



Angle-resolved photoemission spectroscopy of gallium arsenide using synchrotron radiation
by James Arthur Knapp

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF
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Abstract:

Angle-resolved photoemission spectroscopy is a relatively new, powerful technique for studying the electronic properties of solids. Measuring the direction as well as the energy of photoemitted electrons provides both energy and wavevector information about the electronic states of the material. To achieve this capability, a cylindrical mirror electron energy analyzer was modified to permit collection of photoemission spectra with 4° angular resolution. Since the parallel component of the electron's momentum (Formula not captured by OCR) is conserved upon leaving the sample, surface band structure information was directly accessible. Observed bulk transitions were limited by the technique to those which occur only along certain lines in (Formula not captured by OCR)-space. Three methods of photoemission spectroscopy were employed; angle-resolved electron energy distribution curves (EDO's), angle-resolved constant final energy spectra (CFS's), and angle-resolved constant initial energy spectra (CIS's).

Angle-resolved photoemission from the (110) face of Gallium Arsenide was studied using synchrotron radiation. The 4° resolution, in conjunction with the wide photon energy continuum of synchrotron radiation ($h\nu < 30$ eV), permitted the gathering of considerable dispersion information about the electronic states of the material, both at the surface and in the bulk. Two occupied surface states were identified and portions of their band structure mapped out. The observed states, centered at ~ -1 eV and a, ~ -6 eV measured from the valence band maximum, have been predicted in several theoretical calculations, but have not been observed previously in experiment due to their degeneracy with bulk valence bands. Observations of bulk transitions concentrated on emission normal to the surface, for which the transitions occur primarily along the ζ symmetry line in the bulk Brillouin zone. Data was collected for several different orientations of the electric polarization vector ϵ relative to the crystal symmetries. A simple, direct-transition model proved sufficient to explain much of the phenomena, including the identification of several bulk energy band critical points.

ANGLE-RESOLVED PHOTOEMISSION SPECTROSCOPY OF GALLIUM ARSENIDE
USING SYNCHROTRON RADIATION

by

JAMES ARTHUR KNAPP

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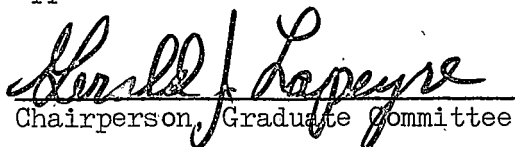
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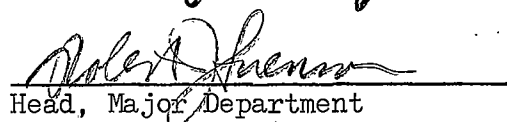
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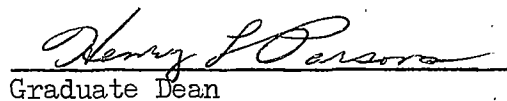
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ABSTRACT

Angle-resolved photoemission spectroscopy is a relatively new, powerful technique for studying the electronic properties of solids. Measuring the direction as well as the energy of photoemitted electrons provides both energy and wavevector information about the electronic states of the material. To achieve this capability, a cylindrical mirror electron energy analyzer was modified to permit collection of photoemission spectra with 4° angular resolution. Since the parallel component of the electron's momentum $\hbar k_{||}$ is conserved upon leaving the sample, surface band structure information was directly accessible. Observed bulk transitions were limited by the technique to those which occur only along certain lines in $\vec{k}$ -space. Three methods of photoemission spectroscopy were employed; angle-resolved electron energy distribution curves (EDC's), angle-resolved constant final energy spectra (CFS's), and angle-resolved constant initial energy spectra (CIS's).

Angle-resolved photoemission from the (110) face of Gallium Arsenide was studied using synchrotron radiation. The 4° resolution, in conjunction with the wide photon energy continuum of synchrotron radiation ($h\nu < 30$ eV), permitted the gathering of considerable dispersion information about the electronic states of the material, both at the surface and in the bulk. Two occupied surface states were identified and portions of their band structure mapped out. The observed states, centered at ~ -1 eV and ~ -6 eV measured from the valence band maximum, have been predicted in several theoretical calculations, but have not been observed previously in experiment due to their degeneracy with bulk valence bands. Observations of bulk transitions concentrated on emission normal to the surface, for which the transitions occur primarily along the Σ symmetry line in the bulk Brillouin zone. Data was collected for several different orientations of the electric polarization vector $\vec{\epsilon}$ relative to the crystal symmetries. A simple, direct-transition model proved sufficient to explain much of the phenomena, including the identification of several bulk energy band critical points.

I. INTRODUCTION

Most of the observed properties of solids are determined by the electronic structure of the valence, or outer shell electrons. Elucidation of this structure is therefore a primary concern of those interested in understanding and predicting the behavior of solid materials under various conditions. There have been many theoretical and experimental efforts applied to this end over the years.¹ The development of large-capacity, high-speed computers has facilitated the development of several approaches to calculating the electronic structure (band structure) of metals, insulators, and semiconductors. These techniques are all based on the one-electron approximation, which has proved its value in comparison to experiment. Experimental methods for determining the energy and wavefunctions of the electrons in solids have centered on exciting those electrons to higher energy states with either photons or other electrons. Information about the transitions is then derived from measurements of the rate of excitation, such as an optical absorption spectrum, or from measurements of electrons which are ejected from the material after excitation. Conventional angle-integrated ultraviolet photoemission spectroscopy (UPS) is of the latter type of measurement. Electrons which are excited to sufficient energy by the incident ultraviolet light may be

emitted from the solid and detected. The number of these photoelectrons as a function of kinetic energy provides much useful information about the strength and energies of the optical transitions. However, since the detection includes all or most of the emission hemisphere, any information which may be contained in the directional dependence of the emission is lost. None of the conventional experimental techniques, including UPS, provide much information about the wavevectors of the electron wavefunctions, in general measuring all transitions regardless of origin in reciprocal lattice space.

In 1964, Gobel, Allen, and Kane² demonstrated that a substantial portion of photoemitted electrons escape the sample without losing momentum to phonons or imperfections in the bulk or at the surface. For these electrons, the component of wavevector parallel to the surface is conserved, while the perpendicular component is modified in the process of escape. This demonstration of wavevector conservation implied that, subject to certain limitations, both the energy and the wavevector of the valence electrons might be measured by determining the energy and direction of photoemitted electrons. Mahan calculated in 1970 that the photoemission from a free-electron-like metal (sodium) should have a highly anisotropic angular distribution.³ Tentative experimental work proceeded at several laboratories, concentrating on the variation of emission

with polar angle⁴⁻⁷ or on emission from several crystal faces.⁸ The first study of both polar and azimuthal dependence of photoemission was done, coincidentally enough, on the (110) face of GaAs at a photon energy of 10.2 eV by Smith and Traum in 1973.⁹ Interpretation of these spectra was inhibited by the lack of conservation of the perpendicular component of momentum.^{9,10} Further experiments by Smith and his co-workers on two-dimensional systems, such as the layered compound TaS₂^{11,12} and surface states on Si(111),^{13,14} provided for the first time tangible success in actually mapping out energy bands with experiment. Angle-resolved photoemission spectroscopy was beginning to show substantial promise.

Concurrently with the early development of angle-resolved photoemission spectroscopy, the use of synchrotrons and storage rings as a source of radiation began to receive ever increasing attention.¹⁵ In accelerators or storage rings, electrons radiate as they are accelerated by bending magnets. In their frame of reference, the electrons radiate in a Larmor radiation pattern, but in the laboratory frame, with a velocity approaching that of light, they radiate strongly in the forward direction. This synchrotron radiation, as it is called, is a highly collimated, intense, continuous spectrum, which includes many photon energies not available from other sources. The use of a monochromator with the radiation provides a continuously tunable source that in the last

ten years has been used in a wide variety of experimental applications. Facilities to provide this radiation to research groups have been built around the world, including three in the U.S. One is the synchrotron radiation facility at SPEAR, the electron-positron ring in California. Another is SURF-II, a storage ring at the National Bureau of Standards in Washington, D.C. The third is Tantalus I, a 240 MeV storage ring at the University of Wisconsin, which provides synchrotron radiation for groups from around the country. Tantalus I was the first facility dedicated completely to providing synchrotron radiation for research. The Montana State University photoemission group has been using the Wisconsin facility since 1971 for photoemission studies.

The use of synchrotron radiation as an excitation source for doing angle-resolved photoemission spectroscopy is a natural development that greatly enhances an already promising technique. The wide continuum of photon energy permits the study of a large region of momentum and energy space. Furthermore, the radiation is strongly polarized in the plane of the electron's orbit, adding still another factor in the optical transition which can be investigated.

A primary purpose of this research project has been to develop equipment and techniques, compatible with existing equipment, with which angle-resolved photoemission spectroscopy could be performed

on single crystals using synchrotron radiation. This goal was attained. Preliminary studies of TaS_2 , done in collaboration with N.V. Smith and M.M. Traum of Bell Laboratories using the equipment to be described herein, are believed to be the first studies of this kind on single crystals using synchrotron radiation.^{16,17}

Another goal of the research project has been to demonstrate the usefulness of the technique by a careful study of a material which is interesting from both theoretical and application standpoints. GaAs was chosen as the subject of the study for several reasons. First, clean (110) surfaces could be prepared in situ by cleaving, simplifying sample preparation. Second, several theoretical calculations of bands exist with which the data could be compared, both in the bulk¹⁸⁻²⁰ and at the surface.²¹⁻²⁵ Lastly, GaAs is an important semiconductor in terms of its present and potential application to solid-state devices.

The study was successful in identifying surface states at ~ 1 eV and ~ 6 eV below the Fermi level. These states had been predicted by the theoretical calculations,²²⁻²⁵ but not previously observed in experiment.²⁶ Bulk energy band positions were identified that are difficult to discern in conventional photoemission. Emission from initial states located at Σ_1^{min} , X_5 , and L_3 was isolated, fixing the energy position of these levels more positively than has been previously possible. Several conduction band energy

levels were identified, many of which have been inaccessible with other techniques. The bulk emission features, as a whole, correlated very well with existing band calculations, providing confidence in the one-electron approximation and demonstrating a valuable technique for checking and refining future band calculations.

The discussion of the project will begin with a short review of the band theory of solids and the optical transition which is the source of photoemitted electrons. The three modes of collecting photoemission spectra are presented, with particular emphasis given to methods of data analysis unique to angle-resolved photoemission spectroscopy. The experimental details are then discussed in Chapter III, including a description of the angle-resolving modification of the electron energy analyzer. Sample preparation and orientation is detailed. Chapter IV compiles the experimental results. Emission from the two occupied surface states is described, along with tests of its surface character. Observations of an unoccupied surface state are presented and compared to results from other experiments. Finally, emission due to bulk transitions is detailed, with demonstrations of bulk band critical point identifications. The last chapter summarizes the experiment and its results.

II. THE PHYSICS OF PHOTOEMISSION SPECTROSCOPY

A. Energy Bands of Solids

1. Band Theory. The one-electron approximation is the basis of the band theory of solids.¹ The electron is assumed to behave as an isolated entity immersed in a potential due to the periodic array of atomic cores plus an overall potential due to the other valence electrons. All wave functions are then single-electron wave functions. The solutions of the Schrodinger equation

$$\left\{ \left(\frac{1}{2m} \right) \vec{p}^2 + V(\vec{r}) \right\} \psi = E\psi \quad (1)$$

for a periodic crystal potential $V(\vec{r})$ are Bloch functions

$$\psi(\vec{k}, \vec{r}) = U_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \quad (2)$$

where $U_{\vec{k}}(\vec{r})$ is a function with the periodicity of the lattice.

The simplest solution to Eq. (1) is for the case $V(\vec{r}) = 0$, the "free electron" solution. The wave functions are then plane waves and the energy of an electron is given by

$$E = \hbar^2 k^2 / 2m \quad (3)$$

The energy vs. wavevector relation in Eq. (3) embodies the electron energy bands for the free electron. Energy here is a simple parabolic function of $\vec{k}$. If we include the lattice periodicity, leaving

the potential arbitrarily weak, we can write

$$E = \left(\frac{\hbar^2}{2m} \right) |\vec{k} + \vec{G}|^2 \quad (4)$$

where $\vec{G}$ is a reciprocal lattice vector. The bands can then be represented in the reduced zone scheme. Figure 1a shows the free electron bands plotted along the (110) direction in the reduced zone. As the potential $V(\vec{r})$ is "turned on" partially, degeneracies are lifted and band crossings eliminated, resulting in the "nearly free" electron energy bands of Fig. 1b. The energy bands for the complete potential for GaAs²⁰ are shown in Fig. 1c, with the bands labelled according to the symmetry points and the Fermi energy E_F indicated. The crystal field has produced an energy gap of 1.4 eV between the bands below the Fermi energy and those above. Those states represented by the bands below E_F are normally occupied at room temperature and are called the valence bands (VB's) while the states which lie above E_F are unoccupied and called conduction bands (CB's). The location of E_F in the band gap is of course determined by the impurity doping of the material, but this study concentrated on p-type GaAs, putting E_F at the bottom of the gap. The spin-orbit interaction, when included, will split even more degeneracies, but this effect is smaller than our experimental resolution¹⁹ and will be neglected in the interpretation of the results.

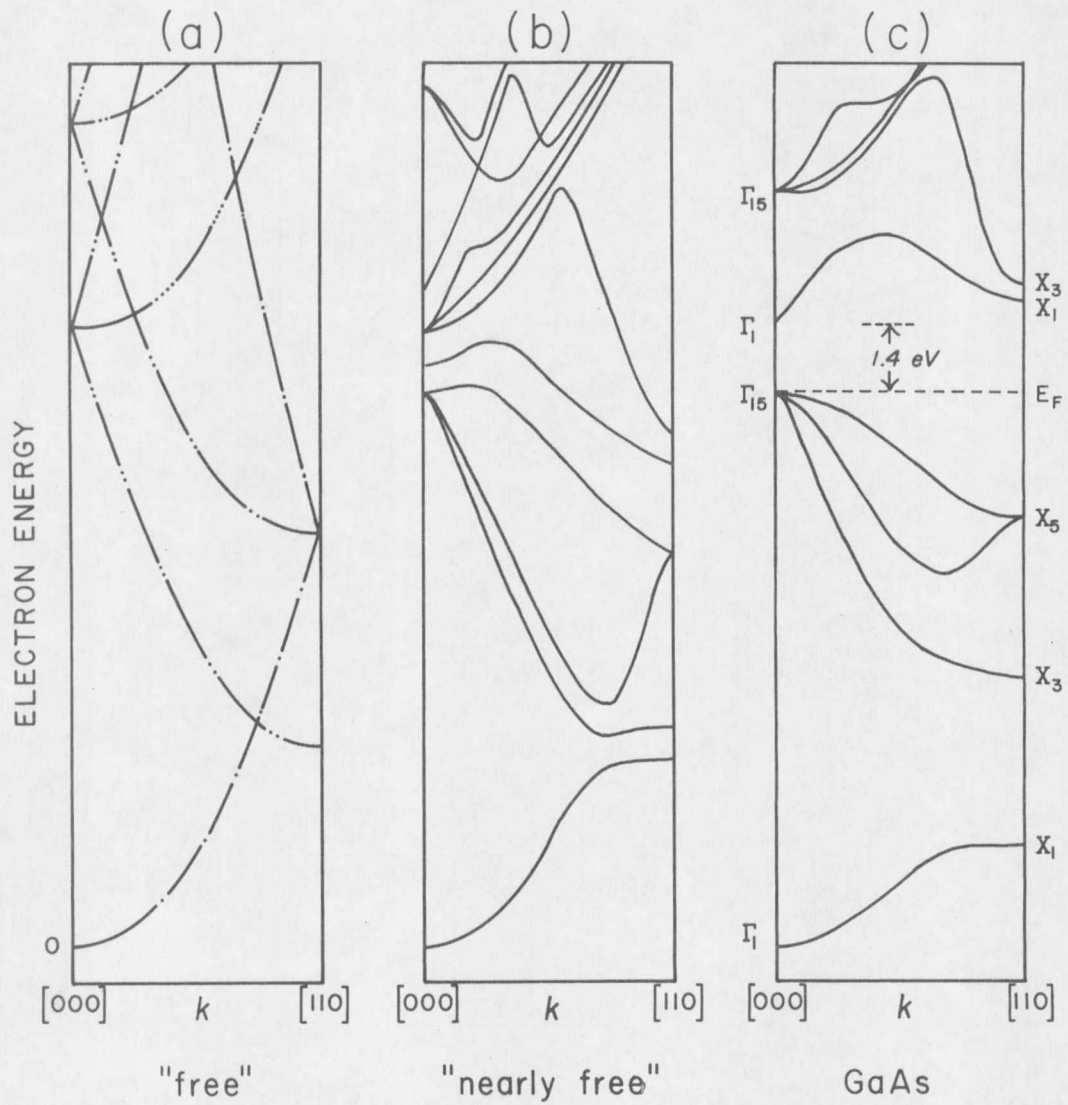


FIG. 1. Energy band structure along the (110) direction in k -space for three different crystal potentials.

2. Repeated Zone Scheme. The concept of a repeated zone scheme should be expanded upon, since its use is central to the data interpretation. If we encounter a Bloch wavefunction written as in Eq. (2) with $\vec{k}$ lying outside the first zone, we can always find a reciprocal lattice vector $\vec{G}$ such that

$$\vec{k}' = \vec{k} - \vec{G} \quad (5)$$

lies inside the first zone. We then rewrite Eq. (2) as

$$\begin{aligned} \psi(\vec{k}', \vec{r}) &= U_{\vec{k}'}(\vec{r}) e^{i\vec{k}' \cdot \vec{r}} = (e^{i\vec{G} \cdot \vec{r}} U_{\vec{k}}(\vec{r})) e^{i\vec{k} \cdot \vec{r}} \\ &= U_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} \\ &= \psi(\vec{k}, \vec{r}) \end{aligned} \quad (6)$$

where

$$U_{\vec{k}}(\vec{r}) = (e^{i\vec{G} \cdot \vec{r}} U_{\vec{k}'}(\vec{r})) \quad (7)$$

is periodic in the lattice as required. It follows that energy $E_{\vec{k}}$ outside the first zone is equal to an $E_{\vec{k}}$ inside the first zone. Translating the bands back into the first zone is the basis of the reduced zone scheme. Since the bands can be translated back into the first zone with appropriate reciprocal lattice vectors, they can also be translated to any other or every zone. Then the bands become periodic in the reciprocal lattice:

$$E_{\vec{k}} = E_{\vec{k}+\vec{G}} \quad (8)$$

This procedure is called the repeated, or periodic zone scheme. It is of use in the interpretation of the data because the results may be plotted in reciprocal lattice space directly, without adding or subtracting reciprocal lattice vectors to translate everything back to the first zone. The repeated zone scheme may be thought of as an unfolding of a wavevector description (reduced zone scheme) into a "momentum space". In this "momentum space", each band has a different "momentum" weighting in each repeated zone. The word "momentum" is used somewhat loosely here, since a wavevector $\vec{k}$ is directly proportional to momentum only for a free particle.

B. The Three Modes of Photoemission Spectroscopy

1. Photoemission. When light of sufficient energy shines on a material, it may excite a transition between a filled valence state and an empty conduction state. If the final state has sufficient energy, the electron may escape the solid as a photoemitted electron, either with or without undergoing a scattering event. The Hamiltonian H including the electron-photon interaction, with the charge of the electron as $-e$, is

$$H = \frac{1}{2m} \left(\vec{p} + \frac{e}{c} \vec{A} \right)^2 + V(\vec{r}) \quad (9)$$

where $\vec{A}$ is the vector potential of the radiation field.²⁷ Letting $\vec{\nabla} \cdot \vec{A} = 0$ and dropping terms of order A^2 , Eq. (9) reduces to

$$H = \frac{1}{2m} \vec{p}^2 + V(\vec{r}) + \frac{e}{mc} \vec{A} \cdot \vec{p} \quad (10)$$

The first two terms are just the unperturbed Hamiltonian H_0 . The last we shall call the perturbing Hamiltonian H_{if} .

$$H_0 = \frac{1}{2m} \vec{p}^2 + V(\vec{r}), \quad H_{if} = \frac{e}{mc} \vec{A} \cdot \vec{p} \quad (11)$$

Using Fermi's Golden Rule of time-dependent perturbation theory,²⁷ the transition rate W_{if} for excitation from an initial density of states N_i at initial energy $E_i = E - h\nu$ to a final density of states N_f at final energy $E_f = E$ is

$$W_{if} = \frac{2\pi}{\hbar} \left\{ \langle f | \left(\frac{e}{mc} \vec{A} \cdot \vec{p} \right) | i \rangle \right\}^2 N_i(E - h\nu) N_f(E) \quad (12)$$

Energy conservation has been put into the formula explicitly, using $E_i = E_f - h\nu$. The initial and final state wave functions are indicated as $|i\rangle$ and $\langle f|$ respectively. The quantity which is squared in Eq. (12) is called the matrix element and is in general not known, since we lack exact forms for the wave functions.

Substitution of Bloch wave functions into a more general form of Eq. (12) also leads to a selection rule between initial and final

wavevectors.²⁸ Without interaction with lattice imperfections or phonons, the transition is allowed only between wavefunctions with the same reduced wavevector. Transitions fulfilling this requirement are termed direct transitions and will be discussed in more detail later.

Neglecting for the moment the directionality of the emission, the number of electrons emitted with a particular final energy E is then basically proportional to the initial density of states (DOS) which are excited to that energy convoluted with the final DOS at that energy. This simple convolution is modulated by the matrix elements and added to or subtracted from by inelastic scattering. The emission intensity at all possible combinations of initial and final DOS at all $h\nu$ constitutes a three-dimensional surface which we shall call the emission surface. The axes of this surface are photoemission intensity $N(E_i, E_f, h\nu)$, photon energy $h\nu$, and final energy E_f . (Again, this discussion neglects the directionality of the emission; such an emission surface exists for each direction of emission and also for the total, angle-integrated emission.) In studying the photoemission from solids, we have used three different modes of photoemission spectroscopy to analyze the emission surface in three different but complementary ways. These three modes are Electron Energy Distribution Curves, Constant Final Energy Spectra, and Constant Initial Energy Spectra.

2. Electron Energy Distribution Curves. The first method of photoemission spectroscopy is also the most established, the Electron Energy Distribution Curve (EDC). In this mode the photon energy $h\nu$ is fixed and the intensity of emission as a function of kinetic energy in the vacuum is recorded. Figure 2 shows a schematic of this process. Valence and conduction band DOS are shown as cross-hatched areas on the left side, representing the sample. The right side represents the vacuum, with the vacuum level E_v indicated. (The vertical axis in the figure is energy.) E_v is the minimum final energy for which an electron may escape the solid. The fundamental threshold for emission of an electron into the vacuum is E_{th} , the difference between E_v and the top of the valence bands at E_{vbm} . The work function Φ is the difference between E_v and E_F . For heavily doped p-type semiconductors, Φ corresponds to E_{th} . The measured kinetic energy E_k of an unscattered photoelectron is

$$E_k = h\nu + E_i - E_{th} \quad (13)$$

where E_i is measured relative to the top of the valence bands at E_F . Since $h\nu$ and E_{th} are fixed, Eq. (13) shows that the EDC measures a spectrum of initial energies, each excited to a different final energy.

Two types of photoelectrons are shown in Fig. 2, a "primary"

and an inelastically scattered "secondary" electron. Electron "a" is a primary electron; it is excited to a CB state by the photon energy $h\nu$ and escapes without further change in final energy. Electron "b" is also excited to a CB state, but then inelastically scatters with electron "c", giving up a portion of its energy and escaping at reduced final energy as a scattered secondary electron. Electron "c" is excited to a CB state by the scattering event, but may still be below E_v and thus not escape the solid. The overall appearance of an EDC is a combination of unscattered primaries and scattered secondaries at lower kinetic energies.

