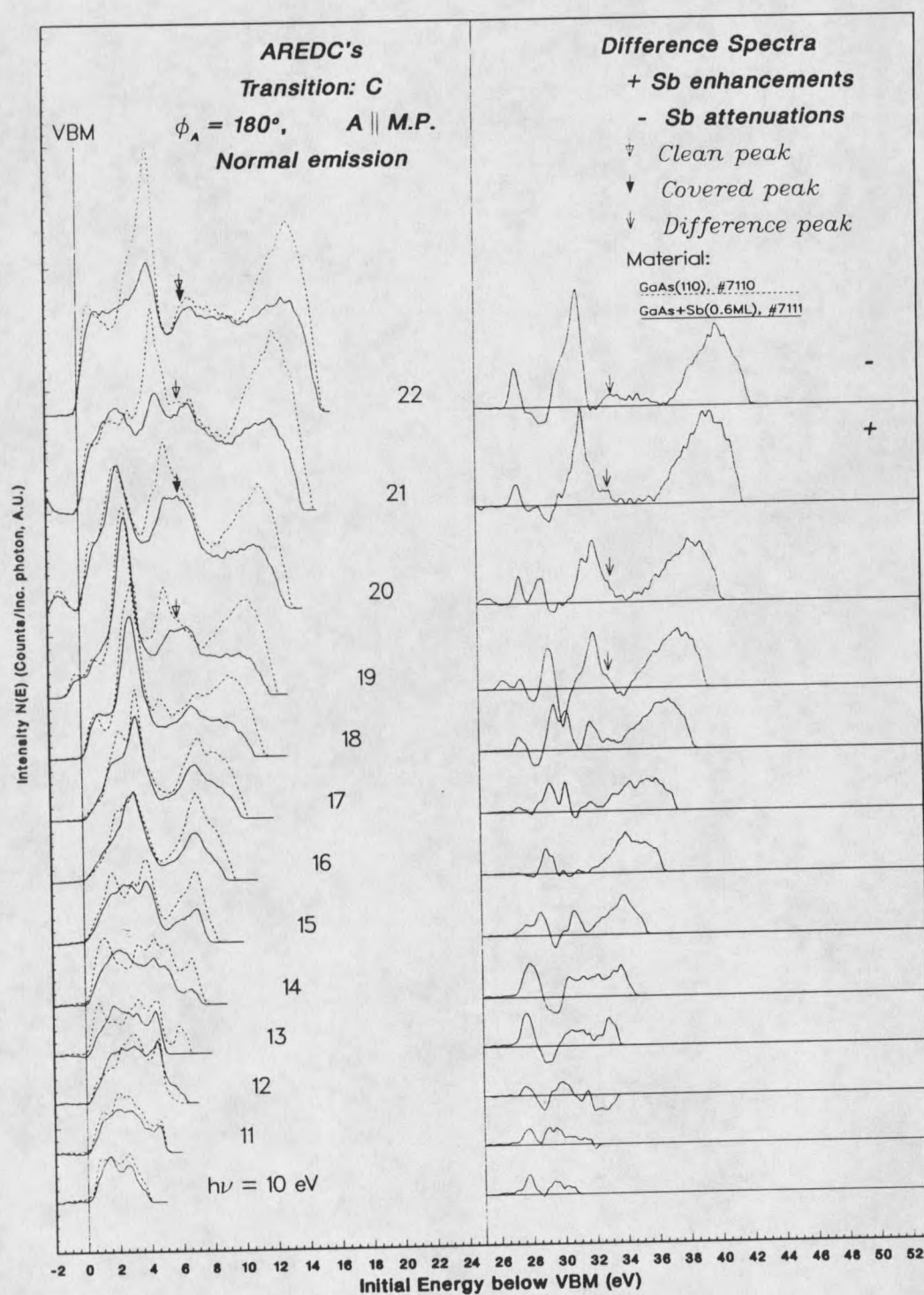


Figure 99. EDC difference spectra, transition C, pol. 180, $h\nu=10-22$ eV.

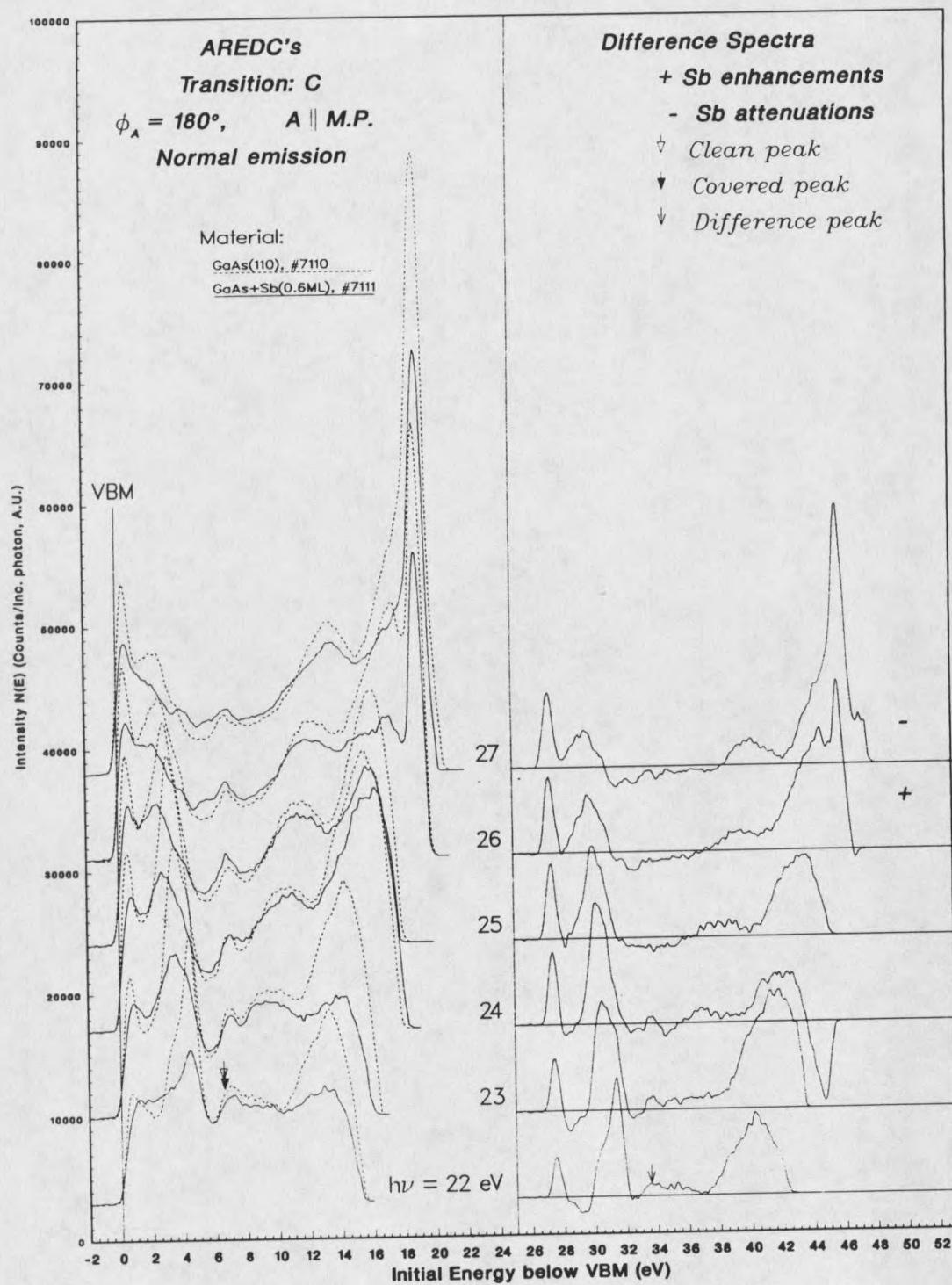


Figure 100. EDC difference spectra, transition C, pol. 180, $h\nu=22-30 \text{ eV}$.