3. Constant Final Energy Spectra. The second mode of photoemission spectroscopy is an outgrowth of its application to synchrotron radiation.²⁹ The continuous, smooth spectral dependence of that light source permitted the acquisition of spectra for which photon energy was scanned, rather than held constant. In Constant Final Energy Spectroscopy (CFS) the analyzer energy window is set at one fixed kinetic energy and the photon energy is then scanned, exciting in turn different initial states to that fixed final energy. Figure 3 diagrams the process. Initial and final DOS are as in Fig. 2, with energy levels labelled as before. The analyzer window is fixed at some value of E_k and $h\nu$ is scanned, increasing from $h\nu_1$ through $h\nu_2$ and $h\nu_3$. Electrons excited to

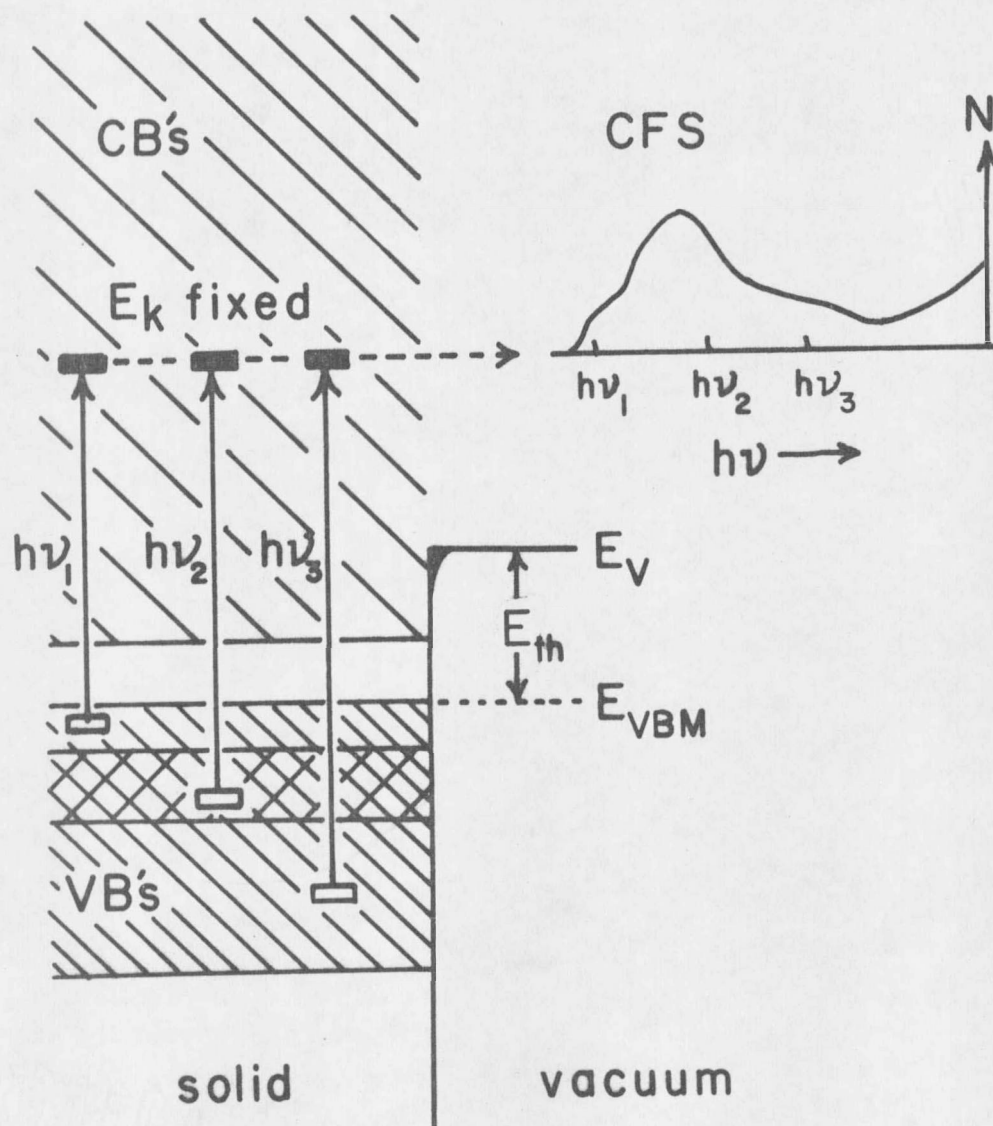


FIG. 3. Schematic of the Constant Final Energy Spectrum mode of photoemission spectroscopy.

the chosen final energy are shown for each of these three photon energies. The resulting CFS represents the spectrum of initial states excited to that particular final state. Thus a CFS is similar to an EDC in that it measures a spectrum of initial states, but different in that the convolution with final states has been removed, showing the effects of only one final state energy. A CFS taken at another final energy will show the same spectrum of initial states but may have a different appearance due to differences in how the initial states couple into the new final states.

4. Constant Initial Energy Spectra. The third mode of photo-emission spectroscopy again uses the synchrotron radiation continuum in scanning photon energy.²⁹ However, instead of fixing the final energy, the final energy is scanned synchronously with the photon energy, which in the one-electron picture fixes the initial energy of those electrons which are detected. Figure 4 diagrams this mode, the Constant Initial Energy Spectroscopy (CIS). Energies and VB DOS are the same as in the two previous figures. However, two areas of high CB DOS are indicated by cross-hatched sections. As the photon energy is scanned, increasing through $h\nu_1$, $h\nu_2$, and $h\nu_3$, the kinetic energy window of the analyzer is also increased such that the initial energy E_i stays constant. Rewriting Eq. (13), this can be expressed as

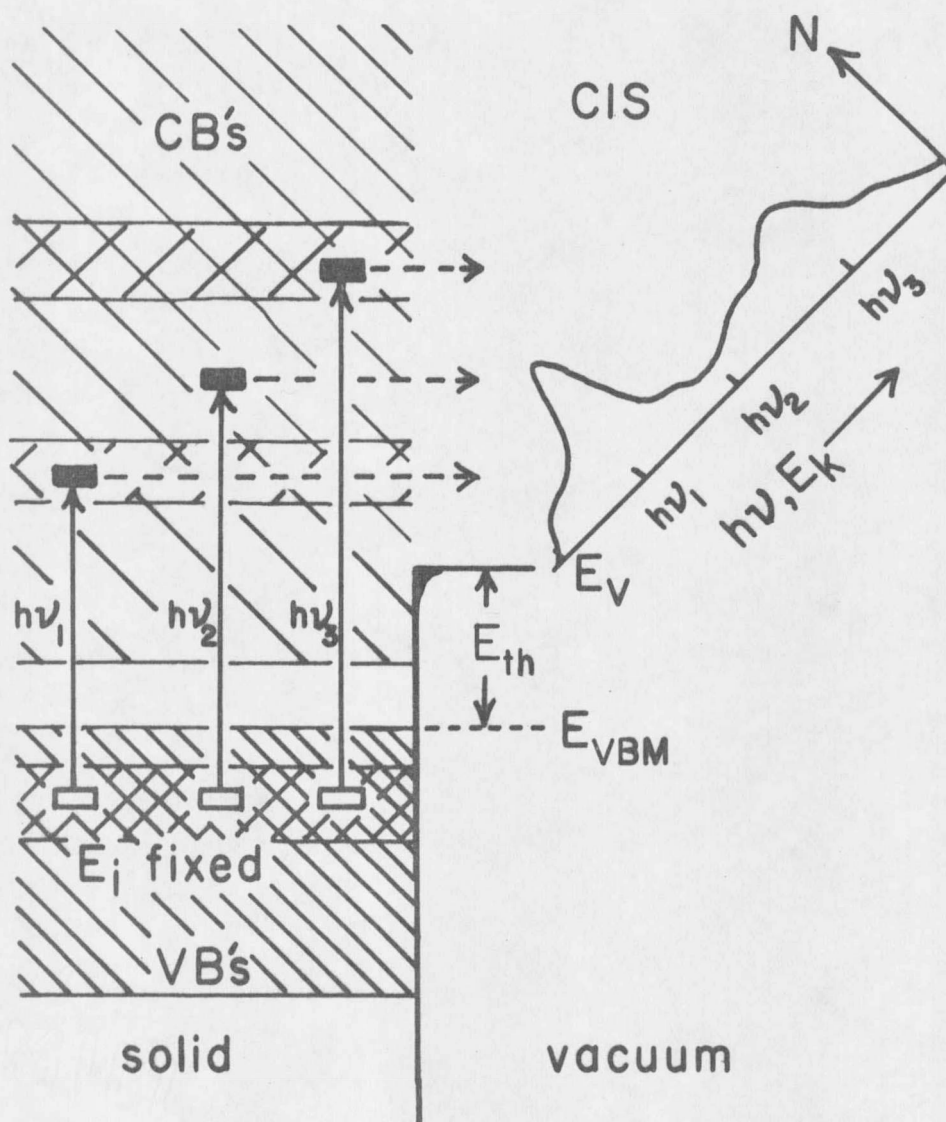


FIG. 4. Schematic of the Constant Initial Energy Spectrum mode of photoemission spectroscopy.

$$E_i = \text{constant} = E_k - h\nu + E_{th} \quad . \quad (14)$$

Since E_{th} is a constant, $h\nu$ and E_k must be increased at an equal rate to hold E_i fixed. The CIS obtained in this manner represents the spectra of how states at that particular initial energy couple to the final states at a range of final energies. The figure shows two peaks in the CIS corresponding to peaks in CB DOS. A CIS taken for a different value of E_i will show how a different set of initial states couple to final states in the same range of final energies, and will in general be different in appearance due to matrix element and other effects.

C. Angle-Resolved Photoemission.

It was pointed out some years ago that measuring the direction as well as the energy of the photoemitted electron should give much more information about the optical excitation than measuring energy alone.^{2,3} In particular, it was hoped that measuring E_k and momentum $\vec{p}$ of the electron in vacuum would enable one to deduce E_i and the wavevector $\vec{k}$ of the original transition in the solid, thus permitting the "mapping" out of the band structure experimentally. For this to be possible, two conditions must be met. First, the wavevector must be conserved in the optical transition. Second, the wavevector information must not be destroyed during

transport across the surface into the vacuum.

1. Direct vs. Indirect Transitions. Conservation of wave-vector during the optical transition leads to the "direct transition" model.²⁸ Interaction of electrons in a perfect lattice with an electromagnetic field obey the following conservation law

$$\vec{k}_f + \vec{G} = \vec{k}_i + \vec{q} \quad (15)$$

where $\vec{G}$ is a reciprocal lattice vector and $\vec{q}$ is the photon wave-vector. In the reduced zone $\vec{G} = 0$, and since $\vec{q}$ is much smaller than a reciprocal lattice vector, we have

$$\vec{k}_f = \vec{k}_i \quad (16)$$

Transitions of this kind are termed direct transitions. The reduced wavevectors of the initial and final states are identical.

If the lattice contains imperfections in the form of quantized vibrations (phonons), a phonon of wavevector $\vec{Q}$ can interact with the electrons and modify the wavevector equality of Eq. (16). In this case the initial and final wavevectors are no longer the same and the transition is termed indirect. Figure 5 diagrams a hypothetical band structure with both a direct and an indirect transition indicated. An initial state of energy E_i and wavevector $\vec{k}_i$ is excited by a photon of energy $h\nu_0$. Transition A is direct,

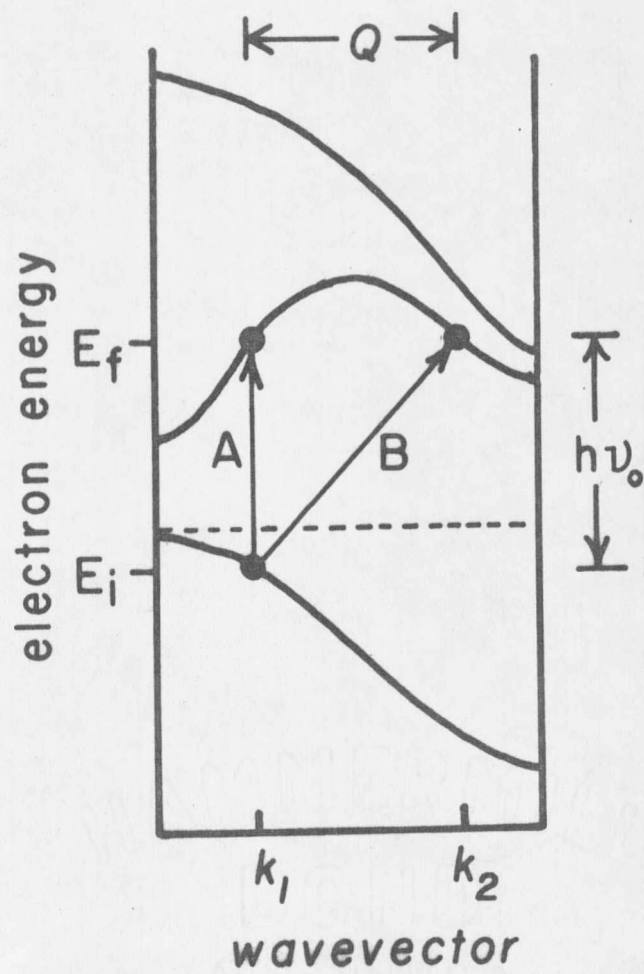


FIG. 5. Schematic of two types of transitions:

"A" - direct, "B" - indirect.

going to a final state of energy $E_f = E_i + h\nu_0$ and wavevector $\vec{k}_1$. Transition B is indirect, going to another final state which also satisfies energy conservation $E_f = E_i + h\nu_0$, but of different wavevector $\vec{k}_2$, equal to $\vec{k}_1$ plus the phonon wavevector $\vec{Q}$.

As we shall show in the data, the direct transition is obviously an important mechanism in the actual transition. Indirect transitions may participate in broadening the emission features and may have some importance in accounting for background emission at energies and momenta where direct transitions are not allowed. Another type of transition which should be considered might best be termed a "cross transition", denoting a transition for which conservation of $\vec{k}$ is not an important selection rule. Measurements of the escape depth of excited electrons by several workers^{30,31} indicate that photoemission is surface sensitive (i.e. the emission originates in the first several atomic layers). Because of this surface character, "cross" transitions need to be considered. The bulk periodicity perpendicular to the surface is broken at the surface, breaking the requirements for considering a band picture of the electronic structure for states near the surface. Thus for emission originating near the surface, "cross" transitions along $\vec{k}$ perpendicular to the surface may be important. These cross transitions may account for background emission and broadening of emission features due to direct transitions.

2. Transport and Escape. Once excited to a conduction band state, the electron may escape from the sample and be detected as a photoemitted electron. The details of this transport of the electron from a Bloch state inside the crystal to a free-electron wavefunction outside the crystal are not understood. However, something is understood about the changes in wavevector during the escape. Kane has pointed out³² that the component of the electron's wavevector which is parallel to the sample surface is conserved in the escape process, but that the perpendicular component is not conserved.

The wavevector of the electron before and after escape from the crystal is diagrammed in Fig. 6. The wavevector inside the crystal is $\vec{k}'$, with parallel component $\vec{k}'_{\parallel}$ and perpendicular component $k'_{\perp}$. The wavevector outside the crystal is $\vec{k}$, with components $\vec{k}_{\parallel}$ and $k_{\perp}$. During escape, the perpendicular component of the wavevector $k'_{\perp}$ is not conserved and in general bears no simple relation to $k_{\perp}$.³³ The surface may, in fact, mix the perpendicular components of the wavevectors of several different transitions in forming $k_{\perp}$. However, the parallel component $\vec{k}'_{\parallel}$ is conserved, equalling $\vec{k}_{\parallel}$. This is extremely important, because the experiment directly measures the $\vec{k}_{\parallel}$ of the electron in the vacuum. Knowing the kinetic energy E_K of the electron and the polar angle θ of emission, one calculates

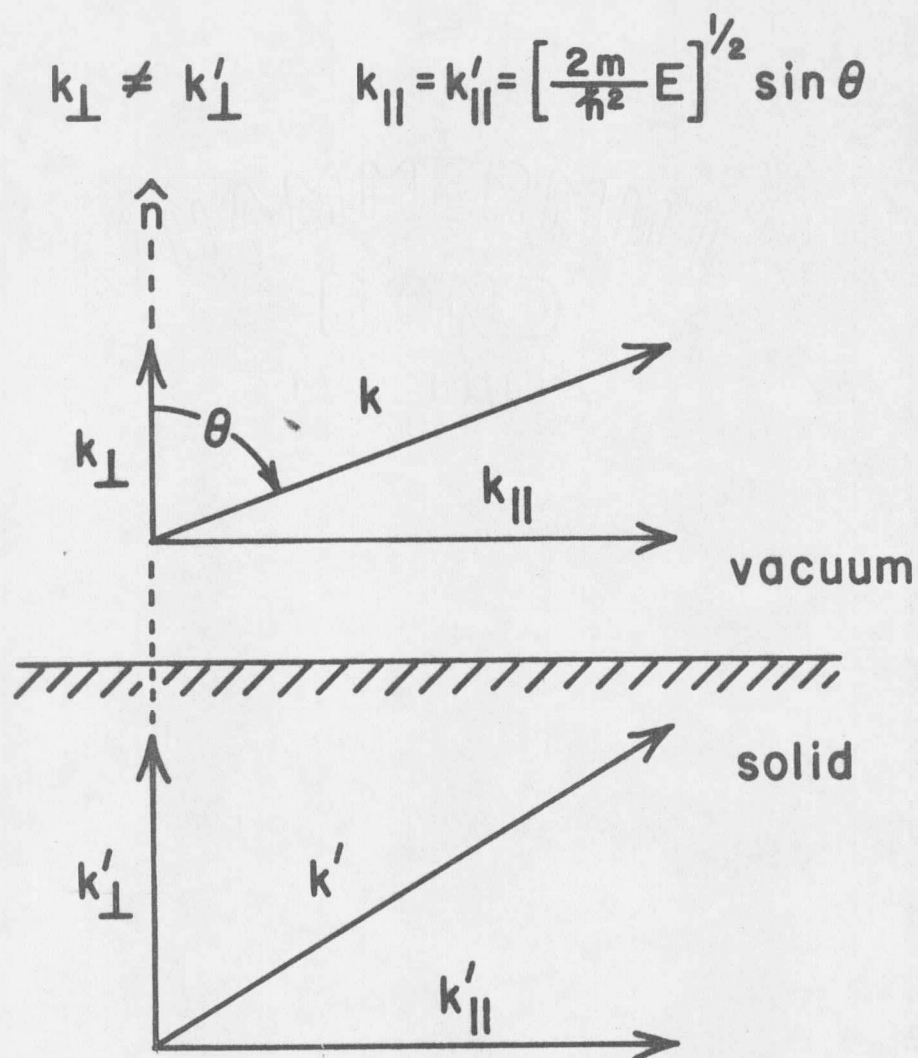


FIG. 6. Relationship between components of the electron wavevector before and after emission from the solid.

$$\vec{k}_{||} = \vec{k}_{||} = (2m E_K / \hbar^2)^{1/2} \sin \theta . \quad (17)$$

The wavevector $\vec{k}_{||}$ is in the repeated zone space. The polar angle θ is the angle between the surface normal and the emission angle.

3. Measurement of Surface State Bands. The direct measurement of $\vec{k}_{||}$ has its most important application in the study of two-dimensional systems, such as layered compounds, adsorbate layers, or surface states. The last is of interest in this study. By measuring $\vec{k}_{||}$ for a surface state feature in the emission and assuming a direct transition, one has identified the wavevector $\vec{k}_i$ of the initial state, within a surface reciprocal lattice vector. Since the bands are periodic in reciprocal lattice space, measuring $\vec{k}_i$ vs. E_i in one zone fixes it for all zones. The initial energy E_i is deduced from the kinetic energy E_K , photon energy $h\nu$, and threshold energy E_{th} using Eq. (13) in the form

$$E_i = E_K - h\nu + E_{th}. \quad (18)$$

Appropriately adjusting the emission direction and photon energy adjusts the measured $\vec{k}_{||}$ to any desired part of the surface reciprocal lattice space. Recording E_i vs. $\vec{k}_{||}$ then maps out the initial band structure in the 2-dimensional reciprocal lattice. This direct, experimental mapping of state band structure is not possible

using any other present technique.

Angle-resolved photoemission spectroscopy not only permits the mapping of the energy bands of surface states which are easily identified as such in the emission, but also aids in the separation and identification of surface emission that is more difficult to identify, due to its degeneracy with bulk valence band emission. At some angles of emission the surface emission may be found to be dominant in the spectra, due to a lack of strong bulk emission in that direction at that energy. Careful searching of the emission hemisphere may thus permit the identification of photoelectrons emitted from surface states which may not be apparent in conventional angle-integrated photoemission spectroscopy.

4. Identification of Bulk Transitions. Conservation of $\vec{k}_{\parallel}$ permits the direct measurement of E vs. $\vec{k}_{\parallel}$ relationships for surface states and other 2-dimensional systems, but does not permit such complete identification of the wavevector of bulk transitions. The wavevector $\vec{k}'$ of any bulk transition which has a possibility of escape from the crystal must have a nontrivial perpendicular component k_1' . Since k_1 , measured outside the sample, bears no simple relationship to k_1' ,³³ the wavevector of bulk transitions cannot be directly measured using angle-resolved photoemission spectroscopy. One can, however, restrict the k_1 of the detected

electrons to certain lines in $\vec{k}$ -space, rather than a volume as in angle-integrated measurements. Since $\vec{k}_{||}'$ is conserved, one can obtain spectra such that $\vec{k}_{||}$ is fixed at some appropriate value. The perpendicular component $k_{\perp}'$ is not fixed in such a process, and may originate from any value along a line in $\vec{k}$ -space corresponding to the fixed value of $\vec{k}_{||}'$. This procedure is particularly valuable if the line in $\vec{k}$ -space is chosen to correspond to a symmetry line in the bulk Brillouin zones. One such line may be the line for which $\vec{k}_{||} = 0$, that is, the emission perpendicular to the surface. Since energy bands are generally calculated only along symmetry lines in the Brillouin zone, such a restriction enables one to compare theory to experiment much more easily. Transitions observed in the data must have originated somewhere on that symmetry line, rather than at a general point in $\vec{k}$ -space. Although the wavevector of bulk transitions cannot be measured directly, data taken at fixed $\vec{k}_{||}$ can be compared with energy band calculations and the bulk transitions identified.

D. The Structure of GaAs.

1. Bulk Lattice and Brillouin Zone. GaAs has the zinc-blende crystal structure, which is common to several III-V and II-VI compound semiconductors and is illustrated in Fig. 7. The

space lattice is face-centered cubic, with four molecules per cubic unit cell. A primitive basis of one molecule of GaAs is associated with each lattice point, a Ga ion at (0 0 0) and an As ion at $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$. If both atoms were identical this would be the diamond structure.

The Brillouin zone (BZ) of the face-centered structure is shown in Fig. 8. Points and lines of high symmetry are labeled with the accepted conventions. Of particular interest in this study of the (110) face of GaAs is the Σ line from Γ to K. This line continues along the boundary of a repeated zone to X, then repeats as X - Γ . The Γ - K - X line in $\vec{k}$ -space is of interest because the normal emission is constituted of transitions originating on this line. By restricting the spectra to the normal emission, $\vec{k}_{||}$ is fixed at 0, as discussed in section IIC, and the data may be compared to bands calculated only along Σ .

2. (110) Surface and Surface Brillouin Zone. The (110) surface of GaAs is shown in Fig. 9a, with both the first and second layers of ions diagrammed. Ga ions are shown as open circles and As ions as filled circles. The unit cell, containing one molecule, is indicated by a heavy-lined rectangle, with dimensions $5.654 \times 3.998 \text{ \AA}$. The convention of azimuthal zero to be used throughout this paper is along the (001) direction lying in the

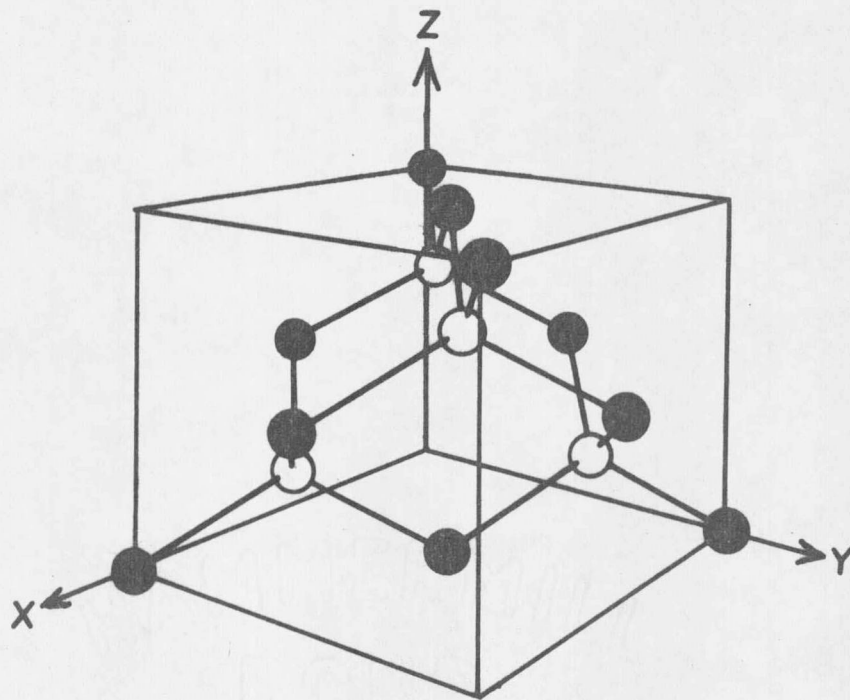


FIG. 7. GaAs space lattice.

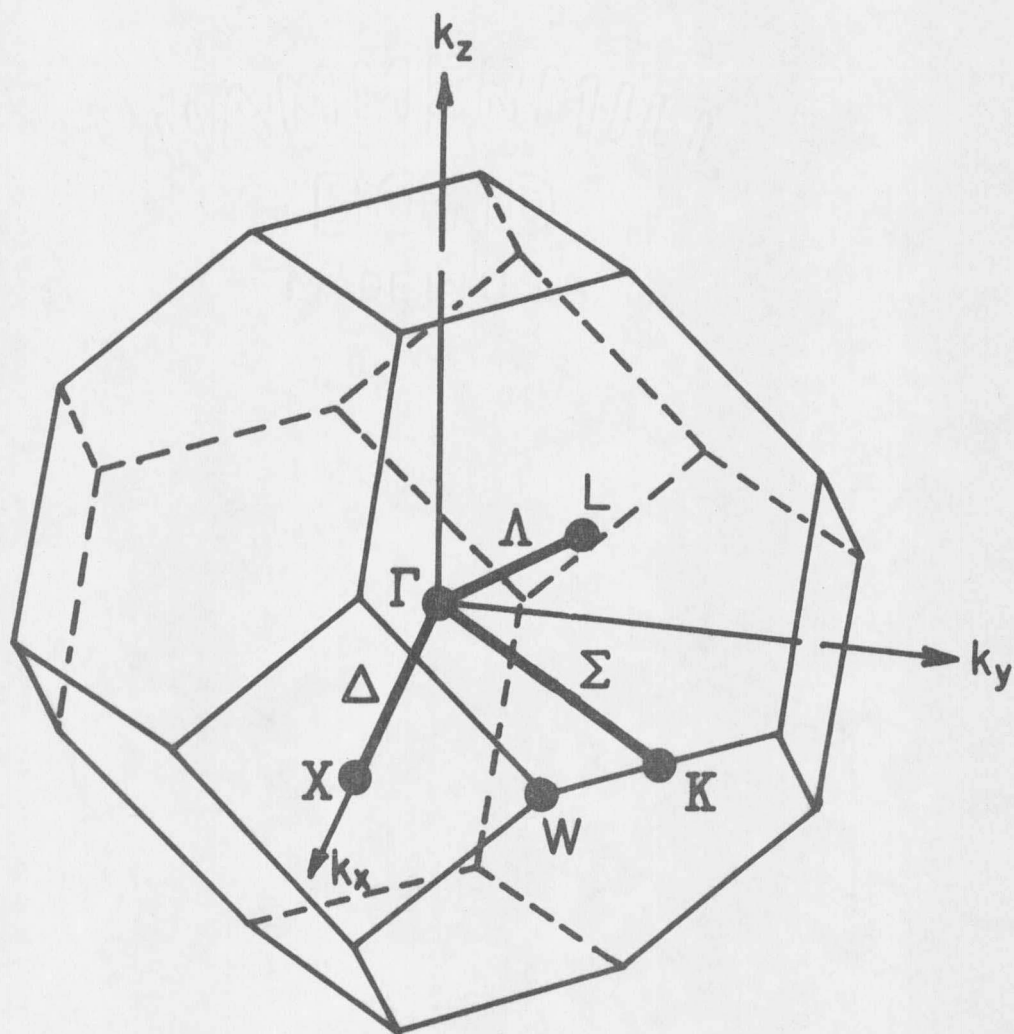
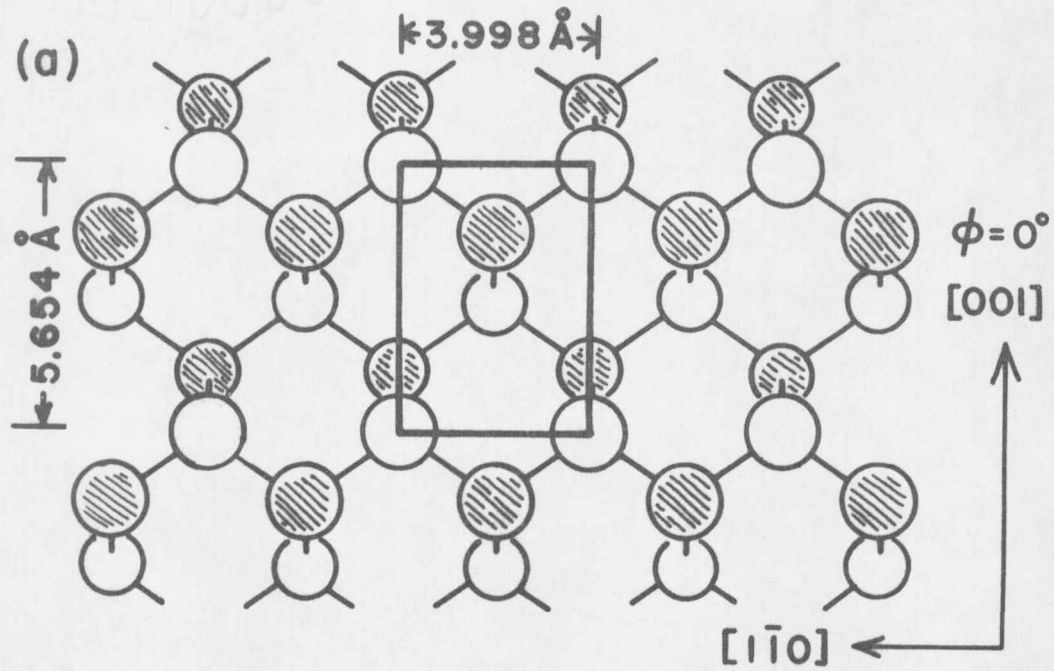


FIG. 8. GaAs bulk Brillouin zone.

surface, which is the azimuth of the Ga "dangling bond". The "dangling bonds" are those bonds broken by the presence of the surface. The only non-trivial symmetry of the surface, a mirror plane, also lies along the $\phi = 0^\circ, 180^\circ$ azimuths.

Most calculations concerning the (110) surface have assumed an ideal surface.²²⁻²⁴ That is, it has been thought that the cleaved (110) face simply terminates the bulk structure, with all ion positions and bonds just as in the bulk. Recent calculations of LEED intensity profiles by Duke and coworkers³⁴ suggest that this has been too simplistic. Their results indicate that the surface relaxes, with the Ga atoms in the surface layer lower and the As atoms raised in such a way as to preserve all bond lengths. A cross-section of an ideal and a relaxed surface are shown in Fig. 9b. The "dangling bonds" on each atom are shown as dashed lines. The symmetry of the surface and reciprocal lattice space are unaffected by the relaxation, but energy band calculations done recently for a relaxed surface²⁵ are in much better agreement with our data than earlier calculations on an ideal surface.^{22,24}

The reciprocal lattice for the (110) surface is shown in Fig. 10. The first Brillouin zone is outlined in solid lines and symmetry points labeled according to the notation of Jones³⁵; $\bar{\Gamma}$ is the center of the zone.



(b) Side view:

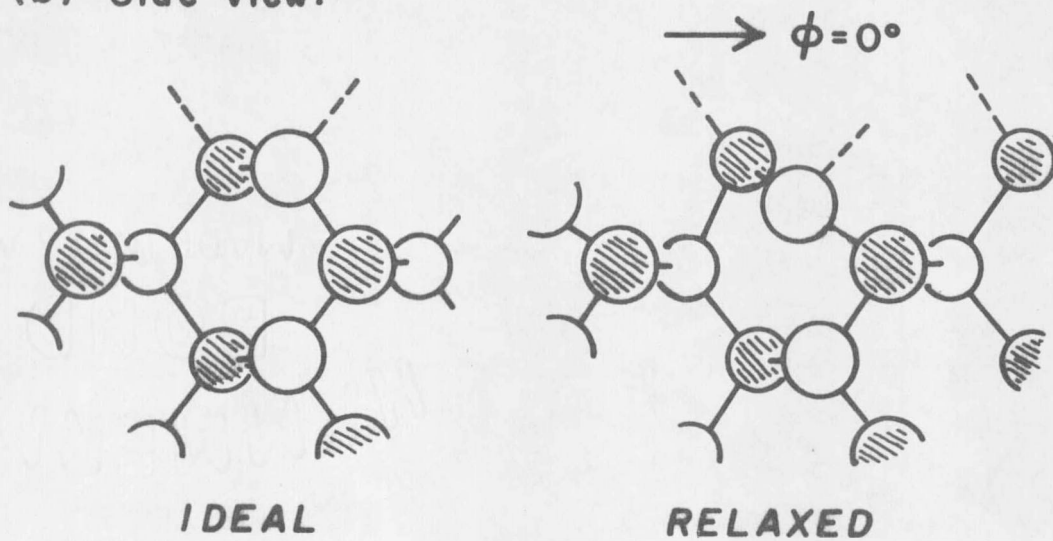


FIG. 9. (a) (110) surface lattice. (b) Side view; ideal and relaxed.

GaAs (110) surface Brillouin zone

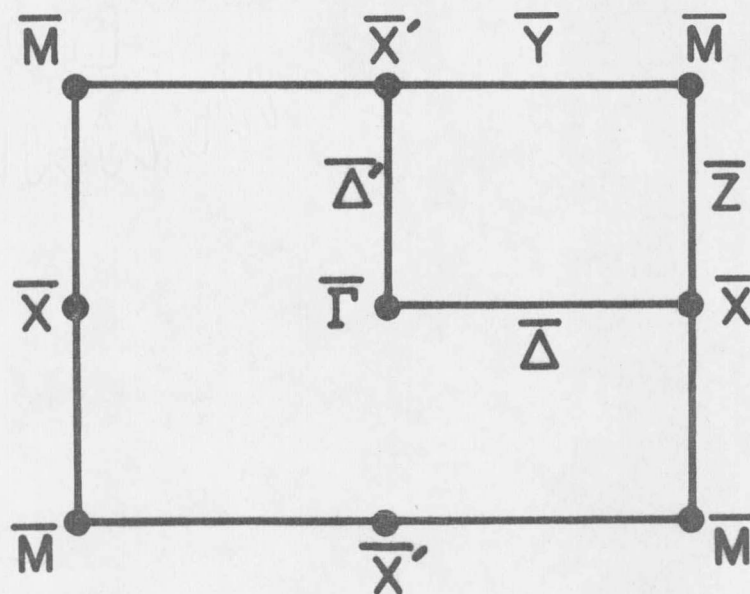


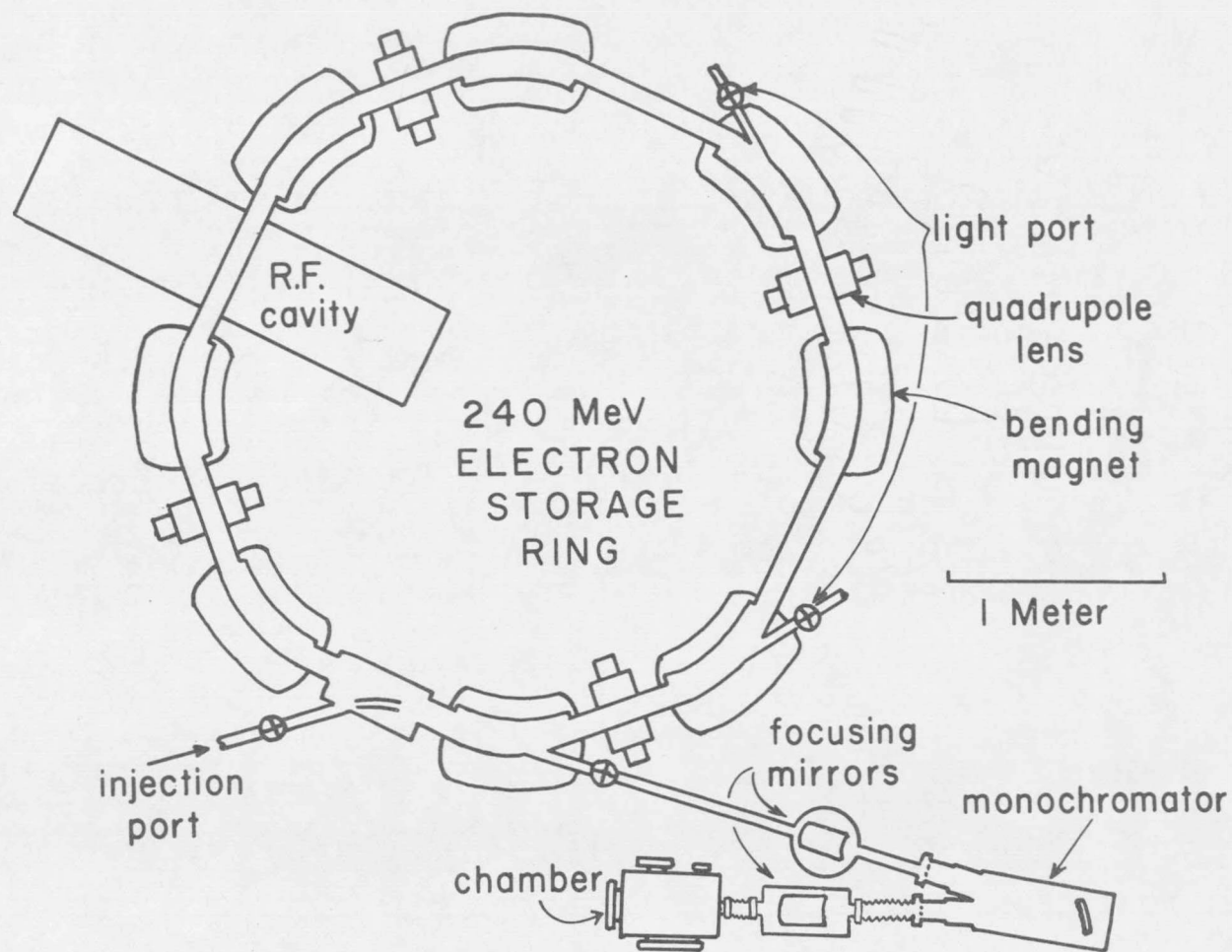
FIG. 10. (110) surface Brillouin zone.

III. EXPERIMENTAL EQUIPMENT AND PROCEDURES

A. Synchrotron Radiation Source.

Synchrotron radiation from the 240 MeV electron storage ring at the University of Wisconsin's Synchrotron Radiation Center was used as the source of high energy photons for the experiment. This type of radiation source has many inherent advantages for use in photoemission spectroscopy.¹⁵ First and most important, the radiation consists of an intense continuum of photon energy which extends from the infra-red to soft X-rays. The use of a monochromator provides a continuously tunable photon source of a brightness and at energies not available by any other means. Second, the radiation is strongly polarized in the plane of the orbit of the electrons, permitting investigations of polarization effects in the photoexcitation process. Third, a good vacuum must be maintained in the storage ring, greatly facilitating the maintenance of ultra high vacuum in the experimental chamber without intervening windows. Last, by its nature the beam of radiation is very stable in both position and intensity.

The radiation used for the experiment was passed through a 1-meter normal incidence monochromator owned by the Synchrotron Radiation Center. Figure 11 diagrams the storage ring layout with



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FIG. 11. Tantalus I storage ring with our monochromator and chamber.

the beam line, monochromator, and chamber used in these experiments indicated. Radiation produced in the field of a bending magnet passes out of the ring and down the beam line to a focusing mirror. This mirror focuses the beam of radiation at the entrance slit of the monochromator. Our equipment (shown) attaches to the exit slit housing of the monochromator.

The light curve, or spectral dependence of the intensity of the light beam after passing through the monochromator, is plotted in Fig. 12 as a function of photon energy $h\nu$, in eV. The greatest intensity is near $h\nu = 18$ eV. The useful limit of photon energy, as determined by intensity fall-off, was generally near $h\nu = 30$ eV. The light curve, which is sensitive to chamber alignment and which changes slowly over a period of months as the reflecting surfaces age, was obtained for each session of experiments by depositing a thin film of sodium salicylate on the vacuum side of a small Boro-silicate window in line with the photon beam. A photomultiplier tube was then positioned behind the window to detect the fluorescence of the synchrotron radiation striking the sodium salicylate. The monochromator was scanned through the spectrum as the output of the photomultiplier was monitored with a picoammeter. The resulting light curve was used to normalize all spectra to a constant intensity level, greatly facilitating data interpretation.

The dispersion of the monochromator was $8.3 \text{ \AA/mm}$ of slit width.

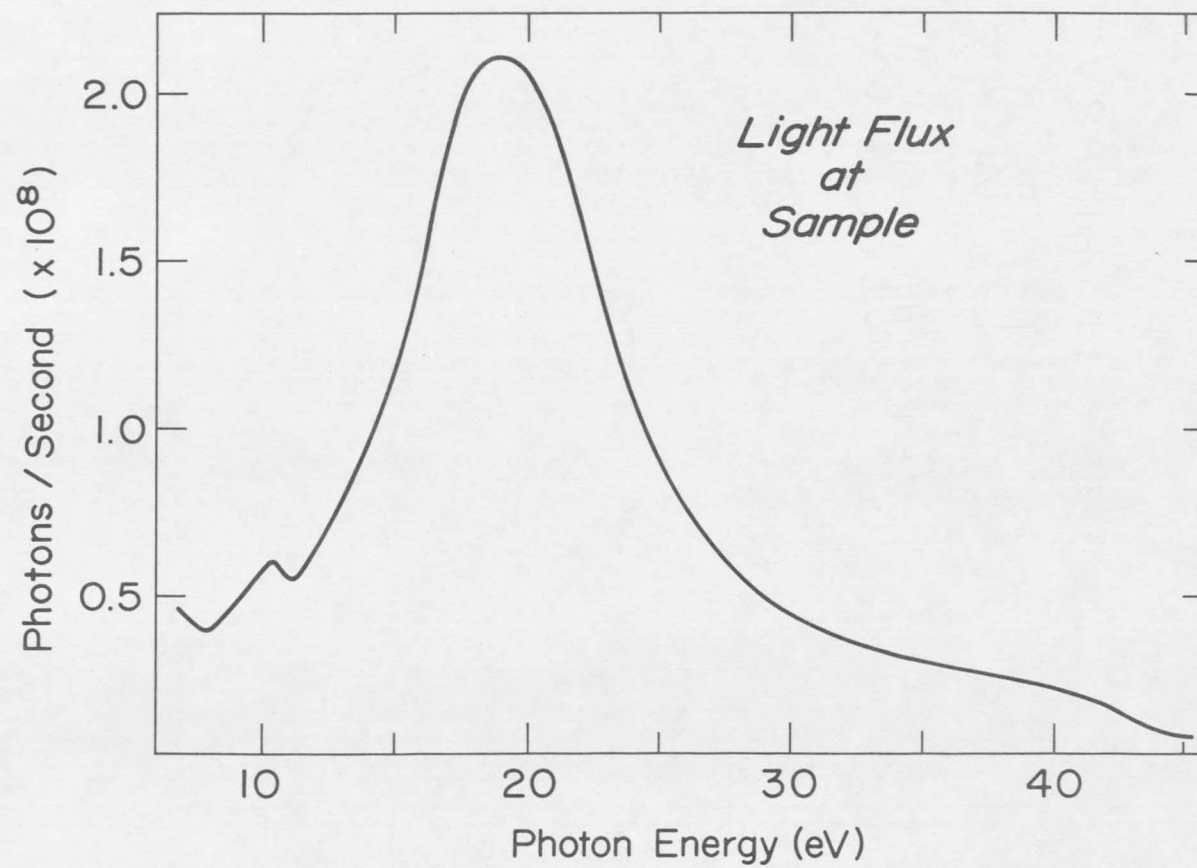
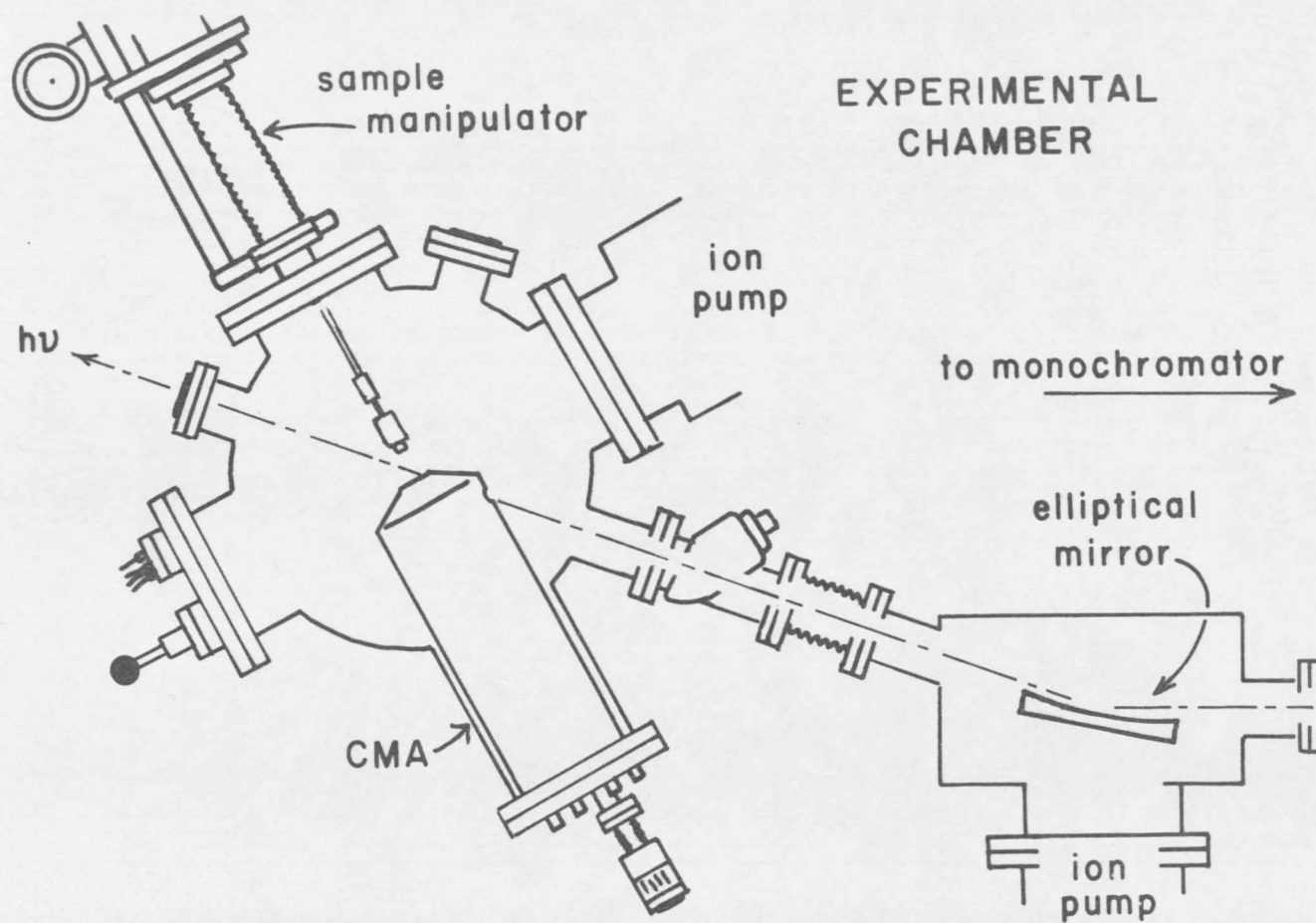


FIG. 12. Light curve.

The slits were opened to 0.75 mm for all angle-resolved measurements, resulting in a constant wavelength bandpass of $\Delta\lambda = 6.2 \text{ \AA}$. Since all spectra are referenced to photon energy $h\nu$ rather than wavelength λ , it is more useful to refer to an "energy bandpass". For $\Delta\lambda = 6.2 \text{ \AA}$, $\Delta(h\nu)$ is a variable function of the photon energy, varying from $\Delta(h\nu) = .05 \text{ eV}$ at $h\nu = 10 \text{ eV}$ to $\Delta(h\nu) = .44 \text{ eV}$ at $h\nu = 30 \text{ eV}$.

E. Experimental Chamber.

The photoemission measurements were made in an all-metal, ultra-high vacuum experimental chamber maintained by the MSU photoemission group at the Synchrotron Radiation Center. The chamber, diagrammed in Fig. 13, has been used to study a wide variety of materials by conventional photoemission spectroscopy. UV light from the monochromator is focused by an elliptical mirror to a 1 mm square spot at the source point of a double-pass cylindrical mirror analyzer (CMA). The CMA is positioned such that the light beam passes through part of the analyzer before reaching the source point; holes are positioned in the side of the CMA and through its hemispherical screens to accommodate the beam. The source point of the CMA is at the center of the chamber and is surrounded by a variety of vacuum ports. The following were mounted in these ports for a typical experimental session; (1) two samples, mounted



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FIG. 13. Schematic of the experimental chamber.

on two different sample manipulators, (2) a cleaving blade at one port and a cleaving anvil at an opposing port, each on a linear motion feedthrough, (3) leak valves for bleeding in controlled amounts of gases such as O_2 and H_2 , (4) an electrical feedthrough to an evaporating basket of Sn, (5) a crystal oscillator for monitoring evaporation rates, and (6) several viewing ports. The use of each of these will become apparent in the description of the experimental procedures. Vacuum inside the chamber, after baking, was maintained at a base pressure of 1×10^{-10} Torr. Surface contamination rates at such pressures are very low, allowing the examination of clean sample surfaces for extended periods of time.

C. Angle-Resolving Analyzer.

Energy and direction of the photoemitted electrons were detected in the two-stage cylindrical mirror analyzer, which was modified to permit the angle-resolving capability. In its normal mode of operation, the CMA detects electrons from a wide range of emission directions, forming a cone. The modification, within the inner cylinder and consisting of an axially mounted, rotatable drum with two small apertures in its side, blocks all but a small segment of this electron flux. The beam of electrons which passes through the selected aperture and is subsequently detected corresponds to a specified small range of emission angles. Rotational reposi-

tioning of the drum selects any part of the electron flux by repositioning the aperture. The drum may also be translated along the axis of the CMA, permitting 1) the selection of the second aperture of different angular width, or 2) the removal of the drum from the electron flux altogether, restoring the analyzer to its normal mode of operation. These motions are accomplished quickly and easily by means of a rotary/linear feedthrough without breaking vacuum.