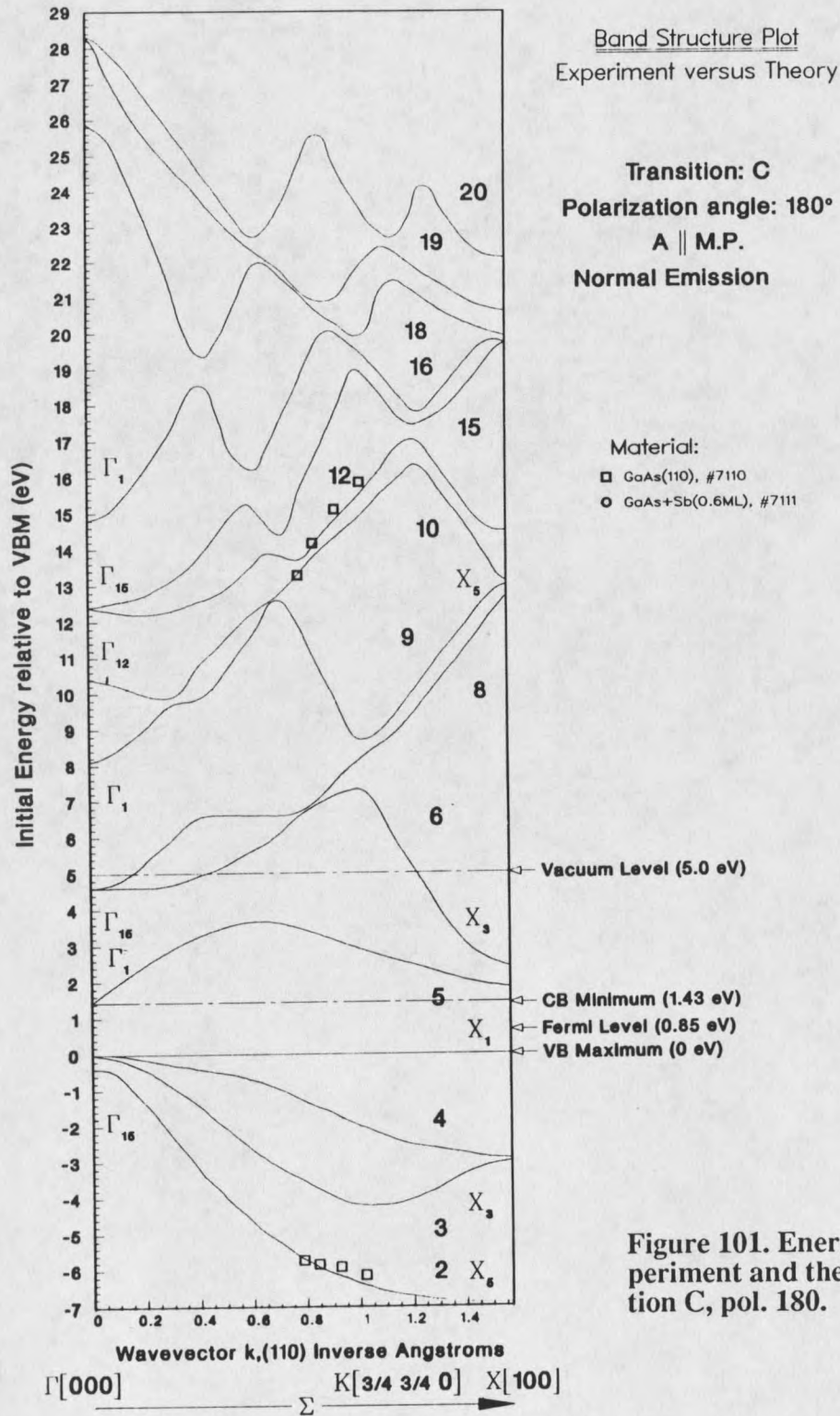


Figure 101. Energy bands ex-
periment and theory, transi-
tion C, pol. 180.

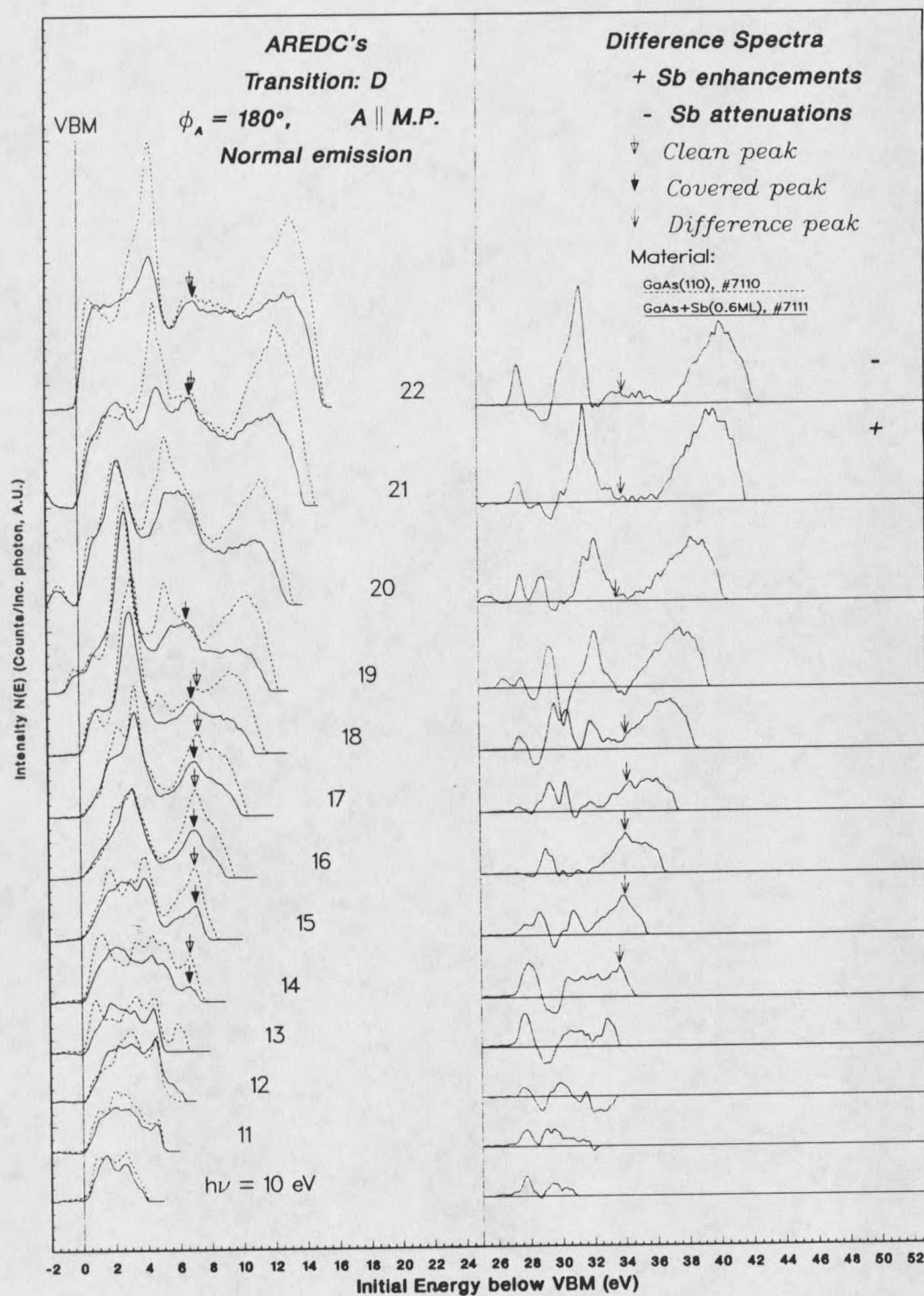


Figure 102. EDC difference spectra, transition D, pol. 180, $h\nu=10-22 \text{ eV}$.