Figure 14 shows a schematic of the double pass two-stage CMA in angle-integrated mode. The drum is shown in the retracted position, where it does not affect the normal operation of the analyzer. The mounting and feedthrough for the drum are excluded for clarity, and only one aperture is shown in the drum. For photoemission spectroscopy, electrons of the desired kinetic energy are accelerated to a constant pass energy by two hemispherical screens and pass into the fieldfree interior of the first stage inner cylinder. The trajectory through the two cylindrical mirror stages is indicated by dotted lines. The accepted electron flux is determined by the slits through which the electrons pass into and out of the inner cylinders. The accepted flux is in the shape of a cone of half-angle 42.3° and 12° thickness. Two iris's, one at the rear of each stage, serve to define the energy and spatial resolution of the instrument. Electrons exiting the second stage

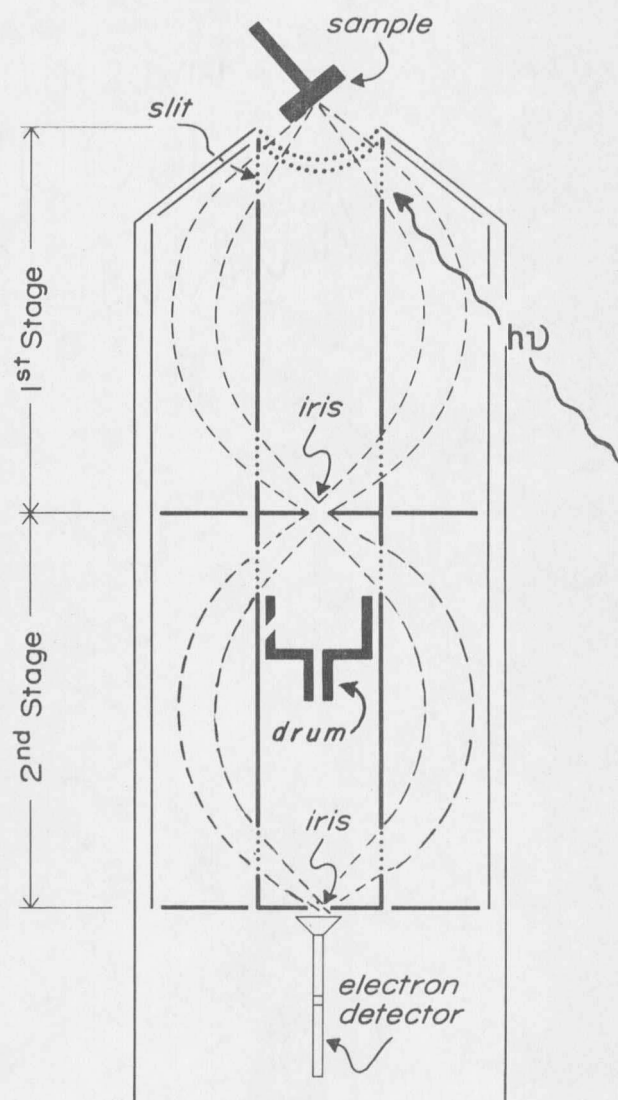


FIG. 14. CMA in angle-integrating mode.

are detected by an electron multiplier.

Figure 15 shows the analyzer in the angle-resolving mode. The hemispherical screens and first stage function just as before. The drum is now positioned between the iris of the first stage and the third set of slits, within the second stage inner cylinder. The drum covers the slits, blocking all of the electron flux except that passed by the selected aperture in the cylindrical surface of the drum. By rotating the drum, any segment of the electron cone can be selected and passed through the second stage to be detected.

To achieve both rotational and linear movement the drum "rides" on an axle fixed at the axis of the CMA by a spindle mounted inside the second-stage inner cylinder. Figure 16 shows the apparatus in position. The spindle is machined to a close fit to the inside diameter of the inner cylinder and is held in place by set screws. A stainless steel shaft with the drive gear fastened at the upper end passes through a vertical, off-axis hole in the spindle. This shaft and gear transmit the linear and rotary motion to the drum. The drum is in the form of a hollow cylinder, closed at the lower end, with a hub extending downward at its center. The axle, as shown in the figure, is fastened rigidly to the spindle and passes up through a hole in the hub, so that the drum moves freely on it. At the upper end of the hub a second gear is staked to the base of the drum, a gear which meshes with the drive gear. When the shaft

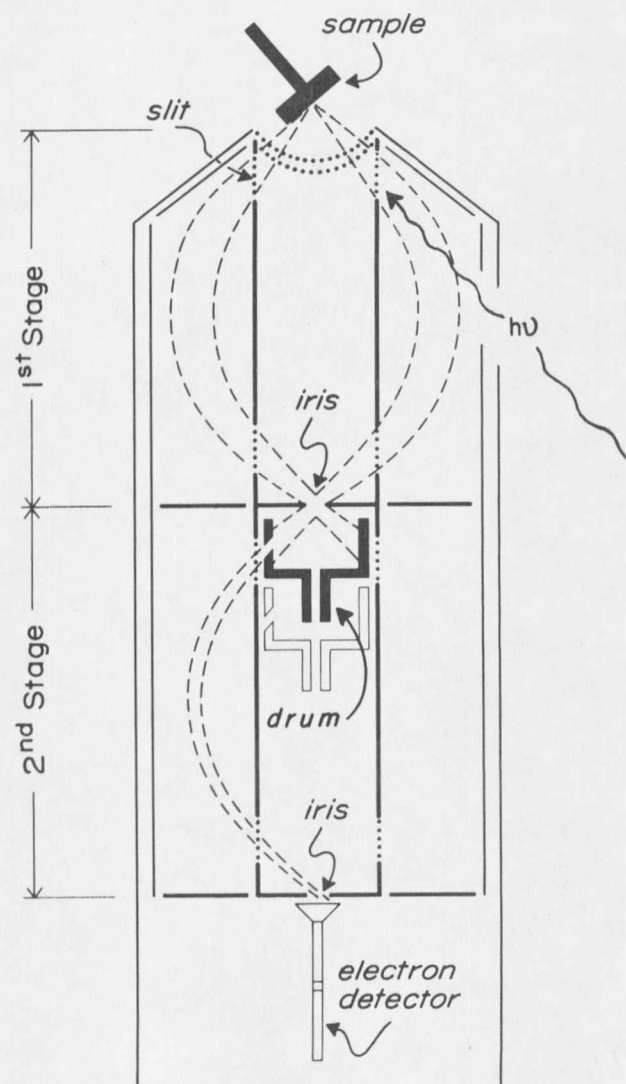


FIG. 15. CMA in angle-resolving mode.

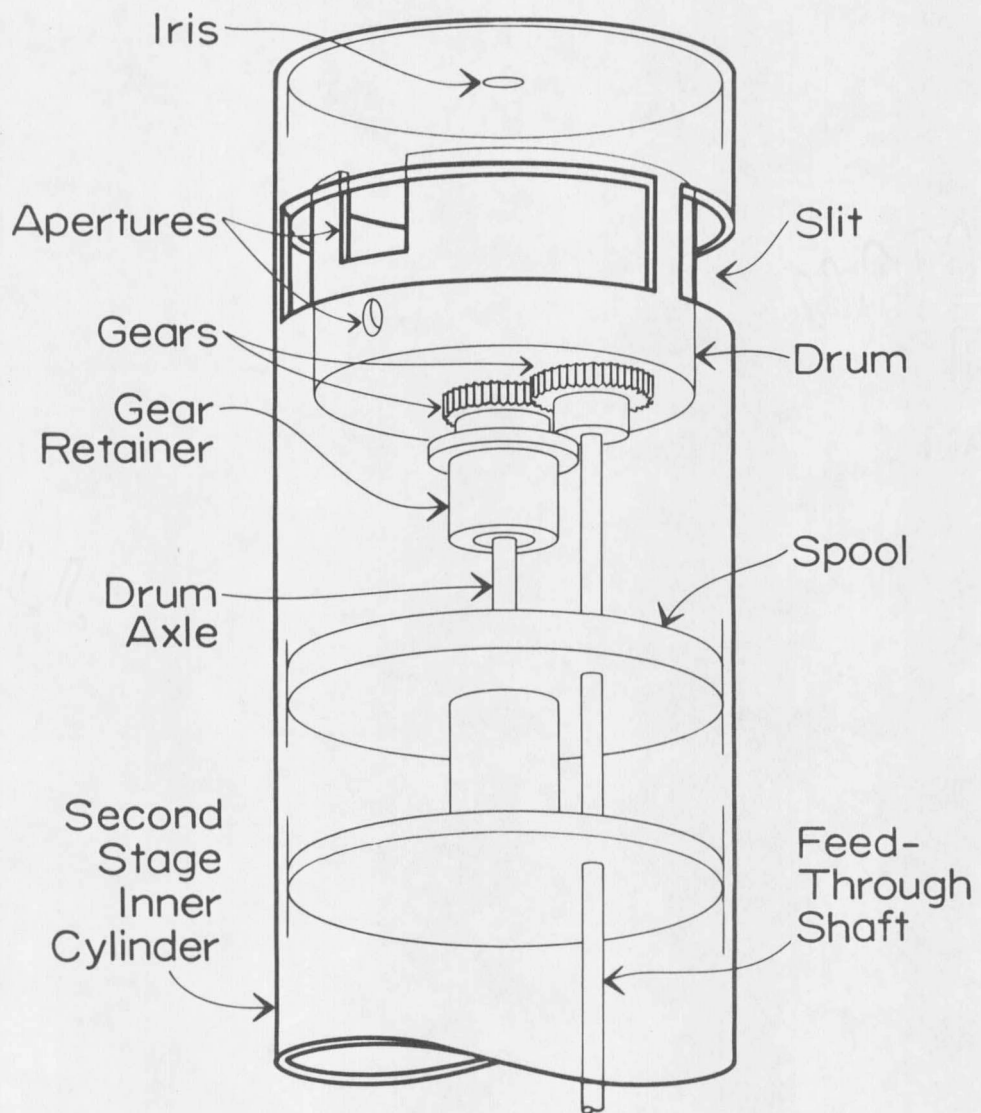


FIG. 16. Angle-resolving CMA modification.

is rotated, the motion is transmitted through the gears to the drum, which rotates on the axle. Below these gears a retaining washer is attached by means of a set screw. The drive gear is captured between this retaining washer and the base of the drum, so that when the shaft is moved upward, the drive gear pushes the drum upwards, sliding up the axle. When the shaft is moved down, the bottom of the drive gear contacts the retaining washer and slides the drum down. The assemblage of gears and retainer is loose enough to permit free rotation of the drum and yet tight enough for positive vertical positioning. Gear ratio for rotation is 1:1.

Two apertures are shown in the side of the drum in Fig 16, a $12^{\circ} \times 12^{\circ}$ rectangle and a 4° hole. Either of these apertures could be selected, but the 4° resolution was used for all angle-resolved spectra taken in the course of this work. The larger aperture is of use when the signal level is too low at 4° resolution.

The drum, spindle, and retaining washer are all machined from Everdur, a copper alloy with good vacuum and magnetic properties and mechanical strength. Most bearing surfaces are Everdur on stainless steel, to minimize vacuum welding problems.

The combination rotary/linear feedthrough at the base of the analyzer is not shown. It consists simply of a standard mechanical rotary feedthrough mounted on a stainless steel bellows. An external

bracket aligns the rotary and holds the bellows at any desired degree of compression, providing the linear degree of freedom necessary to position the drum.

In operation of the analyzer one finds that the transmission through the analyzer is not isotropic. That is, moderate intensity changes occur as the drum rotates to select different portions of the flux cone. These may be measured by fixing the sample and rotating the drum. These fluctuations are primarily due to Moiré patterns between the two hemispherical retarding screens and between the several screens covering the inner cylinder slits. Moiré patterns are shadow patterns produced whenever two screens are interposed over one another.³⁶ In addition, there are shadows, or blank spots, in the flux cone due to the supporting posts through the inner cylinder slits. Because of these anisotropies it was found to be most practical to record spectra at various fixed drum positions, rather than continuously rotating the drum. Counting rates in the angle-resolved mode, when the anisotropy is taken into account, are just as would be expected from the configuration geometry.

In using the CMA to collect spectra in either the EDC or CIS mode, focusing properties of the hemispherical screens³⁷ produce a distortion of the counting rate which is a function of kinetic energy. At low kinetic energy the CMA accepts electrons from a

somewhat larger area of the sample, increasing the count rate if the sample is illuminated over an area larger than the nominal target area. This effect is a smooth function of kinetic energy and will be neglected in the interpretation of the data.

D. Analyzer-Sample Orientation.

1. Emission Cone Orientations. The modified CMA is used for angle-resolved photoemission spectroscopy by mounting the sample on a rotatable shaft such that different polar and azimuthal angles may be selected by sample and/or drum rotation. Two different sample/analyzer orientations proved to be of value in the study. In the configuration diagrammed in Fig. 17 the axis of rotation of the sample is aligned with the axis of the CMA. The cone of electron flux normally accepted by the CMA is then centered about the normal $\hat{n}$ to the sample surface. Only electrons with polar angle $\theta = 42.3^\circ$ (the half-angle of the acceptance cone) may be selected by the drum aperture. The polar angle θ of the emitted electrons is defined as the angle between the surface normal and the emission direction. However, any azimuthal angle ϕ , relative to the sample symmetries, may be selected either by rotating the sample or the drum. The electric polarization vector $\vec{\epsilon}$ of the incident radiation lies in the plane of the surface (s polarization) and may be positioned relative to the sample symmetries indepen-

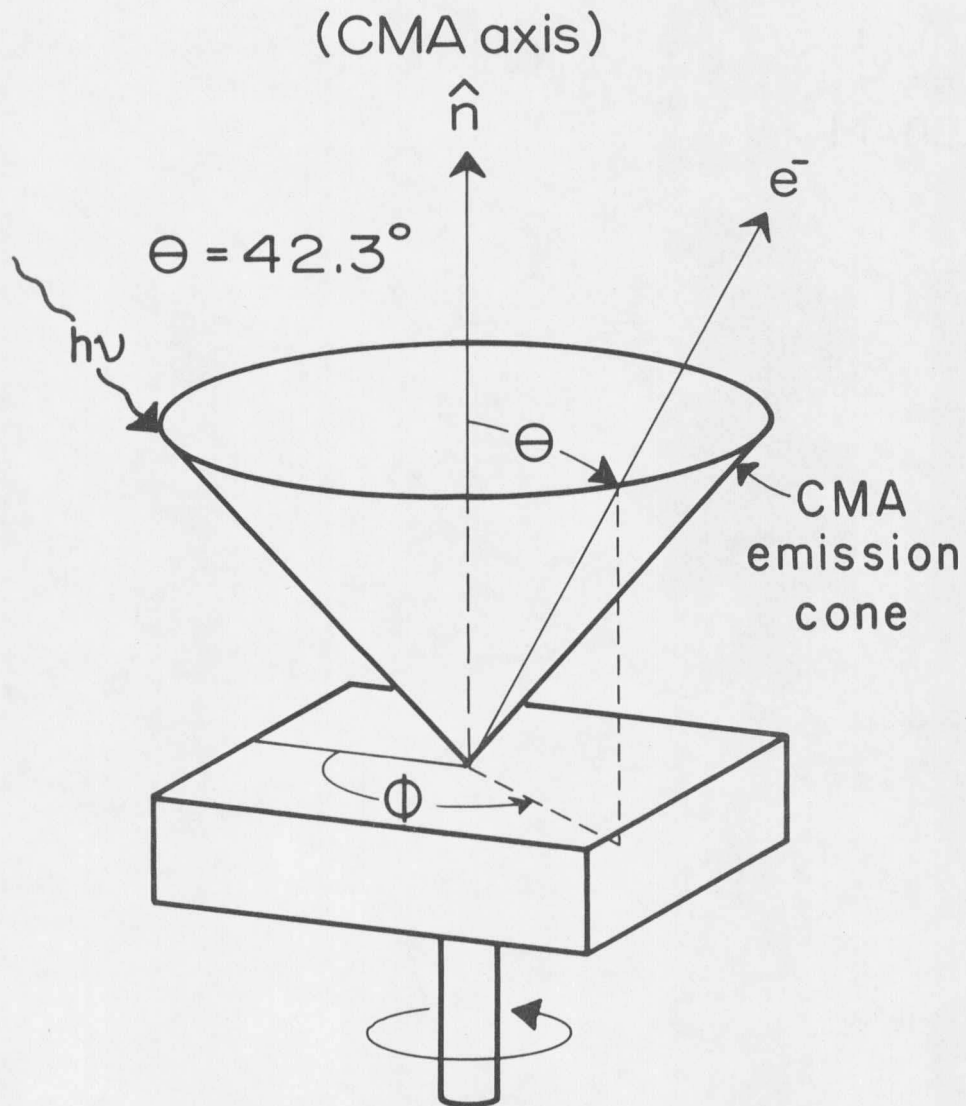


FIG. 17. Sample/emission cone orientation for sample normal aligned with CMA axis.

dently of the electron collection azimuth. Rotating both sample and drum in conjunction fixes the azimuthal angle while rotating $\vec{\epsilon}$ relative to the crystal lattice.

The restriction to one polar angle is eliminated in the second sample/analyzer orientation, shown in Fig. 18. In this configuration the sample normal $\hat{n}$ is aligned with the side of the cone of electron flux normally accepted by the CMA (from which one chooses angle-resolved segments). Examination of Fig. 18 shows that any polar angle between $\theta = 0^\circ$ (normal emission) and $\theta = 84.6^\circ$ (nearly grazing emission) may be selected by rotating the drum. The desired azimuthal angle must then be selected by rotating the crystal. This configuration is much more useful in that nearly the whole emission hemisphere is accessible. However, in this configuration the orientation of the electric polarization vector $\vec{\epsilon}$ may be independently varied only for normal emission ($\theta = 0^\circ$). The angle between $\vec{\epsilon}$ and the azimuth of the collected electrons is fixed for specified polar angle. Polarization effects for data taken in this configuration, except for normal emission, are therefore neglected in the interpretation of the results.

For normal emission in the configuration of Fig. 18 the situation with respect to polarization effects is completely different. Rotating the crystal changes only the orientation of $\vec{\epsilon}$ with respect to crystal symmetries, leaving the collection direction unchanged.

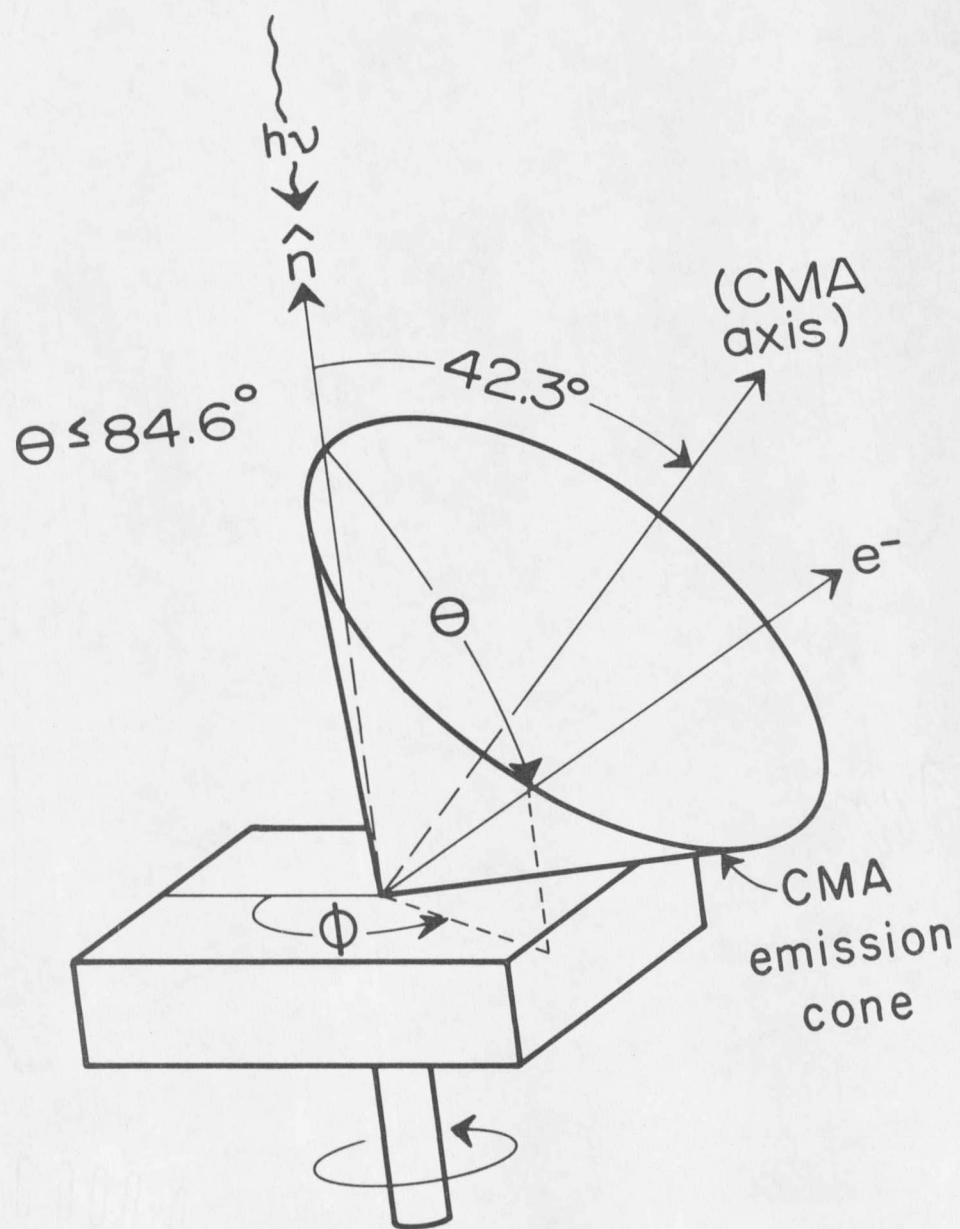


FIG. 18. Sample/emission cone orientation for sample normal 42.3° from the CMA axis.

This configuration then is very useful in studying polarization effects in the normal emission.

2. Polarization Mounting. With the radiation incident along the normal to the surface, as indicated in Fig. 18, $\vec{\epsilon}$ always lies completely in the plane of the surface, resulting in s polarization. In order to study the emission with a substantial perpendicular component in $\vec{\epsilon}$ (p polarization), a special sample manipulator was devised, the effect of which was to enable the rotation of $\vec{\epsilon}$ up out of the surface by 42.3° . The sample/analyzer configuration remains the same as in Fig. 18, but with the radiation incident along the side of the cone 90° around the cone from the sample normal. Rotating the sample rotates $\vec{\epsilon}$ relative to the crystal symmetries as before, but $\vec{\epsilon}$ remains at an angle of 42.3° relative to the plane of the surface. The normal emission from the surface could then be studied as a function of rotating $\vec{\epsilon}$, either in the plane of the surface or in a cone projecting out of the surface. The manipulator was designed so that either of these polarization conditions could be selected from outside the chamber while under UHV conditions.