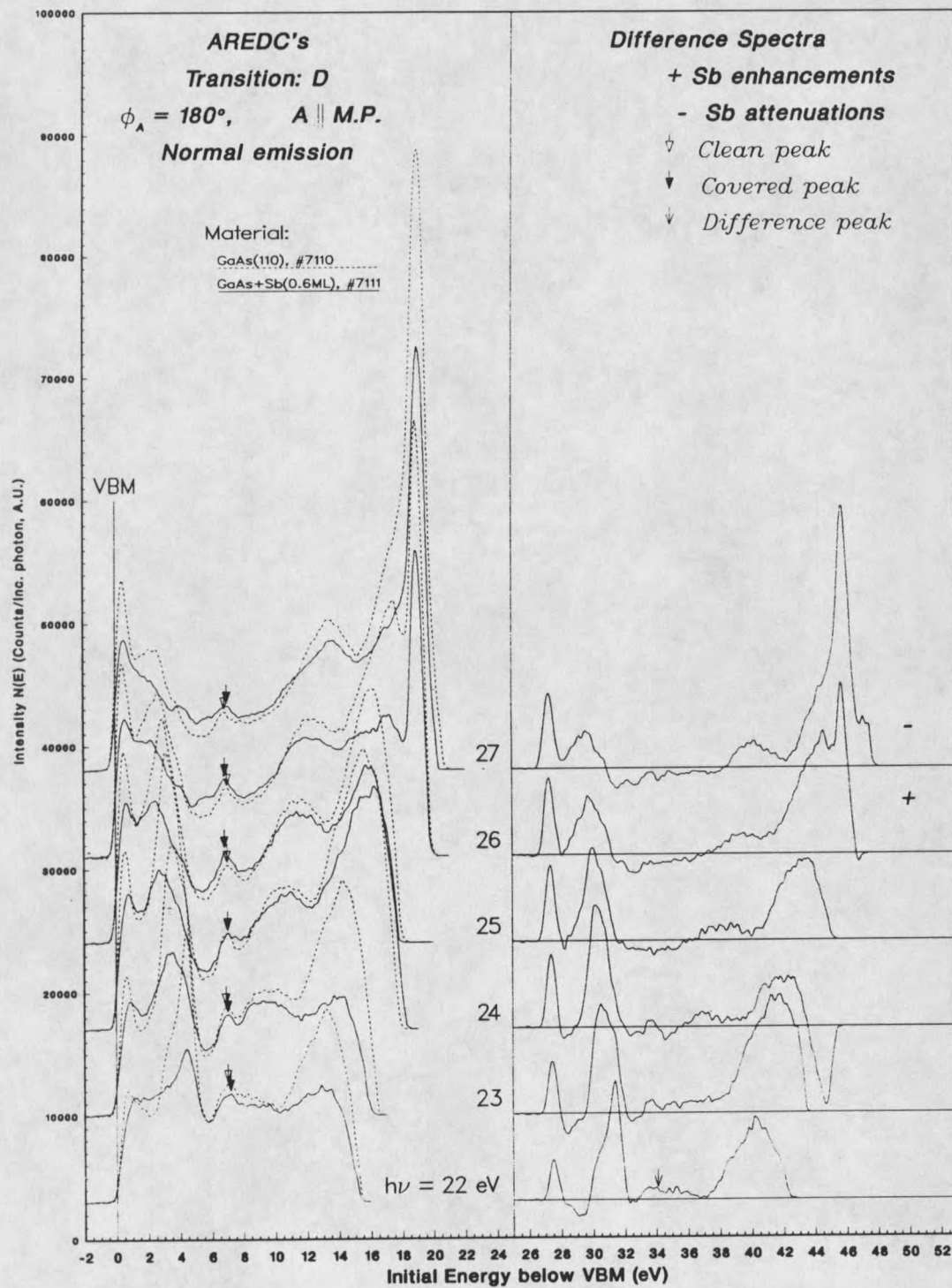


Figure 103. EDC difference spectra, transition D, pol. 180, $h\nu=22-30 \text{ eV}$.

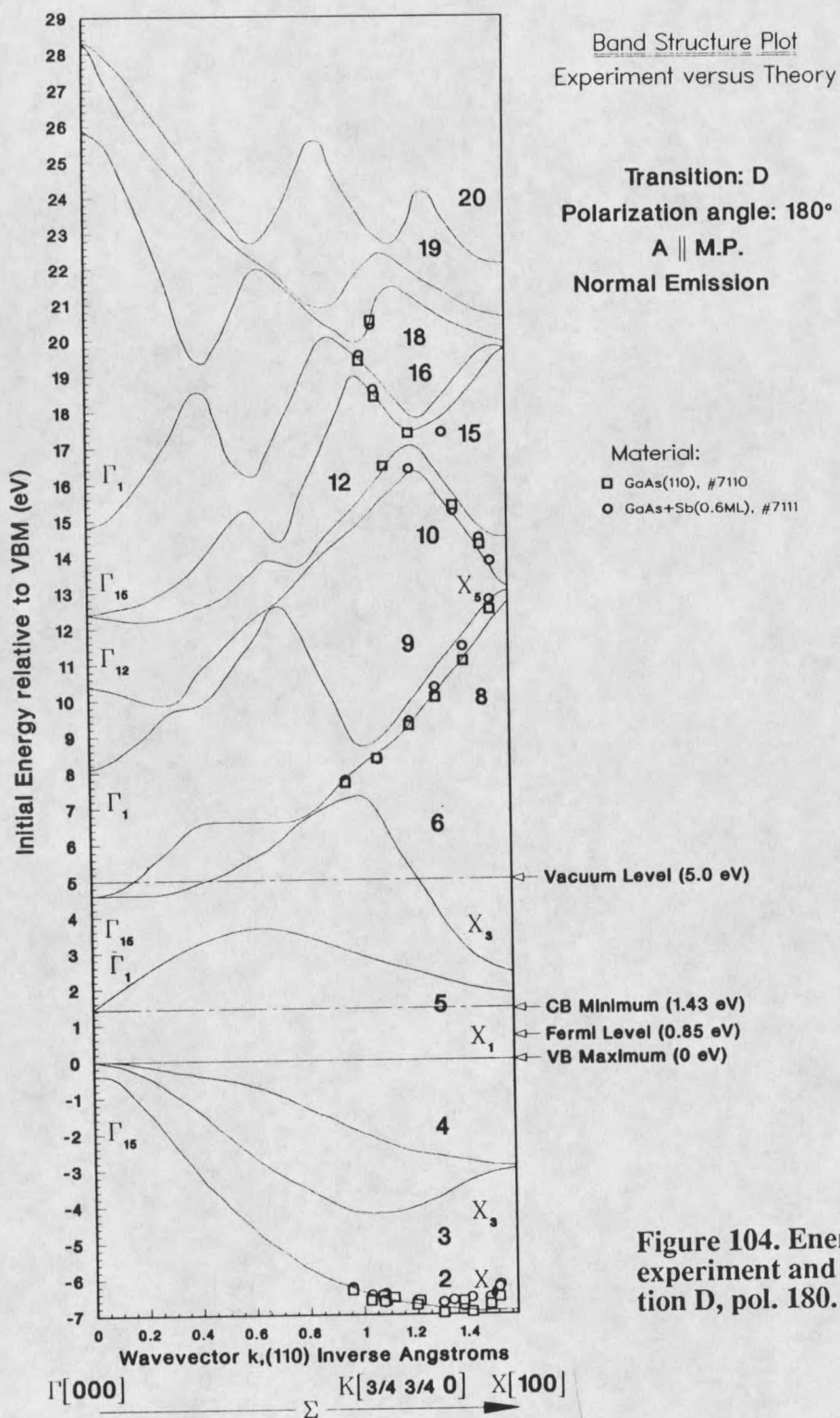


Figure 104. Energy bands of experiment and theory, transition D, pol. 180.

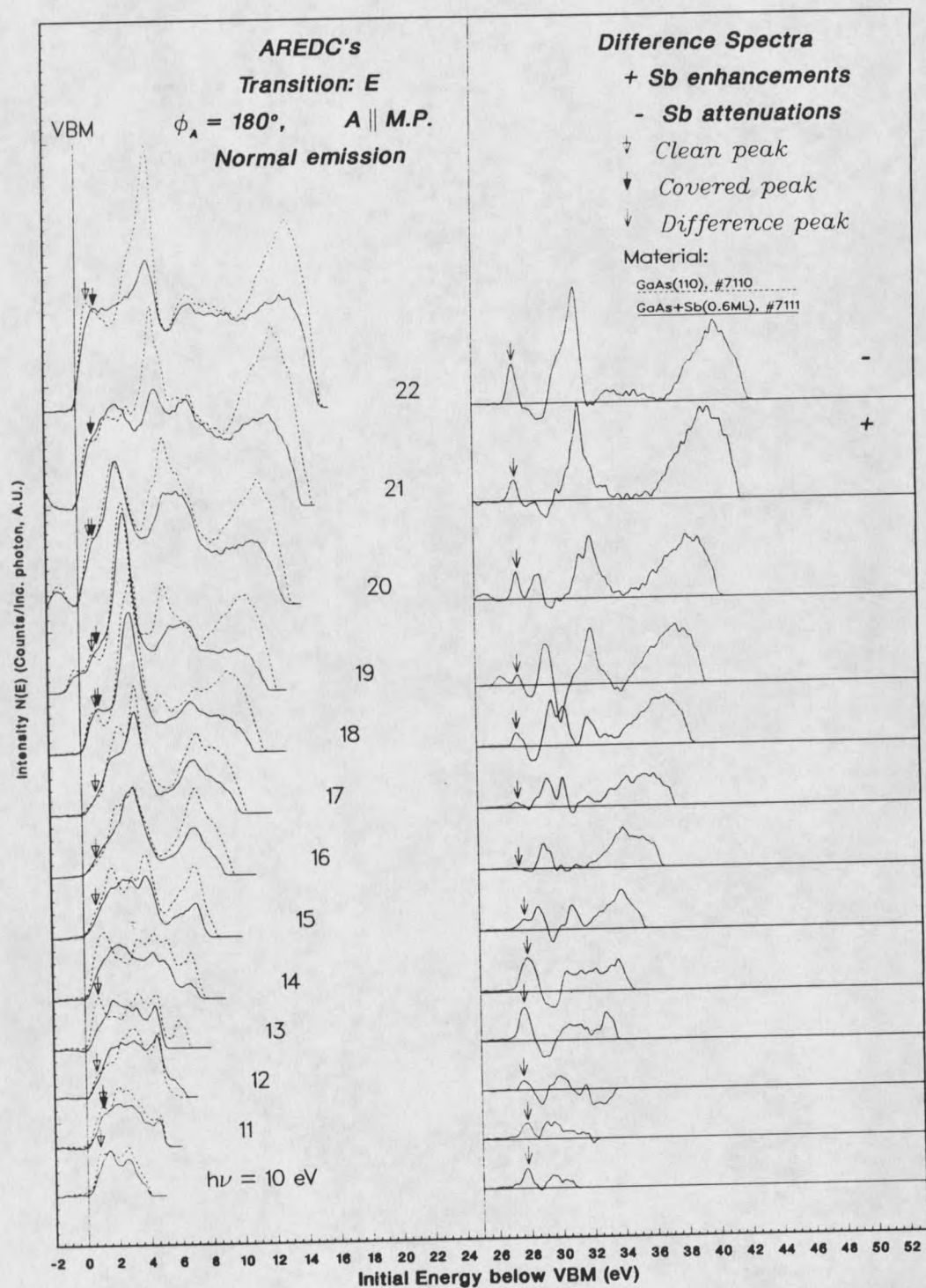


Figure 105. EDC difference spectra, transition E, pol. 180, $h\nu=10-22 \text{ eV}$.