The principle of operation of the "polarization mounting" is sketched in Fig. 19. A pair of Everdur bevel gears transfers rotary motion from a rotary feedthrough, whose axis is parallel

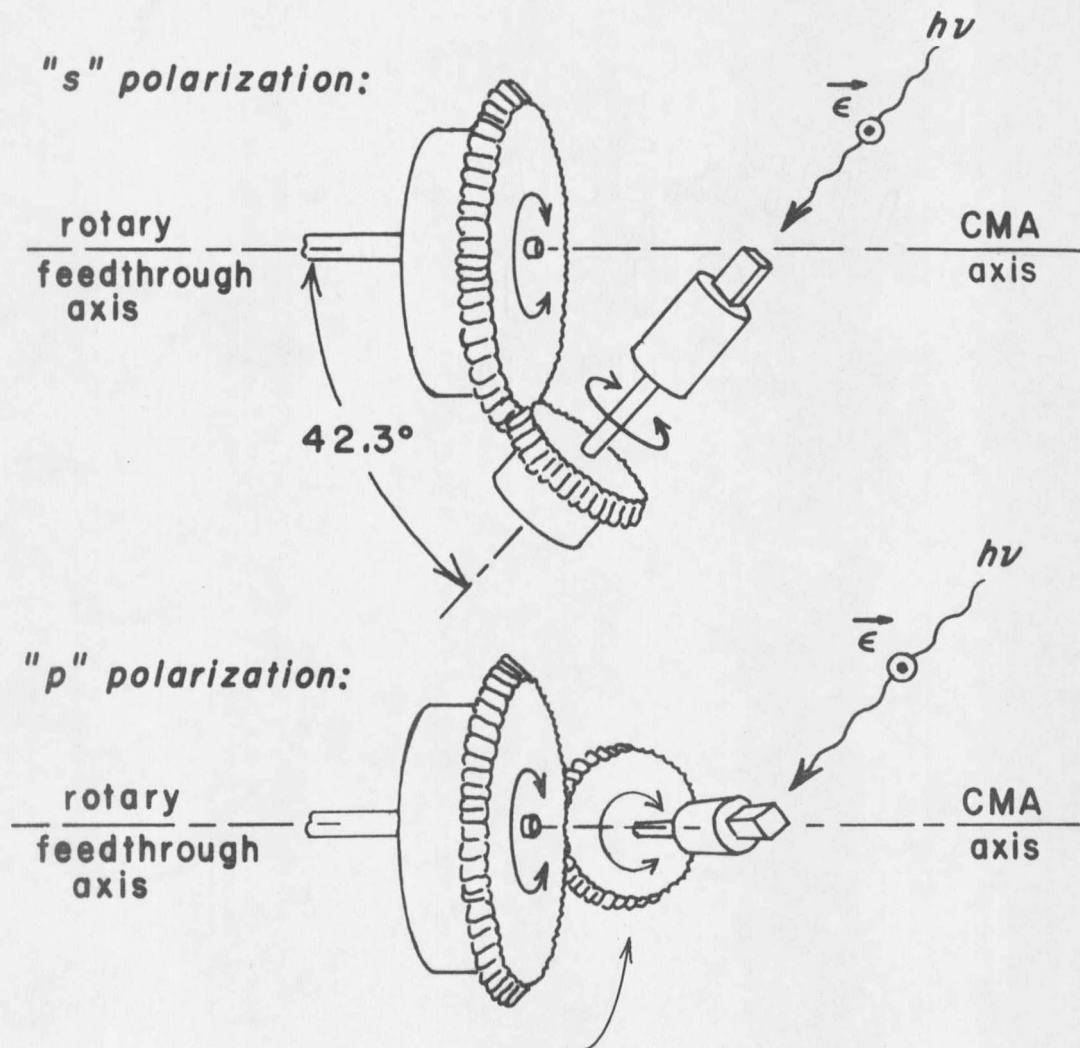


FIG. 19. "Polarization" sample manipulator, shown in two positions.

to the axis of the CMA, to the axis of sample rotation at an angle of 42.3° . The sample is mounted to a shaft on this second axis, duplicating the analyzer/sample alignment of Fig. 18. That is, the normal to the surface is aligned with the side of the acceptance cone of the CMA. The mounting of the second gear and sample is movable, but held in position by a spring-loaded detent. A stop on the rotary feedthrough shaft catches at each end of the available rotary travel and permits rotation of the subassembly around the axis of the CMA to another of the three detent positions. Once set in the new position, the sample may again be rotated freely about the normal to its surface, but now that normal is aligned with a different part of the acceptance cone and the radiation is striking the sample from a different angle. The gear ratio of the bevel gears is 2:1 so that in each position the sample may be rotated by more than $1\frac{1}{2}$ complete turns. The entire assemblage is mounted at the end of a standard sample manipulator, consisting of a rotary feedthrough at the top of a long bellows section, with linear and X-Y motion capability. The manipulator with attachments is mounted in a flange opposite the CMA such that the axis of the rotary feedthrough is parallel to the axis of the CMA.

A photograph of the "polarization mount" is shown in Fig. 20. Figure 20 shows the mount in the s polarization position, where

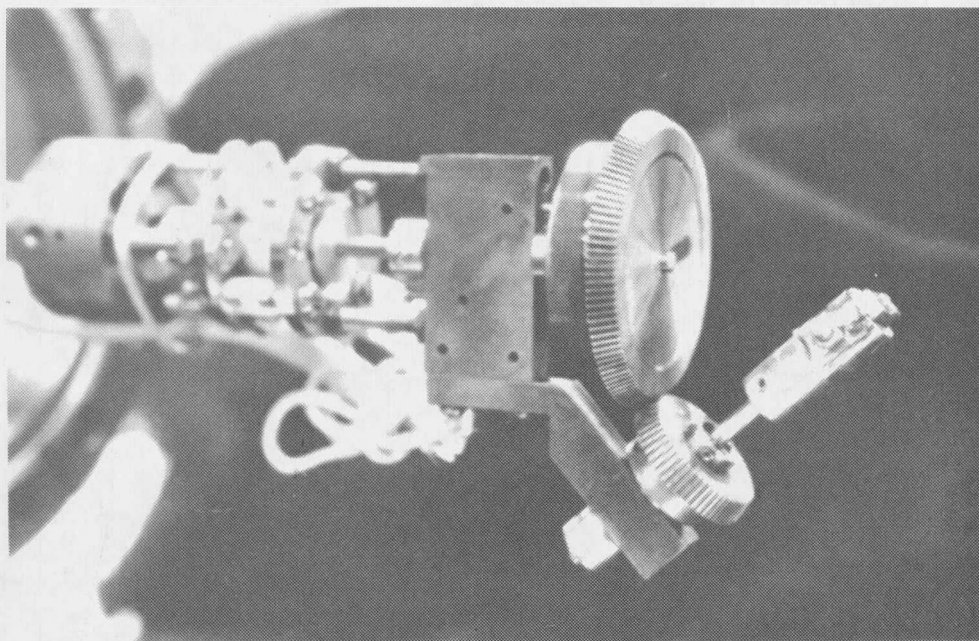


FIG. 20. Photograph of "polarization" sample manipulator.

the light is incident along the sample normal and $\vec{\epsilon}$ stays in the plane of the surface as the sample is rotated. The bevel gears are clearly shown, as is the sample holder with a crystal of GaAs in place. This orientation duplicates the geometry of Fig. 18.

E. Analyzer Electronics.

The cylindrical mirror analyzer had pre-accelerating/retarding grids and was operated in a constant pass energy mode for photoelectron spectroscopy. In the constant pass energy mode the potential between inner and outer cylinders is kept constant, so as to pass only electrons of a specified fixed kinetic energy. Potential between the two hemispherical screens at the front of the analyzer is then adjusted to accelerate or decelerate the photoemitted electrons of the desired kinetic energy to this pass energy as they enter the analyzer. Of the two hemispherical screens, the first is at ground potential by construction. The second hemispherical screen is attached to the first stage inner cylinder, necessitating that the potentials on inner and outer cylinder be changed in unison with the accelerating potential, keeping the difference between inner and outer cylinders constant. The sample could be biased to adjust for contact potentials.

The potentials on the various parts of the analyzer are illustrated in Fig. 21. The difference between inner and outer

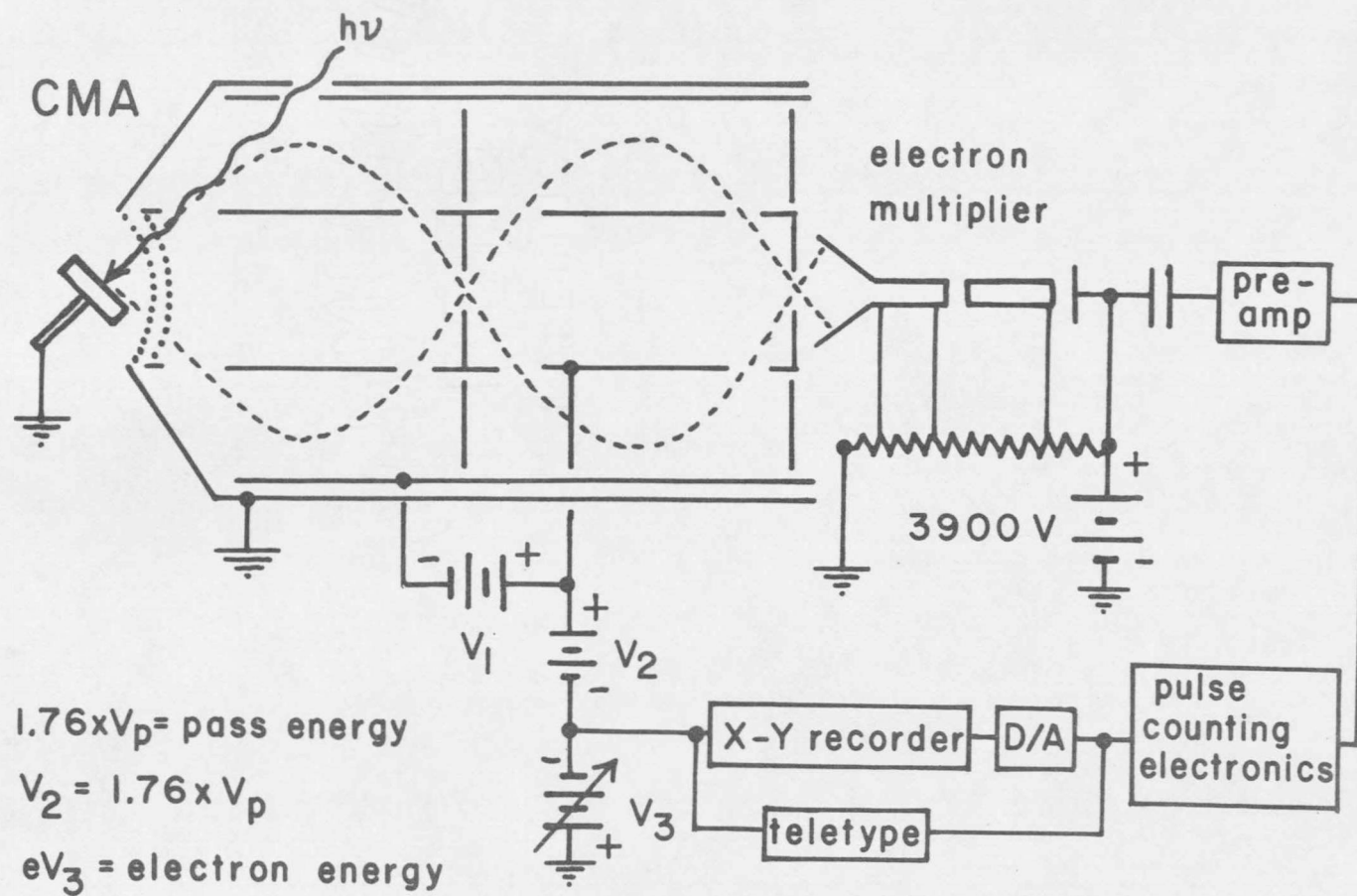


FIG. 21. Analyzer and associated electronics.

cylinders is fixed at V_p , and the resulting pass energy of the analyzer is $E_p = 1.76 \times V_p$. The potential of the inner cylinder and the attached second hemispherical screen is $V_2 - V_3$. When V_3 is set at zero, the hemispherical screens accelerate zero kinetic energy electrons to an energy E_p , and these electrons are passed through the analyzer. Adjusting V_3 to the desired electron energy adjusts the accelerating potential at the hemispherical screens so as to pass those electrons into the analyzer with a new energy equal to E_p . The potential V_3 is fixed or swept as appropriate to accomplish each of the three modes of photoemission spectroscopy described in Chapter II.

Electrons exiting the second stage of the CMA are detected with pulse counting electronics as diagrammed in Fig. 21. Each exiting electron impinges on the Spiraltron continuous dynode electron multiplier, producing a pulse of electrons at the collector. The electron multiplier has a dark count of less than 2-3 per second so the signal to noise ratio was essentially at the theoretical limit (i.e. $\sqrt{n}/n$). The pulse is reshaped in a pre-amplifier and then amplified and counted in a digital ratemeter. The digital output of the ratemeter at the end of a counting interval is sent to a teletype for recording on punched tape and also converted to an analog voltage for display on an X-Y recorder. The energy axis of the recorder and paper tape was the electron energy E_p in the

case of an EDC, or the photon energy $h\nu$ in the case of a CIS or CFS.

F. Sample Preparation.

GaAs is a nearly ideal material for this type of study in that a clean (110) surface can be easily prepared in situ by cleaving within the vacuum chamber. In addition, at the base pressure of the vacuum chamber, 1×10^{-10} Torr, surface contamination rates are so low that no noticeable contamination would accumulate over a period of 5 days. The sticking coefficients are small,³⁸ on the order of 10^{-5} . Thus a crystal could be cleaved on Monday morning and studied for a full week.

1. Source of GaAs Crystals. Eleven different cleaved (110) surfaces on six separate p-type GaAs crystals were studied. All six crystals were Zn doped to a density of from 1.5×10^{18} to $4.8 \times 10^{19} \text{ cm}^{-3}$, coming from three separate batches. The crystals were $4.8 \times 4.8 \times 13$ mm, oriented with a (110) face at the ends and (111) faces at two opposing sides. The crystals were purchased from Laser Diode Laboratories, Inc., 205 Forrest St., Metuchen, N.J.

2. Mounting and Cleaving. Crystals were cleaned in the usual degreasing solutions and then etched lightly in a dilute methanol solution of bromine. They were then mounted in a copper sample

holder with spring steel clips holding the crystal from two sides, allowing a certain amount of movement in the cleaving process. Figure 22 shows a photograph of a sample in its holder, with a cleaved chip and a pencil for scale comparison. The strip of metal inserted between the crystal and the steel clip is soft copper, to reduce the probability of the crystal fracturing at the sharp edges of the steel clip. When mounted, the crystal extended from the holder far enough to attempt 3-4 cleaves from each crystal, taking off ~ 2 mm each time.

The crystals were cleaved using a copper anvil and a tungsten carbide blade, each mounted on linear motion feedthroughs. With the chamber pumped out to its base pressure, the sample was positioned on the line between anvil and blade. The anvil was then moved up to gently contact the crystal on one side and the blade on the other side, positioned parallel to the (110) face and back 2 mm. External supporting mounts permitted the careful positioning and movement of anvil and blade. Once in position, steadily increasing pressure was applied simultaneously to both anvil and blade until the sample cleaved. If alignment of blade with the (110) plane was good, the chip would pop off with only a few pounds of pressure, leaving a mirror-like surface with few discernable steps or imperfections. The chip shown in Fig. 22 was from such a good cleave. If the alignment was less than good, the cleave

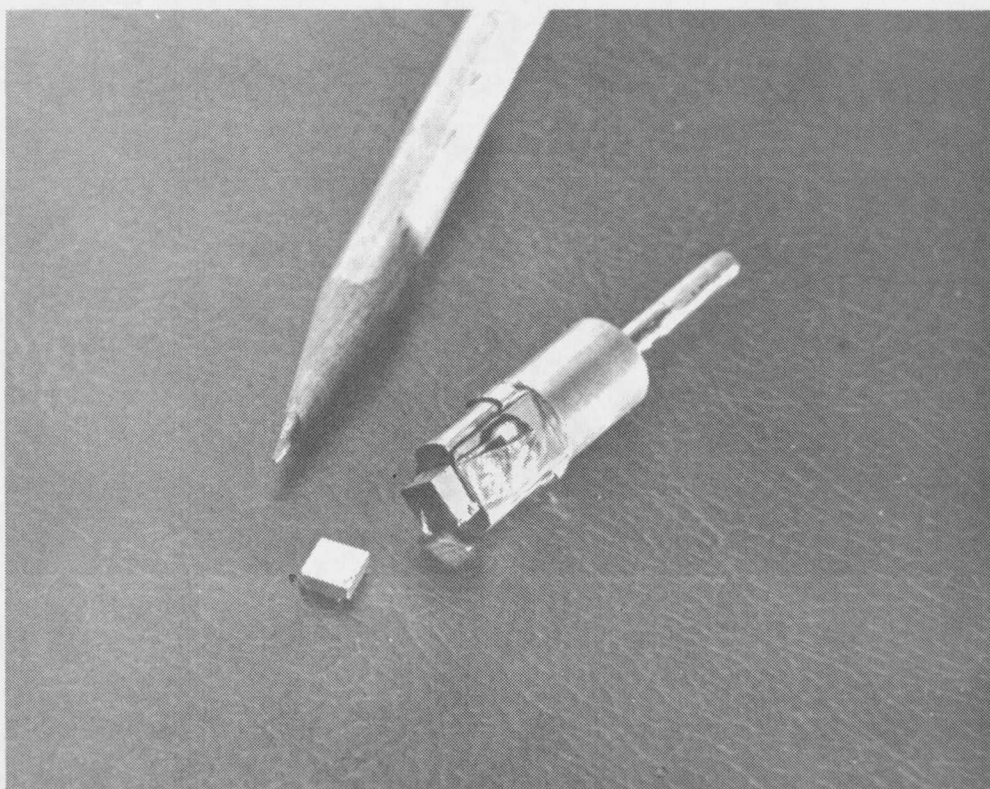


FIG. 22. Photograph of the sample holder, with GaAs crystal in place, and cleaved GaAs chip.

left several large steps or occasional concoidally fractured areas. If alignment was sufficiently poor, the crystal fractured instead of cleaving, generally falling out of the sample holder. Of the cleaves studied, approximately half were very good, with the rest all containing some areas of large step concentration or concoidal fracture. However, even the poorer cleaves which were studied had areas on the surface relatively free of imperfections which could be centered at the light spot and studied. Data from all cleaves was remarkably reproducible from one sample to another, with problems due to major surface imperfections easily identified.

3. Symmetry Determination. Complete orientation of the sample symmetries was not possible by mere inspection of the crystal. The (110) plane contains a mirror plane in which lie the two "dangling bonds", one Ga and the other As in character. Determination of the azimuthal location and direction of these bonds was accomplished by a fairly simple procedure. Since the mirror plane also constitutes a (110) cleavage plane perpendicular to the surface (GaAs cleaves only along (110) planes), inspection of a fractured portion of the crystal with a microscope enabled location of this plane. This also established which two sides of the crystal were (111) planes. Differentiation between As (111) and Ga (111) was accomplished by inspection after an etch with bromine; the As (111)

surface etches to a rough appearance while the Ga (111) takes on a mirror-like quality.³⁹ Once the As (111) and Ga (111) planes are identified and separated, the orientation of the "dangling bonds", and hence the symmetry of the (110) surface, is completely known. This technique was double-checked by back-scattered X-ray diffraction (Laue pattern).

IV. EXPERIMENTAL RESULTS

A. GaAs Bands and Photoemission.

1. Calculated Band Structure. The energy bands along symmetry lines in GaAs have been calculated by a number of workers.^{40, 18-20} The bands diagrammed in Fig. 23 represent the results of one of the most recent and accurate pseudopotential computations, by Pandey and Phillips,²⁰ with band symmetries assigned by examination of the generated wavefunctions. Unfortunately, the pseudopotential calculation is not very accurate at high energy and this calculation was done with a high energy cutoff. Thus the calculated final bands may be somewhat inaccurate at the higher energies accessible in our experiment. The bands are exhibited along three principal symmetry axes of the Brillouin zone, Δ , Λ , and Σ , which are labeled in Fig. 8. As noted previously, the symmetry line Σ extends from $\Gamma\{000\}$ through $K\{3/4\ 3/4\ 0\}$ and on to $X\{1\ 1\ 0\}$. The symmetries of each band are labeled according to the conventions of Parmenter,⁴¹ and each band, starting with the lowest valence band, is assigned a number for convenience in referencing.

The valence electrons are composed of the outermost $4s^2 4p$ levels in gallium and the $4s^2 4p^3$ levels in arsenic (for the neutral atoms). These electrons hybridize in the GaAs crystal to form sp^3 tetrahedral bonds between the atoms. The four valence bands, bands 1-4 in Fig. 23, represent the initial energy E_i of these bonding

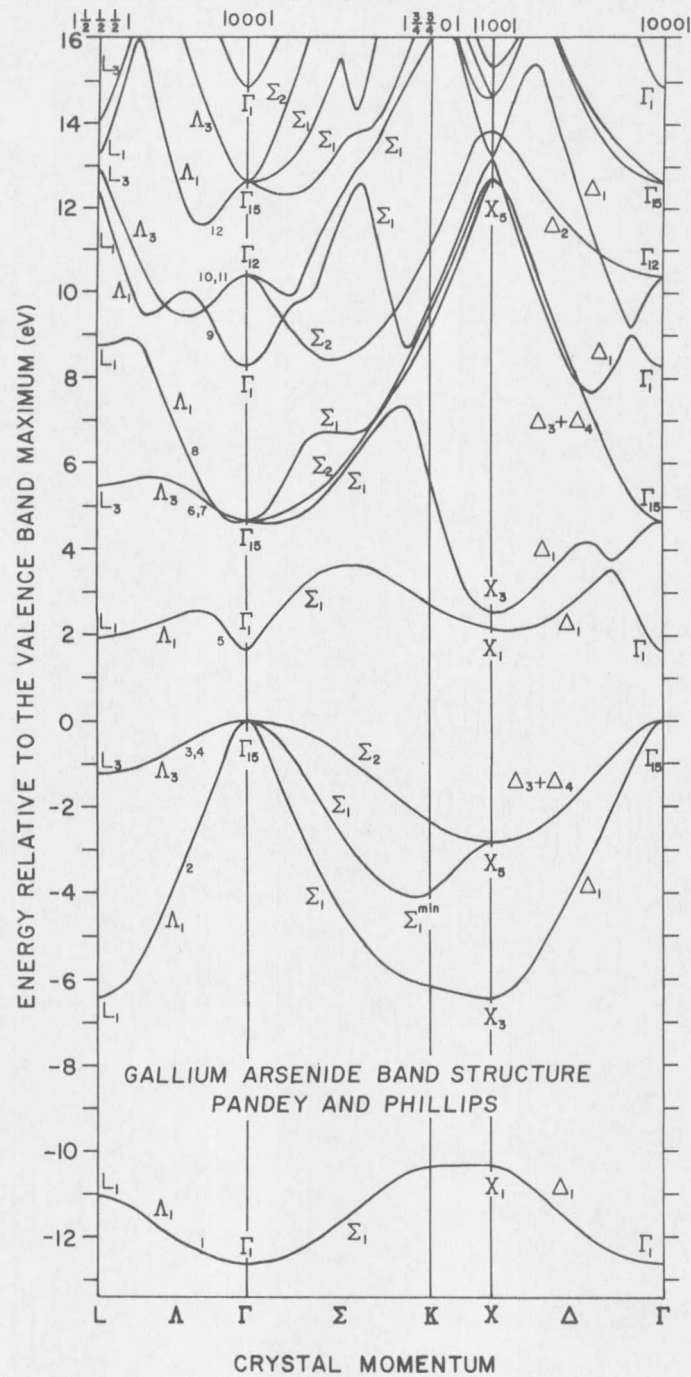


FIG. 23. Bulk band structure of GaAs.

electrons as a function of reduced wavevector in $\vec{k}$ -space. At the center of the zone, Γ , the lowest valence band Γ_1 is "s-like" while the other three VB's are "p-like" and degenerate as Γ_{15} . As one moves away from the zone center the bands are increasingly hybridized and the labels "s-like" and "p-like" can no longer be applied.

The density of initial states summed over the BZ produces three main peaks which exhibit themselves in x-ray photoemission spectra (XPS) and in high energy EDC's. The lowest peak is centered near $E_1 = -12$ eV below the VB maximum and is composed entirely of the "s-like" band 1. The matrix elements for transitions of this band to the lower 20 eV of conduction bands are apparently very weak, as this feature is indiscernable in UPS spectra for $h\nu < 30$ eV. The second, or middle DOS peak is centered near $E_1 = -6.5$ eV and is composed of band 2 along the zone boundaries. Band 2 near Γ and bands 3 and 4 throughout the zone result in the leading DOS peak, which extends from the VB maximum down as much as 4 eV lower. These three VB DOS peaks together with a Ga 3d core level at $E_1 = -18.9$ eV comprise the initial states which are available with normal incidence optics.

For sufficiently high photon energy, angle-integrated photoemission spectra begin to replicate the overall initial DOS. Figure 24 exhibits a CMA-angle-integrated EDC for $h\nu = 30$ eV which

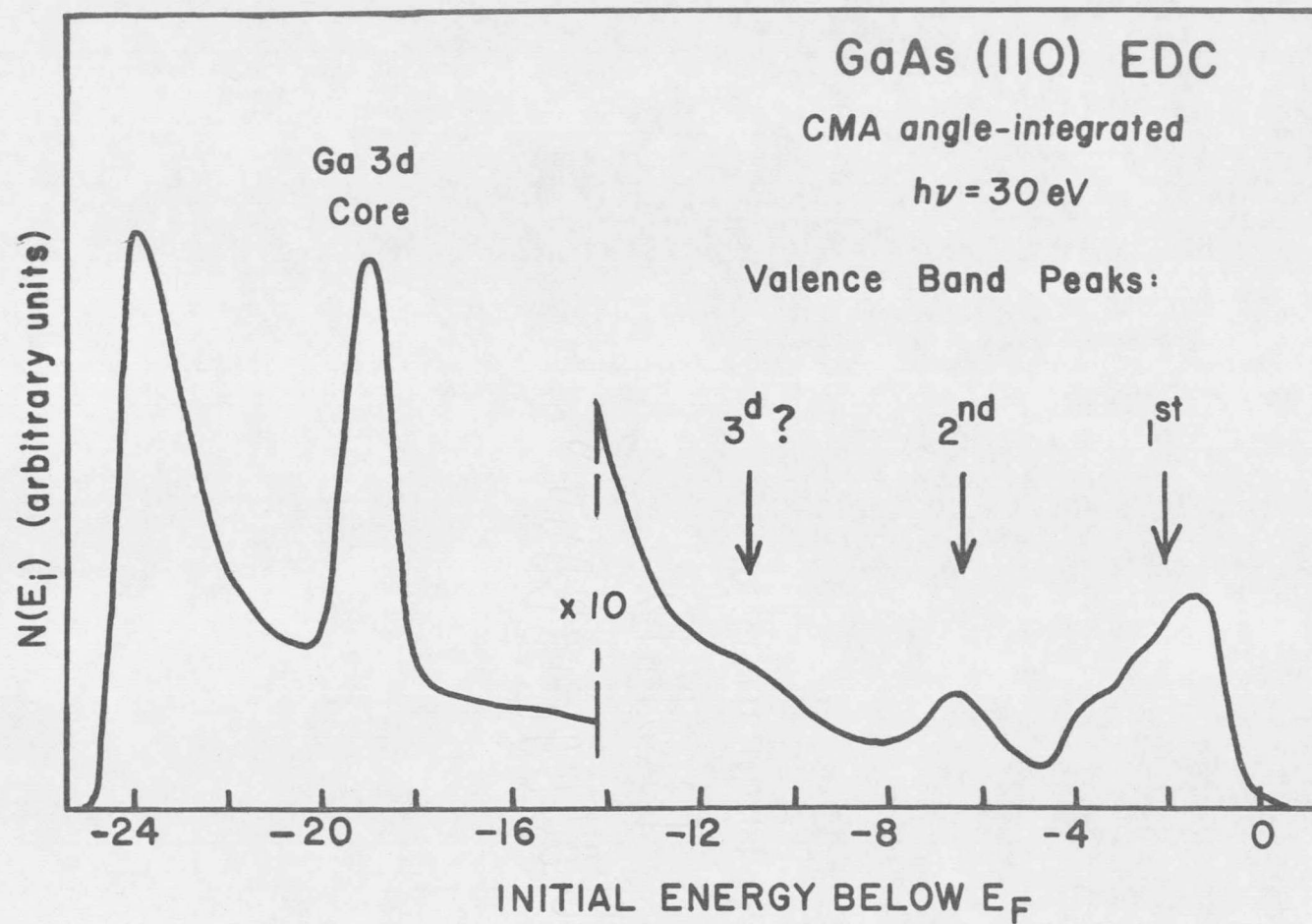


FIG. 24. Angle-integrated EDC obtained at $h\nu = 30 \text{ eV}$.

exhibits clearly most of the valence band features that were discussed above. The leading VB peak extends from the Fermi level E_F to $E_i = -4.1$ eV. The second peak is centered at $E_i = -6.5$ eV and the third peak is only very weakly present near $E_i = -11$ eV. The 3d core level is very prominent near $E_i = -19$ eV. This core level is actually split by spin-orbit interaction into two levels corresponding to total angular momentum $j = 3/2$ and $j = 5/2$. The $3d_{5/2}$ level is at $E_i = -18.7$ eV and the $3d_{3/2}$ is at $E_i = -19.2$ eV; this splitting is not resolved in the spectrum of Fig. 24. The peak at $E_i = -24$ eV is due to inelastically scattered secondary electrons.

2. Angle-Resolved Photoemission and Symmetry. Moving to the angle-resolved mode of photoemission spectroscopy immediately increases the information inherent in each spectrum. Figure 25 exhibits a set of angle-resolved EDC's (AREDC's) taken in the configuration of Fig. 17 with 4° angular resolution. The polar angle θ for all spectra was 42.3° and the azimuthal angles varied in 10° steps from $\phi = 0^\circ$ to $\phi = 180^\circ$. The electric polarization vector $\vec{\epsilon}$ was in the plane of the surface (s polarization) and for each AREDC $\vec{\epsilon}$ was parallel to the azimuthal angle ϕ . Photon energy was 14 eV. The spectra are plotted versus initial energy E_i below E_F . The energy reference here is the Fermi energy E_F , determined by photoemission from an evaporated metal. The first

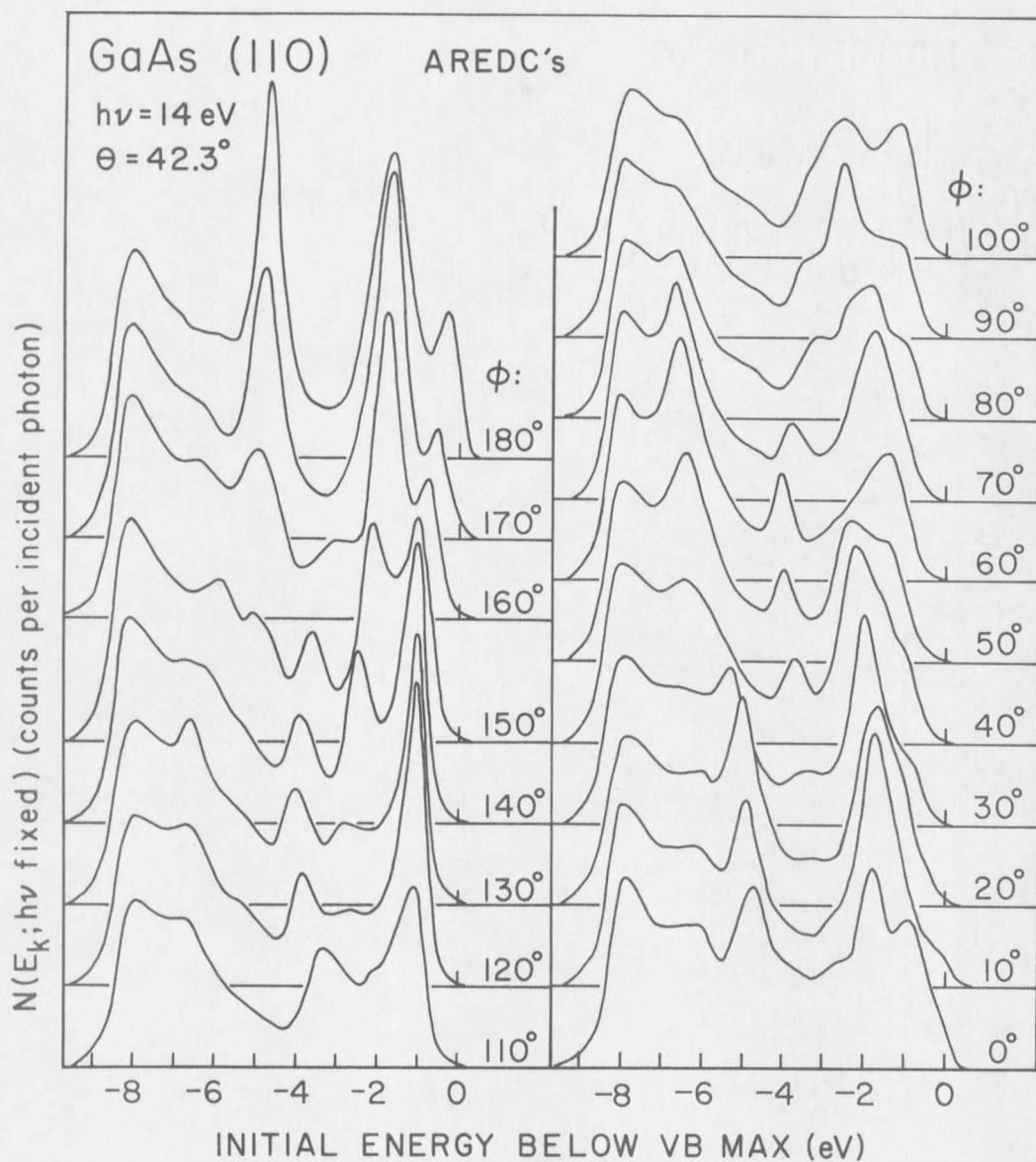


FIG. 25. Angle-resolved EDC's obtained at $h\nu = 14 \text{ eV}$ and $\theta = 42.3^\circ$.

two valence band peaks of Fig. 24 are now resolved into several features which change in magnitude or initial energy as a function of azimuthal angle. These changes represent the fact that each AREDC is sampling transitions from a different segment of momentum space. Details of both initial and final bands are in general different for each two non-equivalent points in the Brillouin zone. Thus spectra taken as little as 2° apart may show substantial differences in the details of transitions that are detected. This, of course, only applies if unscattered electrons are detected, as discussed in section II C. The azimuthal dependence exemplified in Fig. 25 is taken then as evidence for unscattered transport across the surface.

In attempting to sort out and identify the transitions resulting in each of the features shown in Fig. 25, a knowledge of the symmetry of the crystal and hence the symmetry of the photoemission is essential. The spectra of Fig. 25 are displayed only for $\phi = 0^\circ$ to $\phi = 180^\circ$ because these azimuths define a mirror plane in the (110) surface. AREDC's from $\phi = 180^\circ$ to $\phi = 360^\circ$ are identical to the displayed set, with minor discrepancies due to sample misalignment or surface imperfections. This is as it should be, since the Brillouin zone and the energy bands share the symmetry of the crystal. The (110) surface, unfortunately, only possesses this one mirror plane symmetry, rather than the more extensive

symmetries of some other crystal planes commonly studied.

The existence of the mirror plane symmetry in the photoemission is conveniently displayed by what is termed a sample ϕ -pattern. The angle-resolved emission is monitored at a constant kinetic energy and photon energy while the sample is rotated through the full 360° of azimuthal angle ϕ . The polar angle θ is also fixed, so the magnitude of $\vec{k}_{||}$ is constant as well as the initial and final energies. Rotating the crystal thus describes a circle of radius $|\vec{k}_{||}|$ in the surface momentum-space and a cylinder of the same radius in the bulk momentum-space (assuming the surface mixes together $k_{\perp}$; see section II C). Figure 26 shows a sample ϕ -pattern taken in the same sample configuration of Fig. 25, but with a photon energy of 12 eV. The analyzer window was set to accept a constant kinetic energy of 5 eV, corresponding to $E_i = -1.7$ eV. Thus the pattern represents the magnitude of emission in various directions from states near the middle of the first VB peak. The figure is presented as a polar plot and is typical of many ϕ -patterns taken from (110) GaAs; the mirror plane symmetry is easily observed. The slight asymmetry is attributed to a small sample misalignment.

3. Initial vs. Final Energy Dependence. The presence of the appropriate symmetry in the photoemission establishes that the momentum information is not all lost in crossing the surface. It

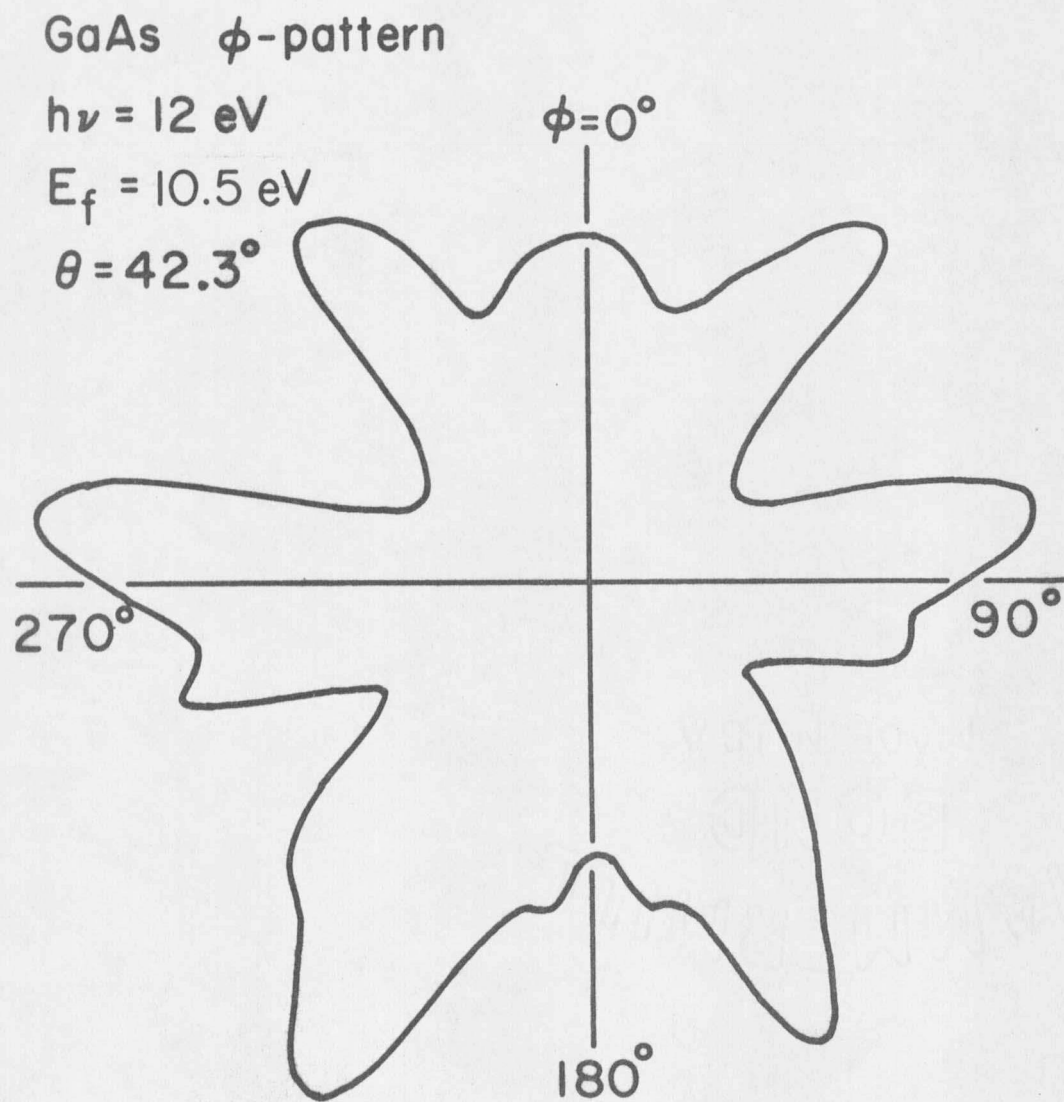
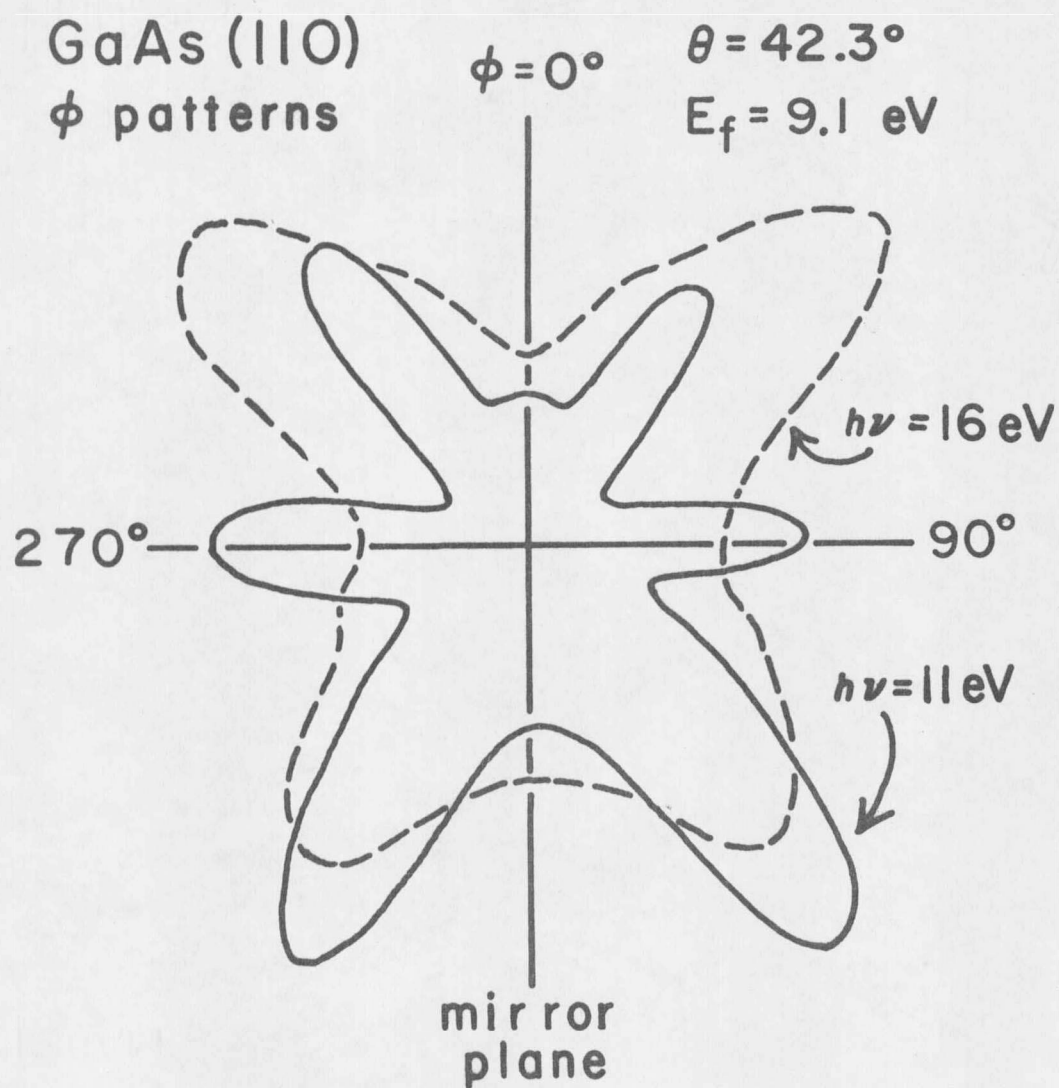


FIG. 26. (110) GaAs ϕ -pattern.

does not establish whether that momentum information comes only from the final state of the electron or also from the initial state. That is, if the transitions are indirect the angular dependence of the emission will depend only on the density of final states, regardless of where the electrons originated. If however the transitions are direct, the wavevector of the final state equals the wavevector of the initial state and the angular dependence is a function of both initial and final state energies. Indirect transitions, as discussed in section IIC, imply elastic scattering of the excited electrons such that all final states at the appropriate final energy are populated, regardless of whether the electrons originated as valence electrons, core electrons, or scattered electrons.

The direct transition model, in which the initial energy influences the angular dependence, is confirmed for GaAs by the ϕ -patterns of Fig. 27. These ϕ -patterns were both taken in the configuration of Fig. 25 at the final energy of $E_f = 9.1$ eV above E_F . The solid curve was taken at $h\nu = 11$ eV, corresponding to an initial energy $E_i = -1.9$ eV. The dashed curve was taken at $h\nu = 16$ eV, corresponding to $E_i = -6.9$ eV. The azimuthal dependence of the emission to that constant final energy is seen to be quite different for states from two different initial energies. This dependence on initial energy is taken as evidence that the

FIG. 27. (110) GaAs ϕ -patterns.

direct transition model is important in understanding the angle-resolved photoemission.

Himpsel and Steinmann,⁴² in similar work done on NaCl and KCl, report that below the threshold for inelastic electron-electron scattering the azimuthal dependence of the emission depends only on the final energy. Above the scattering threshold at $2 E_g$, the emission depends on both initial and final energies as we have seen here for GaAs. The electron-electron scattering threshold is nearly 17 eV for NaCl, but only 2.8 eV for GaAs. The explanation of this phenomenon is that below the electron-electron scattering threshold the escape depth of the electrons is large compared to the electron-phonon scattering length. Electrons which escape have undergone several phonon scattering events, losing all correlation to their initial position in momentum space. Above the threshold for electron-electron scattering the escape depth of the electrons is smaller than the electron-phonon scattering length, such that most electrons which escape have not scattered with phonons. This last case is the situation for all emission from GaAs, since the electron-electron scattering threshold is so low.

4. Polarization Effects. The polarization of synchrotron radiation can sometimes be exploited to help identify the tran-

sitions responsible for certain features in the angle-resolved photoemission. The matrix element of the optical transition in Eq. (12) can be required to be zero by symmetry requirements alone for certain orientations of the electric polarization vector $\vec{\epsilon}$.^{43,44} That is, some allowed transitions can be "turned off" by an appropriate reorientation of $\vec{\epsilon}$ with the crystal symmetries. Examination of the energy and $k_{\parallel}$ of any emission peak which is sensitive to this manipulation may then lead to identification of the initial and final bands in calculated band diagrams.

An example of this technique is shown in Fig. 28. Two AREDC's are exhibited, for which all parameters except the orientation of $\vec{\epsilon}$ are held constant. Both spectra were taken at $h\nu = 14$ eV, $\theta_p = 42.3^\circ$, and $\phi_p = 180^\circ$. (θ_p and ϕ_p are the emission angles previously labelled just θ and ϕ .) For the solid AREDC, the electric polarization vector $\vec{\epsilon}$ was in the surface and parallel to the mirror plane ($\phi_p = 0^\circ, 180^\circ$). For the dashed curve, $\vec{\epsilon}$ was rotated in the surface 90° such that it was perpendicular to the mirror plane. The vector potential $\vec{A}$ of the incident radiation is parallel to $\vec{\epsilon}$. We use the angles θ_A and ϕ_A to denote the direction of both $\vec{\epsilon}$ and $\vec{A}$. Two features present in the solid curve were affected by the reorientation of $\vec{\epsilon}$. The peak centered near $E_i = -5.1$ eV was almost completely eliminated, while a broader structure at $E_i = -2.0$ eV was less dramatically reduced. The

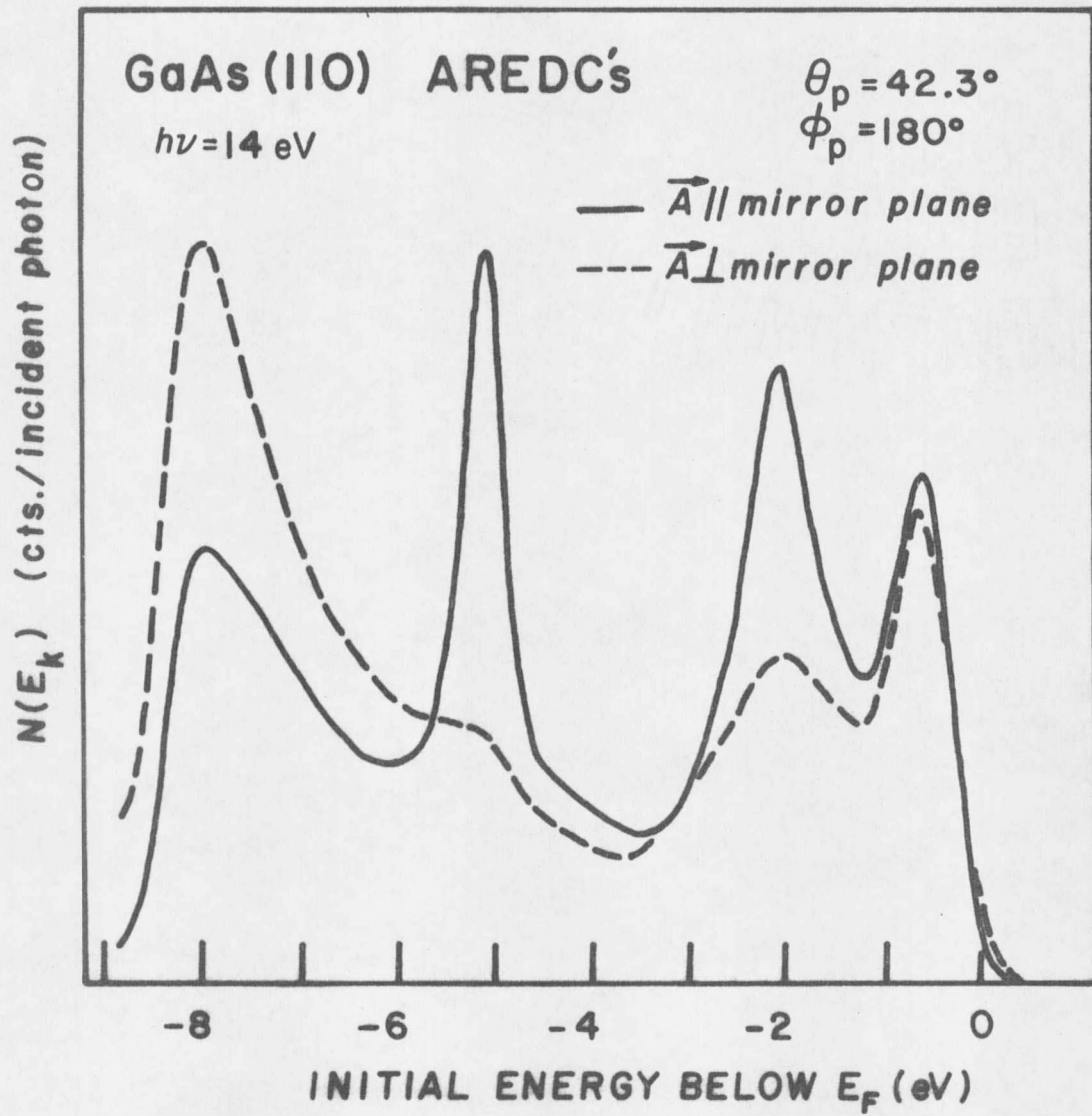


FIG. 28. AREDC's obtained for two different polarization orientations.

increase in low energy scattered electrons at $E_i = - 7.5$ eV is an artifact created by taking spectra such that the electron trajectories were through the holes positioned in the CMA hemispherical screens for passing the light beam (see section IIIC).