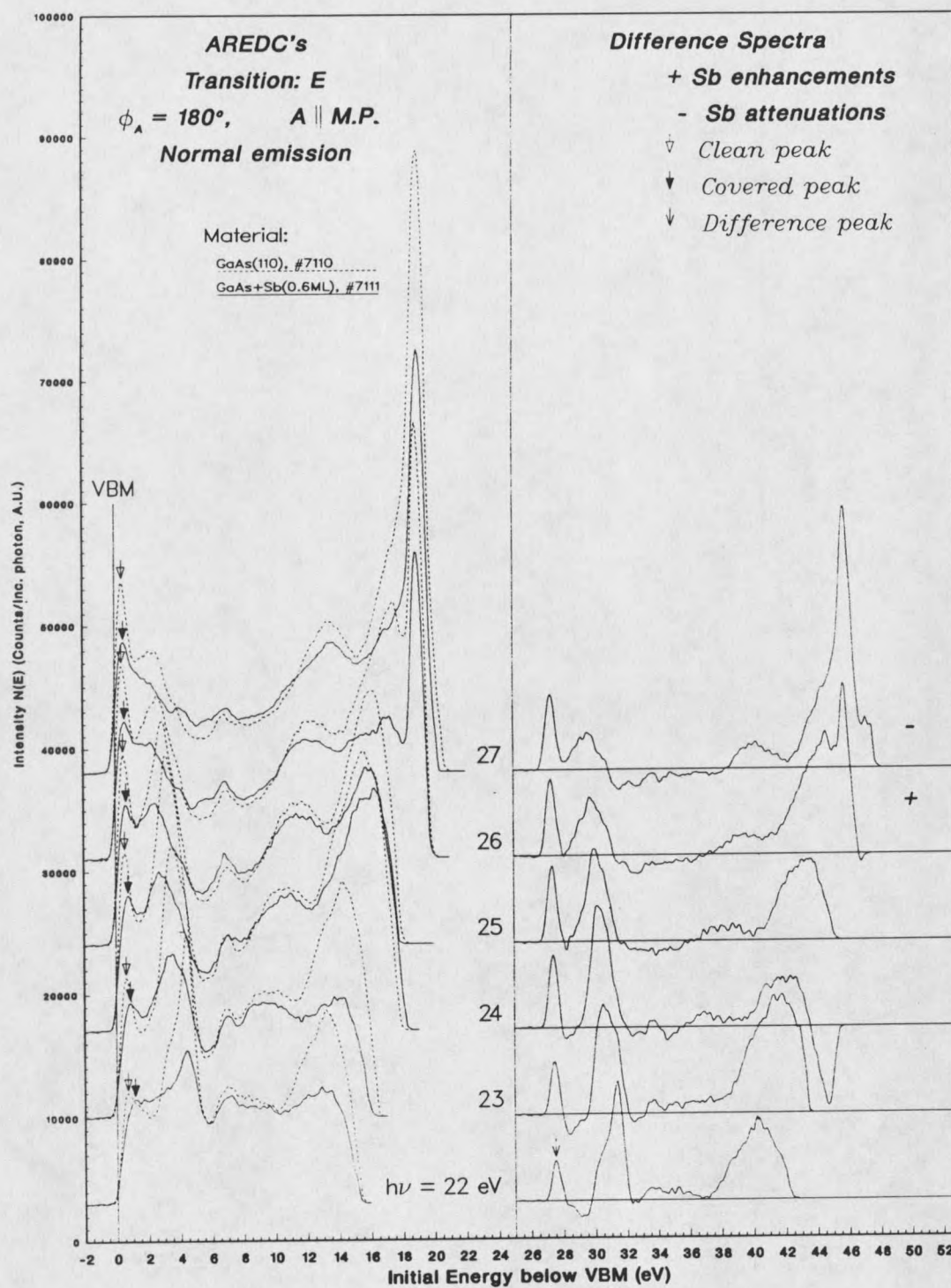


Figure 106. EDC difference spectra, transition E, pol. 180, $h\nu=22-30$ eV.

Figure 107. Energy bands of experiment and theory, transition E, pol. 180.