The feature in Fig. 28 near $E_i = - 5$ eV can be identified in the available band calculations. Since the azimuth for the AREDC's was 180° , all transitions originated somewhere in the mirror plane in $\vec{k}$ -space defined by the real-space mirror plane. The electron states in this mirror plane are either even or odd under reflection in the planes, referred to as even or odd parity. Designate these states as $\langle + |$ and $| - \rangle$. The electron-photon interaction $\vec{A} \cdot \vec{p}$ is itself even under reflection for $\vec{A}$ parallel to the mirror plane and odd for $\vec{A}$ perpendicular to the mirror plane. Since the matrix element of the transition must be invariant under reflection in the plane, it follows that

$$\langle - | \vec{A} \cdot \vec{p} | - \rangle = \langle + | \vec{A} \cdot \vec{p} | + \rangle = 0 \quad (16)$$

for $\vec{A}$ perpendicular to the mirror plane, and

$$\langle - | \vec{A} \cdot \vec{p} | + \rangle = \langle + | \vec{A} \cdot \vec{p} | - \rangle = 0 \quad (17)$$

for $\vec{A}$ parallel to the mirror plane.

For the peak at $E_i = - 5.1$ eV in Fig. 28, the only possible initial band at that energy is band 2, which is even under the

mirror plane reflection. Since the feature is "turned off" by rotating $\vec{A}$ (which is parallel to $\vec{e}$) to the perpendicular position, equations (16) and (17) tell us that the final band must also be even. Calculating $\vec{k}_{||}$ for the peak gives a value of $0.63 \text{ \AA}^{-1}$, which defines a line in $\vec{k}$ -space parallel to $k_{\perp}$ but passing through the boundaries of the BZ very close to the L point. Examination of the band diagram of Fig. 23 reveals that the most likely candidate for the final band is band 9 near L along Λ . Band 9 is even under reflection in the plane, as required, and has a local high density of states relatively parallel to band 2 at the appropriate $\vec{k}$ near L_1 . Furthermore the energy separation of band 9 and band 2 for the appropriate initial energy is very close to 14 eV, the photon energy. This combination of evidence seems sufficient to identify the sharp peak in Fig. 28 as due to a transition between band 2 and band 9 in the area of $\vec{k}$ -space near L on the BZ boundary. This transition is allowed by symmetry when $\vec{A}$ is parallel to the mirror plane, but forbidden when $\vec{A}$ is perpendicular to that plane.

The identification of the other two peaks in Fig. 28 was inhibited by the lack of more detailed band calculations, particularly in the higher conduction bands. The usefulness of the technique will be demonstrated more fully in the interpretation of the normal emission, for which the band calculations are more complete. This will be discussed in section IVD.

B. Occupied Surface States

1. Surface Calculations and UPS Measurements. Investigations of the electronic structure of semiconductor surfaces are of great theoretical and practical interest. Several calculations of surface states on GaAs (110) have been done recently, predicting both occupied and unoccupied states.²¹⁻²⁵ A bond-orbital calculation by Harrison and Ciraci²¹ predicts a filled surface state below the valence band maximum (VBM) and an empty surface state in the optical band gap. The filled state is identified as being derived from the As dangling bond, while the empty state is Ga derived. Calandro and Santoro²³ have made a tight-binding calculation for the GaAs (110) surface which predicts again an As-derived surface state just below the VBM and a Ga-derived empty state 1 eV above the VBM.

A more detailed layer-by-layer tight-binding calculation by Joannopoulos and Cohen (JC)²² finds a total of five surface states. One is high in the conduction band (B_2'), one in the upper part of the band gap (B_1'), one at the VBM (B_1), one about 6 eV below the VBM (B_2), and one near the top of the lowest valence band (B_3). JC have calculated the energy dispersion of each of these states along surface symmetry lines. The two occupied states of interest in the present study are B_1 and B_2 . B_1 has its maximum initial energy at the zone center $\bar{\Gamma}$, where it extends into the band gap

by 0.1 eV. The total width is only 0.2 eV. B_2 was not expected to be easily observable, being nearly degenerate with the second VB DOS peak near $E_i = -6$ eV. B_2 was calculated to be localized near the zone corner $\bar{M}$, increasing in initial energy as one moved away from the zone corner along symmetry lines.

A self-consistent pseudopotential calculation using a periodic array of GaAs slabs has been performed by Chelikowski and Cohen (CC).²⁴ They found surface states very similar to those of JC, centered at $E_i = -9, -5.75, -0.5$, and $+1.0$ eV. In addition, they found some weak surface structure near $E_i = -2.0$ eV. The state at the VBM, corresponding to B_1 in JC's notation, was found to be somewhat wider in energy dispersion and the maximum did not extend past the VBM into the gap.

The identification of the empty surface state at the top of the gap has been made in experiments by several workers⁴⁵⁻⁴⁷ and will be discussed in the next section. Identification of the filled surface states has been much more elusive, apparently because of complete degeneracy with the bulk bands. No emission due to filled surface states was found during a careful UPS study of (110) GaAs by Gregory and Spicer,²⁶ in agreement with other workers.⁴⁷⁻⁴⁹ The narrow surface band predicted in most of the theoretical calculations at or above the VBM is incompatible with these results. Any sharp surface feature at or above the VBM

should be easily observable in conventional UPS. The fact that it was not required that the filled surface band near the VBM be both wider in energy dispersion and lower with respect to the VBM than had been calculated.

The theoretical solution to this disagreement between experiment and theory appears to lie in the consideration of a "relaxed" surface lattice,³⁴ as discussed in section IID. A recent pseudo-potential calculation of a relaxed (110) GaAs surface by Chelikowski, Louie, and Cohen²⁵ shows that B_1 moves to lower energy and broadens in energy dispersion when the relaxation is considered. The surface relaxation is as in Fig. 9b. This calculation is in much better agreement with the UPS results. The maximum initial energy of B_1 is still at $\bar{\Gamma}$ in the surface zone, but is below the VBM, rather than at or above it.⁵⁰

The theoretical predictions for the (110) GaAs surface are summarized by the notation of JC as empty states B_2' and B_1' , and occupied states B_1 , B_2 and B_3 . Of these states, B_2' is inaccessible to us, lying below the vacuum level. B_1' was observed in core resonance decay and will be discussed in section IVC. B_3 , although in theory accessible by our experiment, was not observed in the photon energy range that we have available. B_3 is s-like, as is the third valence DOS peak, and may have very low transition strength to the lower conduction bands.

Of the predicted occupied surface states, we believe we have identified emission due to both B_1 and B_2 in the angle-resolved photoemission from (110) GaAs. As noted above, no emission from occupied surface states has been previously observed in UPS measurements of GaAs.²⁶ The identification in angle-resolved photoemission was possible because emission directions were found for which the surface band transitions were prominent features in the spectra, even though energetically degenerate with strong VB emission in other directions. Specifically, emission attributed to surface states was found to be prominent in spectra obtained for $\theta > 45^\circ$. The width of energy dispersion of both surface features was greater than 1 eV, and completely degenerate with VB energies. Angle-integrated UPS techniques thus have difficulty distinguishing this surface emission from bulk emission.

2. Tests of Surface State Emission. Two tests were used in conjunction to identify emission due to occupied surface states. First, in analogy to experiments on other materials,^{13,14,51} the feature was tested for sensitivity to a light contamination of the surface by a gas or evaporated metal. Second, by varying the available parameters such as photon energy or polar angle, the initial energy of the feature was mapped out in $\vec{k}$ -space as much as possible and the results compared to theoretical surface band

calculations. In mapping out the dispersion of the feature, care was taken in assuring by means of the contamination test that the emission being plotted was indeed surface sensitive for each emission direction. If an emission feature was contamination sensitive and its dispersion agreed well with theory, the identification was complete.

Only very light contamination is needed to affect the emission from a surface state. Adsorbate coverages corresponding to much less than a monolayer interfere with the periodicity of the surface lattice, as well as modifying the actual electronic states at the surface. Bulk periodicity and bulk states are not directly affected, so any emission which is sharply reduced for very light contamination must be associated with the surface.

3. Surface State B_1 . A surface state near the VBM due to the As dangling bond was predicted by all of the calculations discussed above.²¹⁻²⁵ The energy dispersion calculated by JC is in qualitative agreement with the recent calculations for a relaxed surface. The energy is a maximum at the surface BZ center $\bar{\Gamma}$ and lower at all other points in the zone, with minima at $\bar{X}$ and $\bar{X}'$ on the zone boundaries. In referring to the predicted state at the VBM we shall use B_1 , the notation of JC.

Three sets of AREDC's exhibiting the contamination test for

emission which is attributed to B_1 are shown in Fig. 29. Parameters of each pair of spectra were chosen such that $\vec{k}_{||}$ for the peak near the VBM corresponds in each pair to the center $\bar{\Gamma}$ of a different repeated surface Brillouin zone. The magnitude of $\vec{k}_{||}$ for each pair of AREDC's was (A) $1.11 \text{ \AA}^{-1}$, (B) $1.56 \text{ \AA}^{-1}$, and (C) $1.95 \text{ \AA}^{-1}$. The solid curve of each pair was taken from a clean surface and the dashed curve after exposure to a gas. The O_2 exposure corresponds to much less than $\frac{1}{2}$ monolayer coverage³⁸; equivalent exposures of O_2 and H_2 showed similar effects on emission, indicating the sticking coefficients are similar. Each contaminated curve has been shifted toward E_F by 0.4 eV to compensate for band bending effects.⁵² In each case, the emission peak near the VBM is dramatically attenuated by the contamination, while emission structure at other energies remains substantially unchanged. The angular properties of the photoemission features attributed to bulk states, which exhibit the proper crystal symmetries, are unchanged by small gas exposures, corroborating the assumption that adsorbed atoms are not scattering the emission into different directions. The sensitivity to contamination clearly indicates a surface feature near the VBM.

The AREDC's of Fig. 29 were taken such that the surface emission near the VBM originated at three $\bar{\Gamma}$ points in three repeated surface zones. The initial energy in each case is seen to be $E_i \sim -0.8 \text{ eV}$. To sample the dispersion (E_i versus $\vec{k}_{||}$) along the $\bar{\Gamma} - \bar{X}$ line

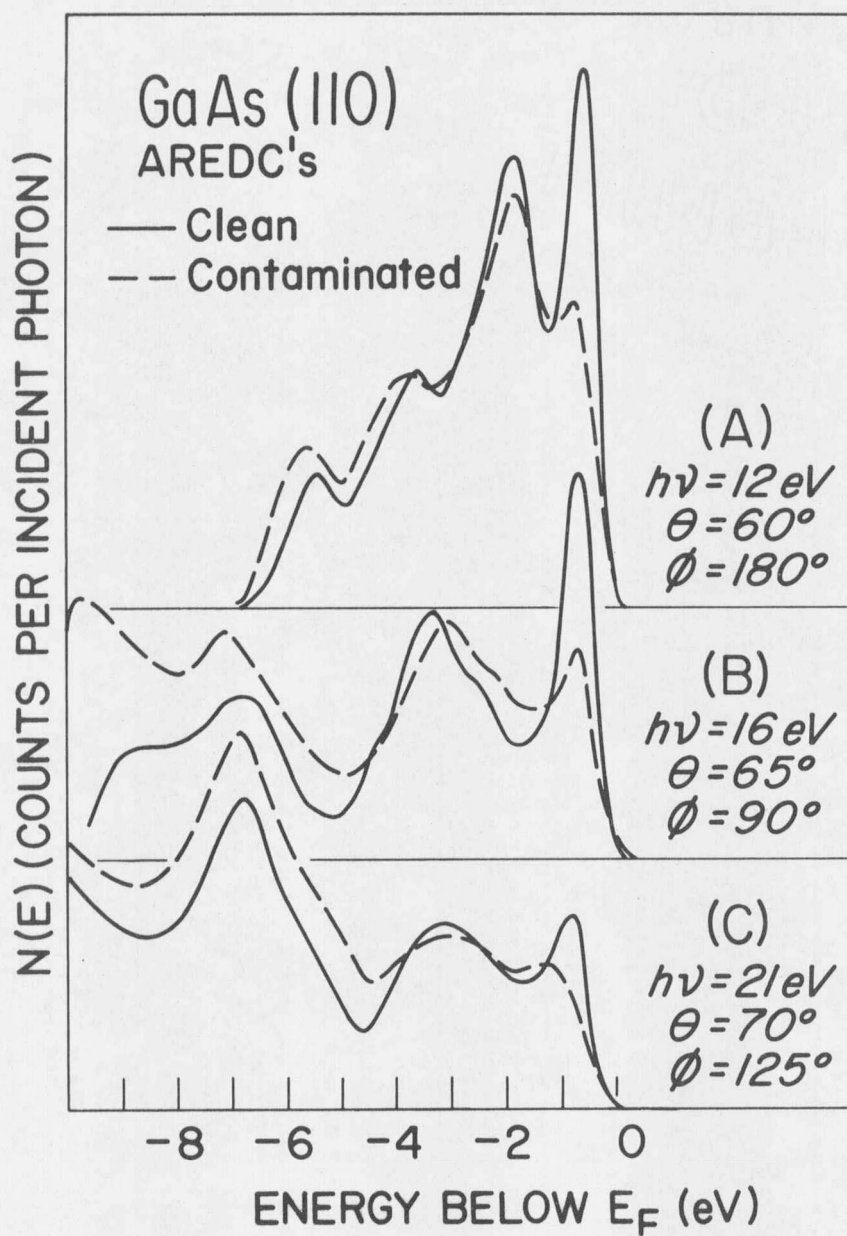


FIG. 29. AREDC's showing surface state emission which is reduced by contamination; (A) and (C) were exposed to 0.7 Torr-sec. of O_2 , while (B) was exposed to 0.15 Torr-sec. of H_2 .

in the surface BZ for the surface state in Fig. 29, AREDC's were obtained by selecting the proper azimuthal angle and varying θ or $h\nu$. A selected set of AREDC's are shown in Fig. 30, where $\vec{k}_{||}$ values for the surface state peak between $1.0 \text{ \AA}^{-1}$ and $2.0 \text{ \AA}^{-1}$ are acquired by varying the photon energy. In the repeated zone scheme the $\vec{k}$ vary from the $\bar{\Gamma}$ point of the second zone along $\phi = 180^\circ$, through $\bar{X}'$, and nearly to the center of the third zone. One notes that the peak nearest the VBM consisting of the surface state emission and any underlying bulk emission moves through an energy minimum.

The dispersion noted in Fig. 30 is best exhibited by plotting the initial energy of the peaks versus $\vec{k}_{||}$. The results of such a plot are shown in Fig. 31, which includes data from the AREDC's in Fig. 30 as well as AREDC's taken at different polar angles. The horizontal axis is labeled with the magnitude of $\vec{k}_{||}$ along $\phi = 180^\circ$ as well as with the surface symmetry points which are sampled. The consistency of the data for different θ values is taken as corroboration of the interpretation. The initial energy of the surface state is at a maximum near $\bar{\Gamma}$ and a minimum near the zone boundary $\bar{X}'$. This behavior was observed for data from several surface zones; that is, the maximum initial energy of the surface state emission is at the zone centers $\bar{\Gamma}$. For comparison, the calculated band B_1 of JC is also shown in Fig. 31, along these

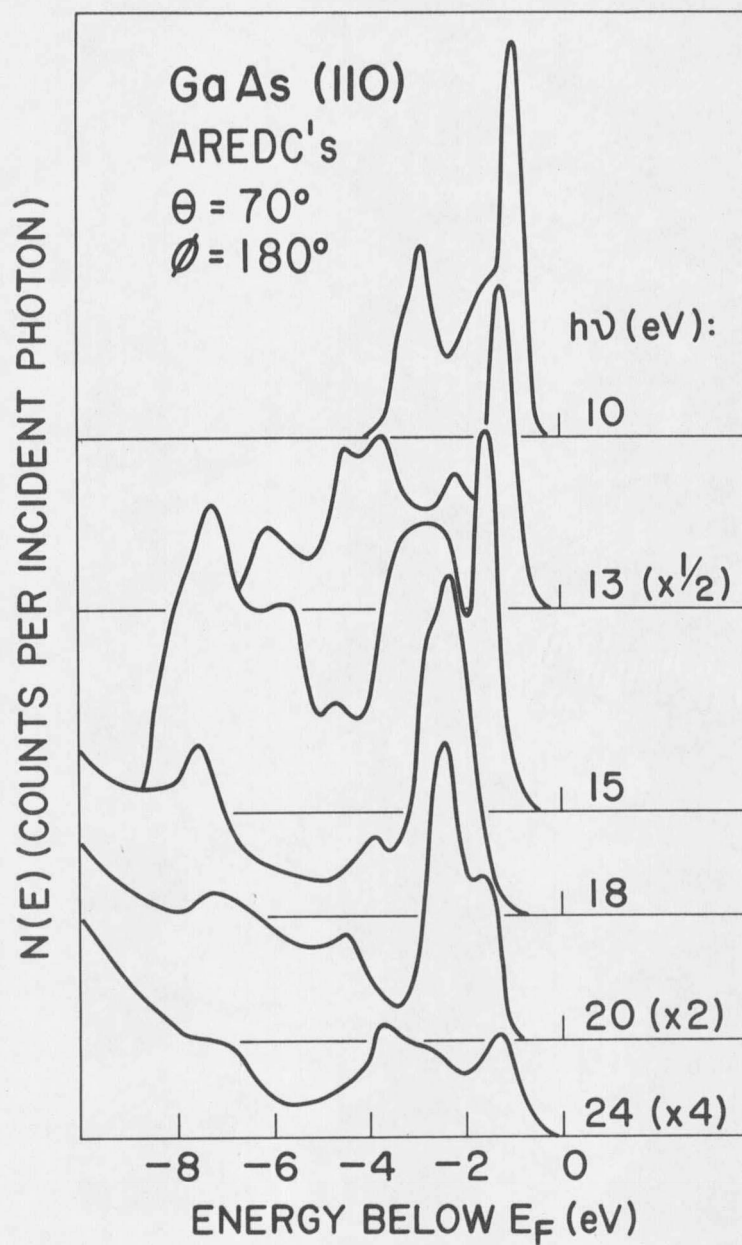


FIG. 30. AREDC's taken at constant $\phi = 180^\circ$ and $\theta = 70^\circ$, showing surface emission at several values of $\vec{k}_{||}$.

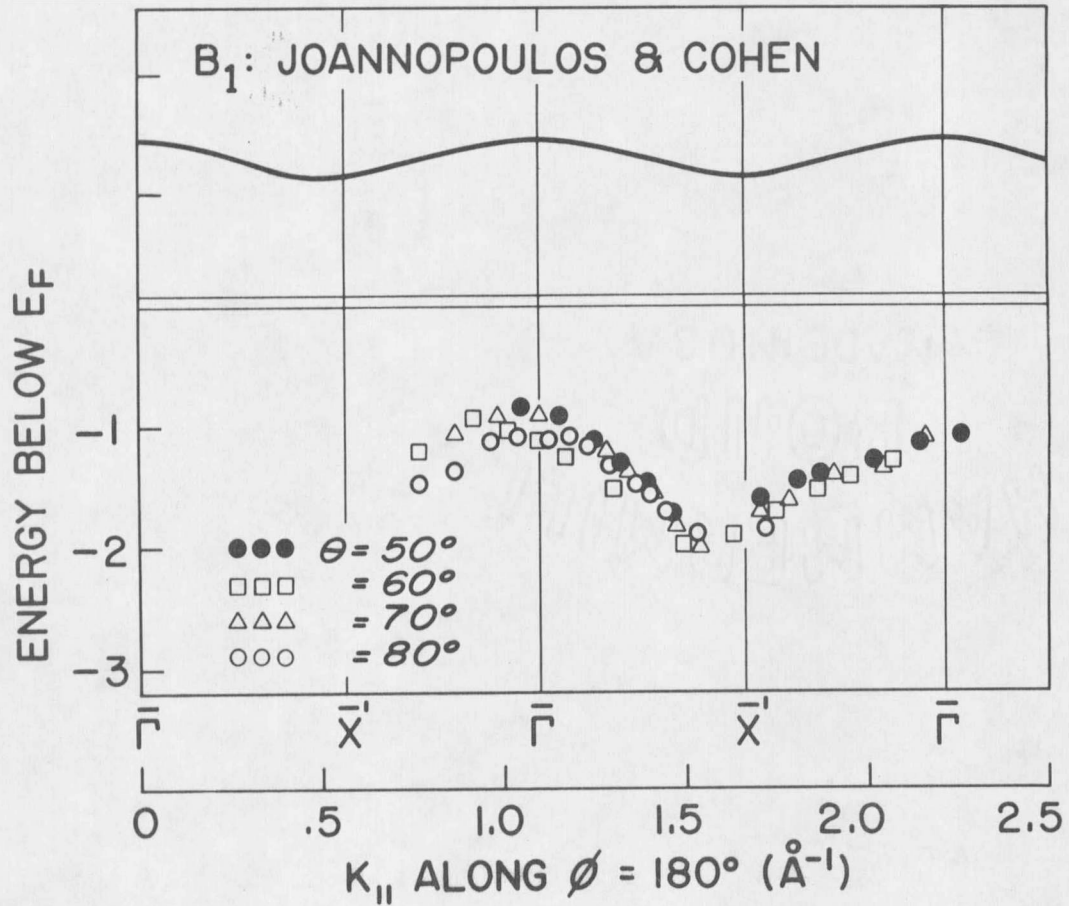


FIG. 31. Initial energy E_i versus $\vec{k}_{||}$ for the surface emission peaks from AREDC's taken at constant $\phi = 180^\circ$ and for various polar angles and photon energies ($10 \leq h\nu \leq 26$ eV). The solid line shows the shape of the calculated surface band B_1 .

symmetries. The position of the JC band relative to the VBM is not indicated, as it is in error. The important point of Fig. 31 is that the positions of the energy maxima and minima of the surface emission agree with the positions predicted in theory for B_1 .

The dispersion behavior throughout the repeated zones may be demonstrated conveniently by the use of ϕ -patterns. An appropriate choice of the parameters $h\nu$, θ , and E_K adjusts the values of $\vec{k}_{||}$ and E_i for the electrons which are detected. E_i is adjusted for each ϕ -pattern such that only electrons near the VBM are passed through the energy window. Several values of the magnitude of $\vec{k}_{||}$ are chosen such that the ϕ -patterns sweep out several concentric circles in the two-dimensional $\vec{k}$ -space of the surface. Since the predicted maximum of the dispersion of B_1 occurs only at the zone center, one may expect emission through the energy window of the analyzer to be strong only when $\vec{k}_{||}$ equals a surface reciprocal lattice vector. That is, the ϕ -pattern will show lobes in the directions for which the circle of radius $\vec{k}_{||}$ crosses the $\bar{\Gamma}$ points of repeated surface zones, if the observed emission agrees with theory.

The magnitude of $\vec{k}_{||}$ for the ϕ -pattern in Fig. 32 is $1.11 \text{ \AA}^{-1}$, the distance in $\vec{k}$ -space to the two closest $\bar{\Gamma}$ points in the repeated surface zone space. The repeated zones for the (110) surface are diagrammed, with a dashed circle representing the circle of $\vec{k}_{||}$

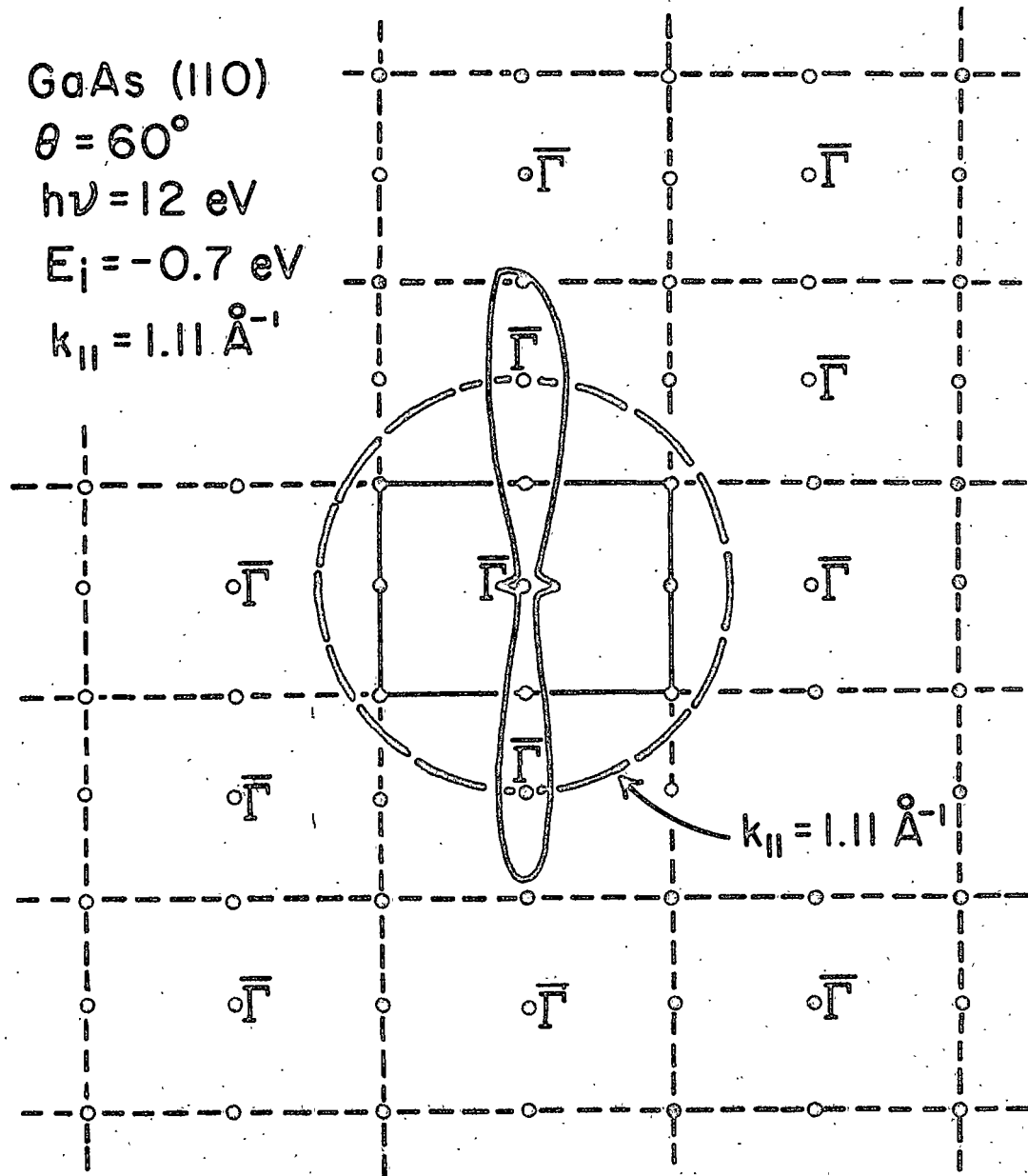


FIG. 32. ϕ -pattern for $\vec{k}_{||} = 1.11 \text{ \AA}^{-1}$.

swept out by the ϕ -pattern. The ϕ -pattern was taken at $h\nu = 12$ eV, $\theta = 60^\circ$, and $E_K = 6.3$ eV, corresponding to $E_i = -0.7$ eV. Only two lobes are present, one at $\phi = 0^\circ$ and another at $\phi = 180^\circ$, each corresponding to a repeated zone $\bar{\Gamma}$.