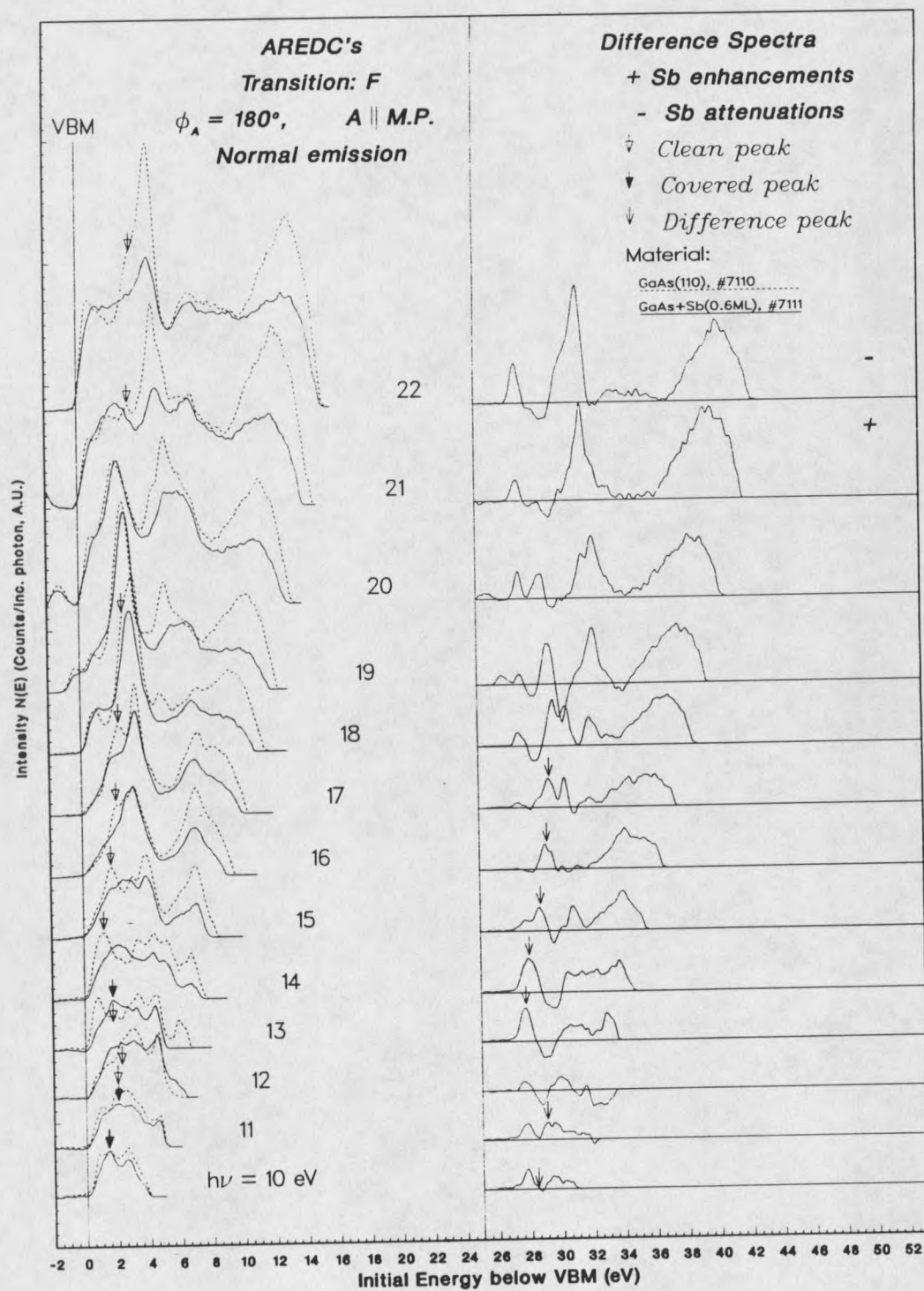


Figure 108. EDC difference spectra, transition F, pol. 180, $h\nu=10-22 \text{ eV}$.

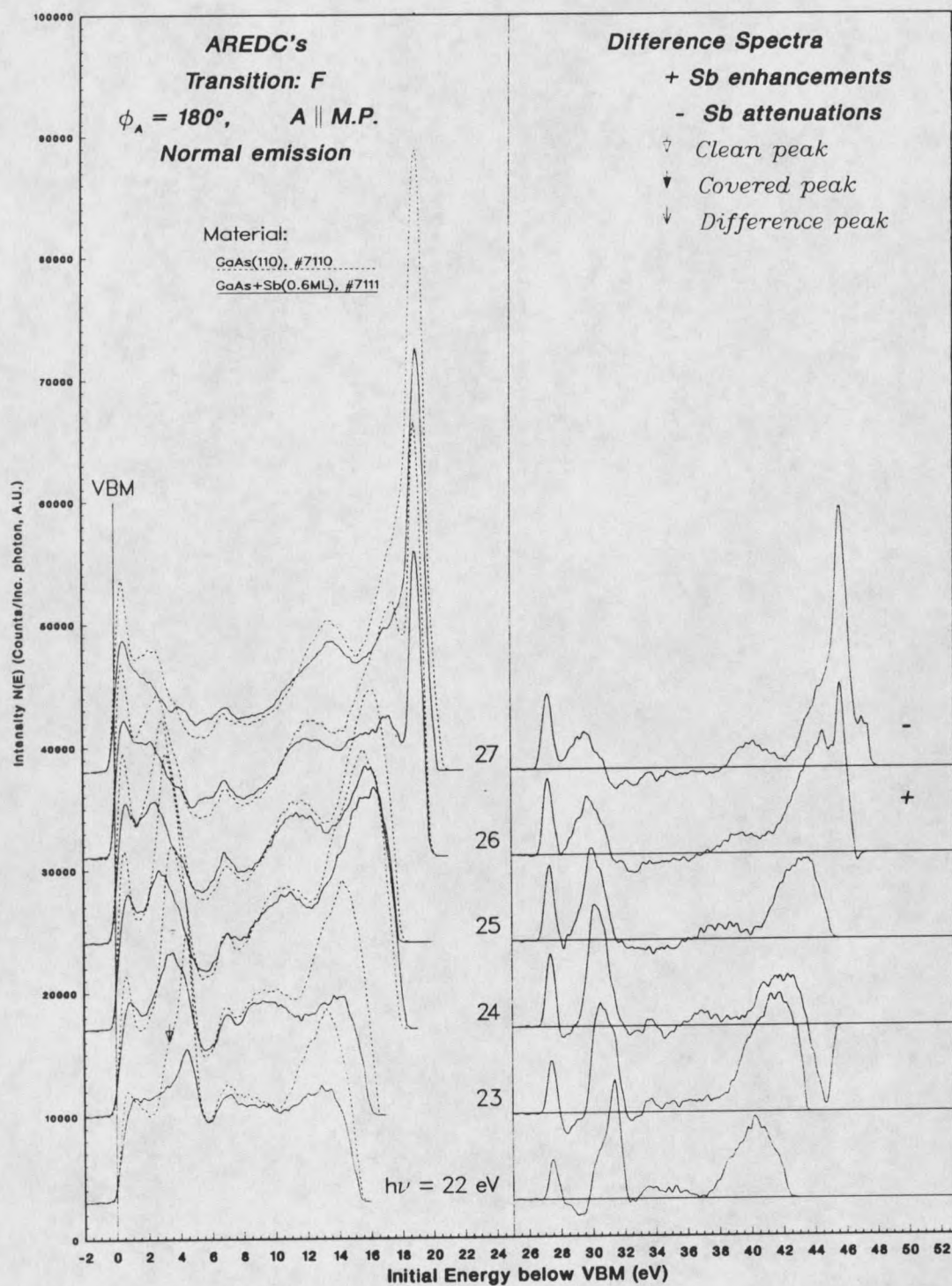


Figure 109. EDC difference spectra, transition F, pol. 180, $h\nu=22-30 \text{ eV}$.

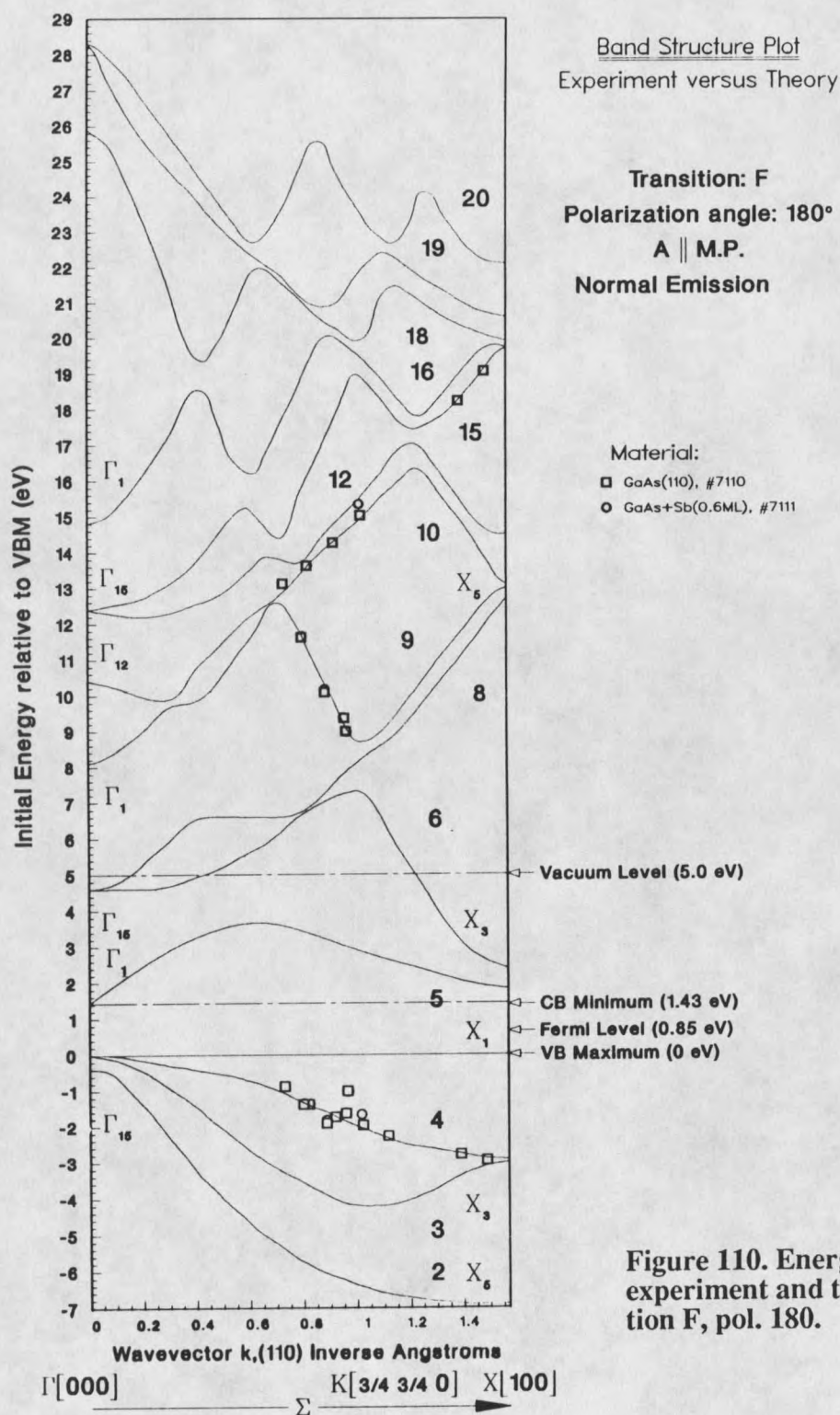


Figure 110. Energy bands of experiment and theory, transition F, pol. 180.

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