When the magnitude of $\vec{k}_{||}$ is increased to $1.54 \text{ \AA}^{-1}$, the ϕ -pattern which results is displayed in Fig. 33. Again, the repeated zones are shown with a circle corresponding to $\vec{k}_{||}$ for the spectrum. The parameters have been increased to $h\nu = 18$ eV, $\theta = 60^\circ$, and $E_K = 12.3$ eV. The initial energy is still $E_i = -0.7$ eV. The emission lobes at $\phi = 0^\circ$ and 180° are now absent and replaced with lobes at $\phi = 90^\circ$ and $\phi = 270^\circ$. These new lobes correspond to emission at $\bar{\Gamma}$ points which are at $1.56 \text{ \AA}^{-1}$. Note also the four small lobes beginning to develop at the azimuths of the $\bar{\Gamma}$ points of the next farthest zones. At these azimuths, the sampled $\vec{k}_{||}$ is within a few tenths $\text{\AA}^{-1}$ of matching these $\bar{\Gamma}$ points. Increasing $\vec{k}_{||}$ in other ϕ -patterns brings these lobes out clearly. The ϕ -patterns of Figs. 33 and 34 demonstrate that photoemission originates at states near the VBM only for $\vec{k}_{||}$ corresponding to surface $\bar{\Gamma}$ points.

The dispersion data on B_1 , exemplified by the AREDC's of Fig. 30 and the ϕ -patterns of Figs. 32 and 33, is in good agreement with the latest calculations for a relaxed surface by Chelikowski, Louie, and Cohen.²⁵ The width of the dispersion is ~ 1 eV, the

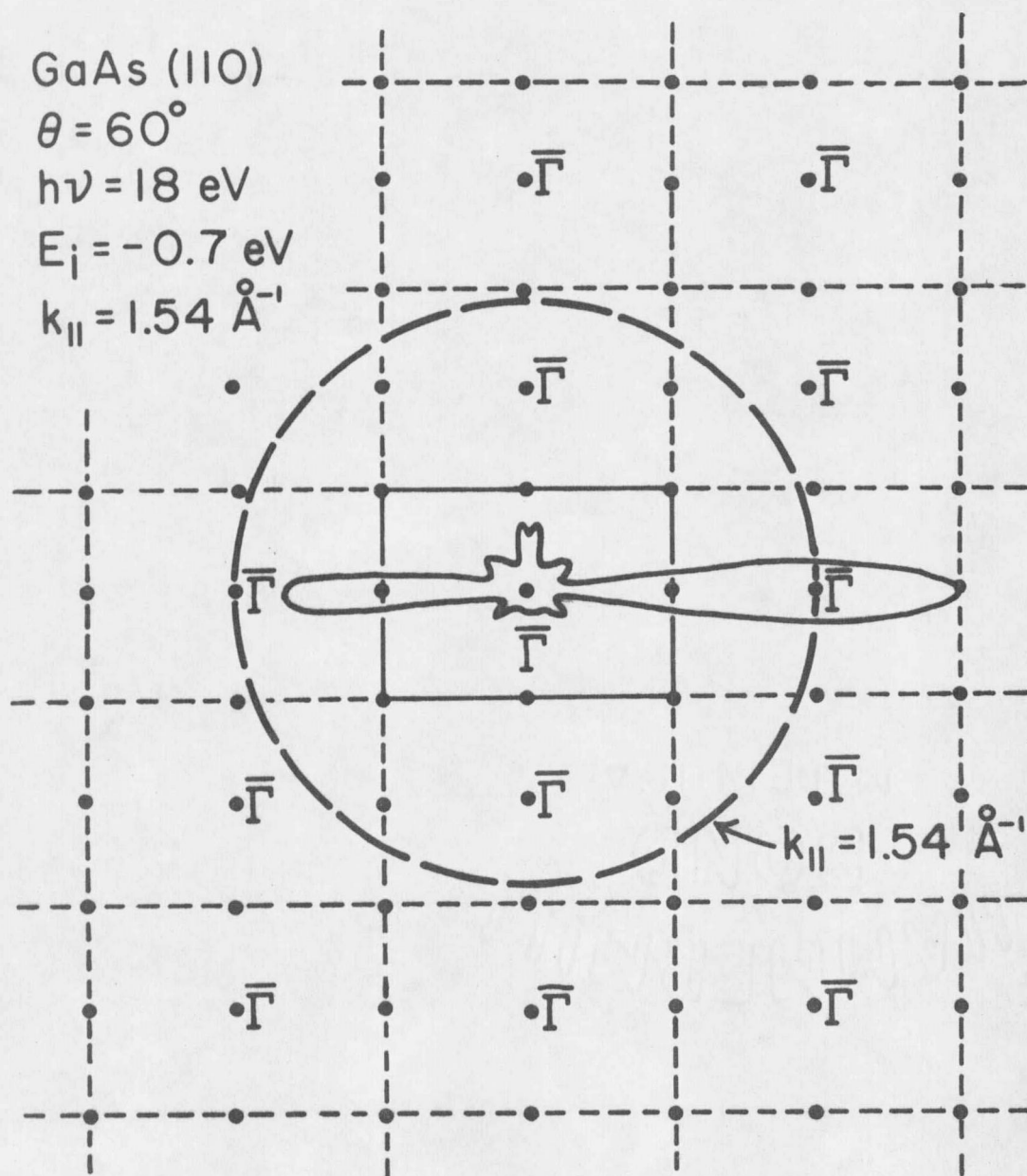


FIG. 33. ϕ -pattern for $\vec{k}_{||} = 1.54 \text{ \AA}^{-1}$.

maximum energy is at $\bar{\Gamma}$ with $E_1 \sim 0.8$ eV, and dispersion minima occur at the zone boundaries. The identification of the emission as due to the predicted surface band just below the VBM is thus easily completed.

Since the bulk Γ points in a plane parallel to the surface form a grid which is twice as large as the grid formed by the surface $\bar{\Gamma}$ points, one might assume that the agreement between the observed periodicity and the surface zone periodicity was sufficient justification for interpreting the peak near the VBM as a surface state. Such a justification is not valid since the surface mixes up the perpendicular components of the electron wavevectors.³³

Figure 34 diagrams a cross section of the bulk BZ's in a plane perpendicular to the surface and including k_z . Also shown are the $\bar{\Gamma}$ points for the surface along k_z . As is evident, there are bulk Γ -points which have the same $\vec{k}_{\parallel}$ values as the surface $\bar{\Gamma}$ points. This is a general result.⁵³ Since $k_{\perp}$'s are mixed in the escape process, then all states of the same $\vec{k}_{\parallel}$ may be detected irrespective of any consideration of $k_{\perp}$. As a result one may observe emission from any state along the vertical line in Fig. 34 corresponding to the selected $\vec{k}_{\parallel}$. In particular, a line corresponding to $\vec{k}_{\parallel}$ which passes through Γ and $\bar{\Gamma}$ will correspond to emission from the centers of the bulk zone and the surface zone. In this case the bulk bands at Γ_{15} might lead to the observed emission periodicity.

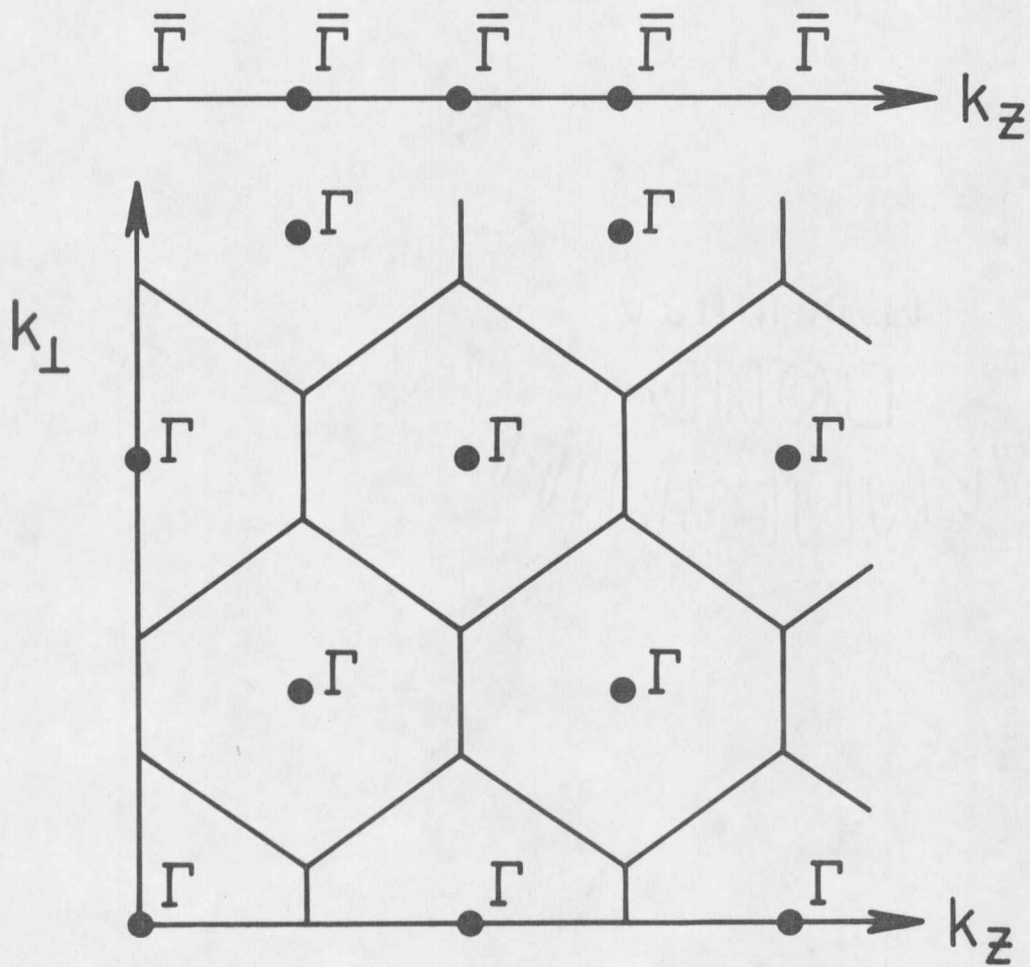


FIG. 34. A cross-section of the repeated bulk Brillouin zones for GaAs, in a plane perpendicular to the surface and including k_z . Surface $\bar{\Gamma}$ along k_z are shown.

The bulk emission; however, should not be sensitive to small coverages of gas, as the surface emission should be. Indeed, for all contamination tests of emission near $\bar{\Gamma}$, significant emission up to the VBM remained after the purported surface state emission was removed. This is interpreted as bulk emission originating near $\bar{\Gamma}$ which is energetically degenerate with the surface state at $\bar{\Gamma}$.

4. Surface State B_2 . The second occupied surface band which has been identified through angle-resolved photoemission corresponds to B_2 in the notation of JC. B_2 was predicted²² to be fairly localized near the zone corners $\bar{M}$, with an initial energy at $\bar{M}$ that would make it degenerate with the second VB peak in angle-integrated UPS. This degeneracy was expected to make detection difficult. However, the dispersion of the band was predicted to move to higher energy as one moved away from $\bar{M}$ toward either $\bar{X}$ or $\bar{X}'$. By examining angle-resolved emission which originated at either side of an $\bar{M}$ point, we were able to identify a peak due to B_2 as it moved to higher energy, away from degeneracy with the second VB peak.

A contamination test for emission attributed to B_2 is shown in Fig. 35. The clean surface data is the solid AREDC and the dashed curve after exposure to 0.1 Torr-sec. of H_2 . Again, the contaminated AREDC is shifted toward E_F by ~ 0.4 eV to correct

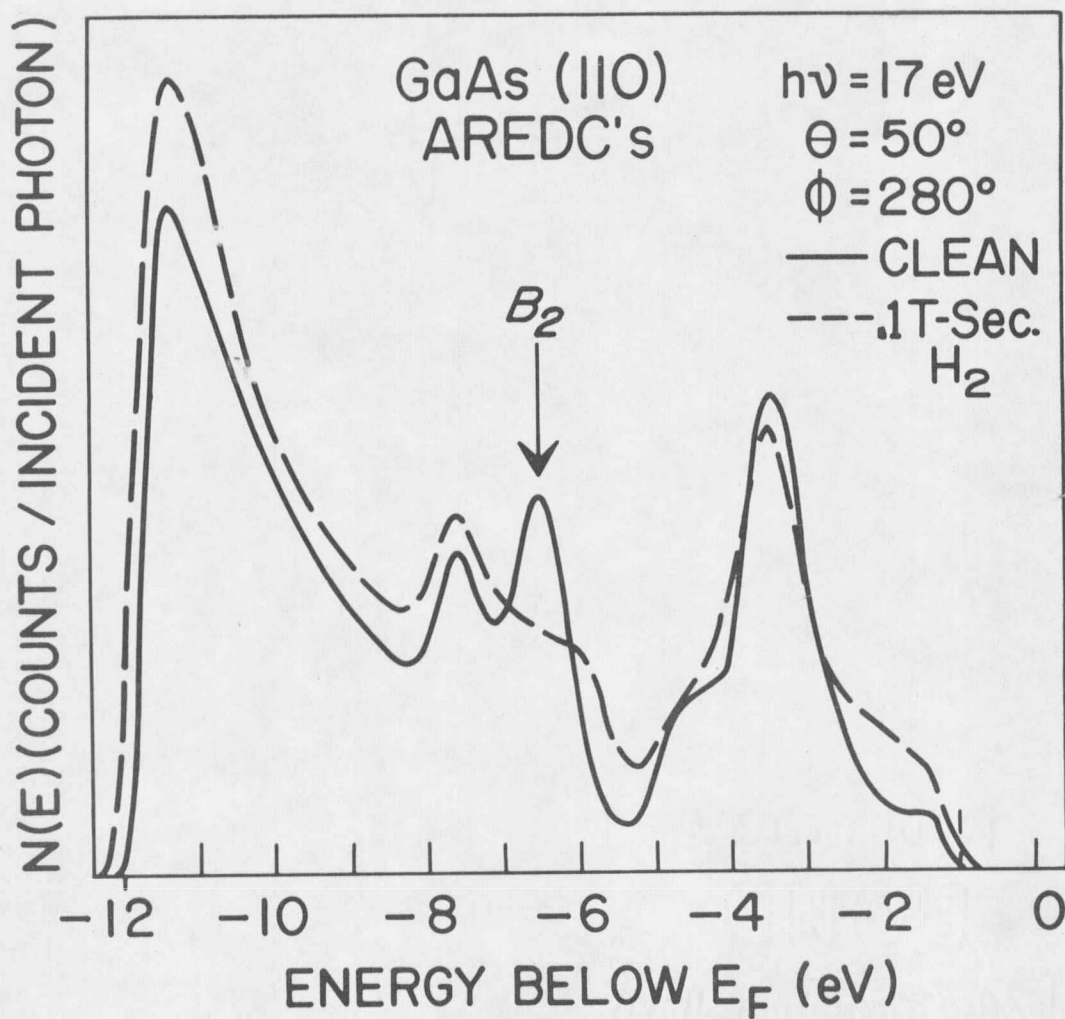


FIG. 35. AREDC's showing the effect of contamination on emission attributed to the surface state B_2 .

for band bending changes.⁵² The parameters $h\nu = 17$ eV, $\theta = 50^\circ$, and $\phi = 280^\circ$ are such that the peak in the clean AREDC at $E_i = -6.5$ eV originates with a $\vec{k}_{||}$ to one side of a zone corner $\bar{M}$. This peak is dramatically attenuated by the H_2 exposure and is thus attributed to a surface feature.

The dispersion behavior of this emission peak is illustrated in Fig. 36. In the set of AREDC's the magnitude of $\vec{k}_{||}$ corresponding to $E_i = -7.0$ eV is set equal to the value of $\vec{k}_{||}$ at $\bar{M}(h\nu = 18$ eV and $\theta = 60^\circ)$ and then the azimuthal angle ϕ is moved from the $\bar{M}$ point into the zone. $\bar{M}$ is at $\phi = 54.7^\circ$. The surface $\vec{k}_{||}$ values corresponding to the peaks labeled B_2 in the AREDC's are shown in the insert of the figure. As ϕ is changed, the emission peak attributed to B_2 moves from coincidence with the second VB at $E_i = -7.4$ eV into the "gap" and the peak vanishes when ϕ reaches 80° near $E_i = -5.0$ eV. The energy position of B_2 moves toward the VBM as the observation point moves away from the $\bar{M}$ point in agreement with the calculated properties. Similar emission features with the same E_i versus $\vec{k}_{||}$ behavior were observed on either side of each of the four $\bar{M}$ points in the first zone. (The corners of the next zones were not accessible with our experimental parameters.) The contamination sensitivity was also confirmed for each corner.

Again, as for B_1 , the contamination tests coupled with E_i

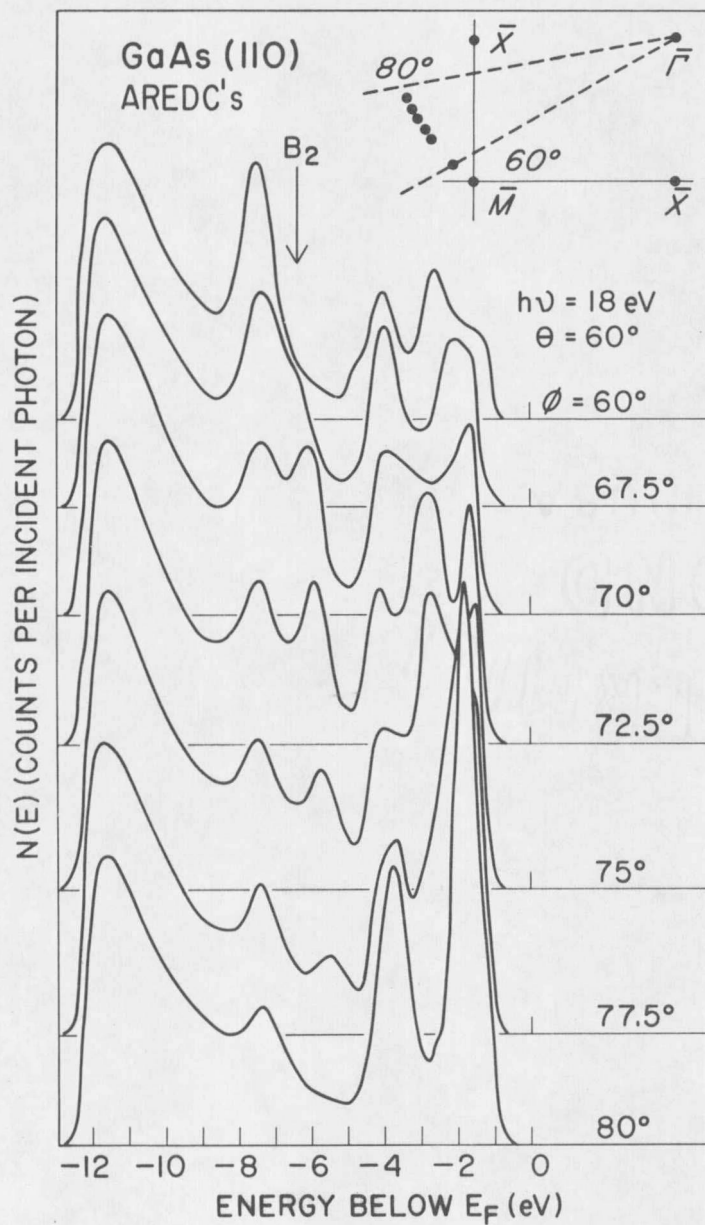


FIG. 36. AREDC's taken at constant $h\nu = 18$ eV, and $\theta = 60^\circ$, and $60^\circ \leq \phi \leq 80^\circ$. The insert shows $\vec{k}_{||}$ plotted for the surface state emission shown in the AREDC's.

versus $\vec{k}$ behavior completes the identification of the emission peak in Figs. 35 and 36 as due to the predicted surface state B_2 . Although it was inconvenient to measure E_i versus $\vec{k}_{||}$ along a zone symmetry line so as to allow an exact comparison with theory, the main energy position and dispersion behavior that are observed seem to agree well with the calculated values. The experimental width of the dispersion is somewhat wider than that of JC's calculation, but is in apparent agreement with the recent calculations for a relaxed surface.²⁵

C. Unoccupied Surface State.

1. Calculations and Experimental Measurements. All of the theoretical calculations of the electronic structure of the (110) surface of GaAs predict a surface state band in the upper part of the optical band gap.²¹⁻²⁵ These calculations have already been discussed. Evidence of the existence of such a state has been found in electron energy loss spectroscopy⁴⁶ and in UPS.^{45,47} The angle-integrated UPS observations of Lapeyre and Anderson (LA)⁴⁵ indicate an excitonic nature for the surface band, rather than a simple density of states model. The observed states may thus be thought of more properly as "surface excitons", rather than surface states in the conventional sense. Recent measurements of the position of the Fermi level at the surface of n-type GaAs⁵⁴⁻⁵⁶

indicate that the surface state does not lie in the band gap as predicted, but above the conduction band minimum. The experimentally observed resonances then imply excitonic binding of at least 0.5 eV.⁵⁵

The angle-resolved observations of the "surface exciton" which have been made in this study are in agreement with the UPS observations of LA. Since the state is well below the vacuum level, no direct photoemission from the empty surface state can escape the sample. The presence of the empty state can only be inferred from enhancements of the photoemission due to the decay of core to surface state excitation.⁴⁵ Measurement of the photoemission with either CFS's or CIS's exhibits this enhancement when the photon energy is swept through the threshold for core excitations. Two processes for the decay of the core hole-exciton have been set forth in the literature²⁹; one is the Auger process and the other is direct recombination. As pointed out by LA, the two processes can be differentiated because they excite electrons to different maximum final energies. In the Auger process, the core hole is filled by a valence electron while another valence electron absorbs the energy and is excited to a CB. In direct recombination (DR), the core hole and excited electron recombine, releasing their energy to a valence electron. The maximum possible final energy above the VBM for the valence electron in the DR process is thus equal to the photon energy of the core excitation, while the maximum

for the Auger process is equal to the energy difference between the core level and the VBM. Since the surface exciton binding energy lies ~ 1.0 eV above the VBM, this means that the maximum final energy for the DR process is equal to the final energy of VBM primary emission, while the maximum for Auger is ~ 1.0 eV less than that. In terms of the CIS's, Auger decay cannot contribute to enhancements for $E_i < 1.0$ eV below the VBM. One of the observations of IA was that the enhancement exists right up to the VBM, implying that the DR process must be present. In turn, the DR process strongly suggests an excitonic model, since the core hole-excited electron pair needs to be quite localized for the process to occur.

2. Angle-Resolved Observations. Angle-resolved CIS's (ARCIS) which exhibit the emission enhancement due to the surface exciton are shown in Fig. 37. These spectra were obtained at normal emission using the polarization mount in the p position. The electric polarization vector $\vec{\epsilon}$ of the incident radiation is out of the surface at a polar angle $\theta_A = 47.7^\circ$. The azimuthal angle ϕ_A of $\vec{\epsilon}$ was rotated around the normal to the surface to the positions 0° , 90° , and 180° relative to the crystal symmetries. Thus for the top ARCIS $\vec{\epsilon}$ is very nearly parallel to the Ga dangling bond, while for the bottom ARCIS $\vec{\epsilon}$ is nearly perpendicular to the Ga dangling bond and parallel to the As dangling bond. The resonant contribution

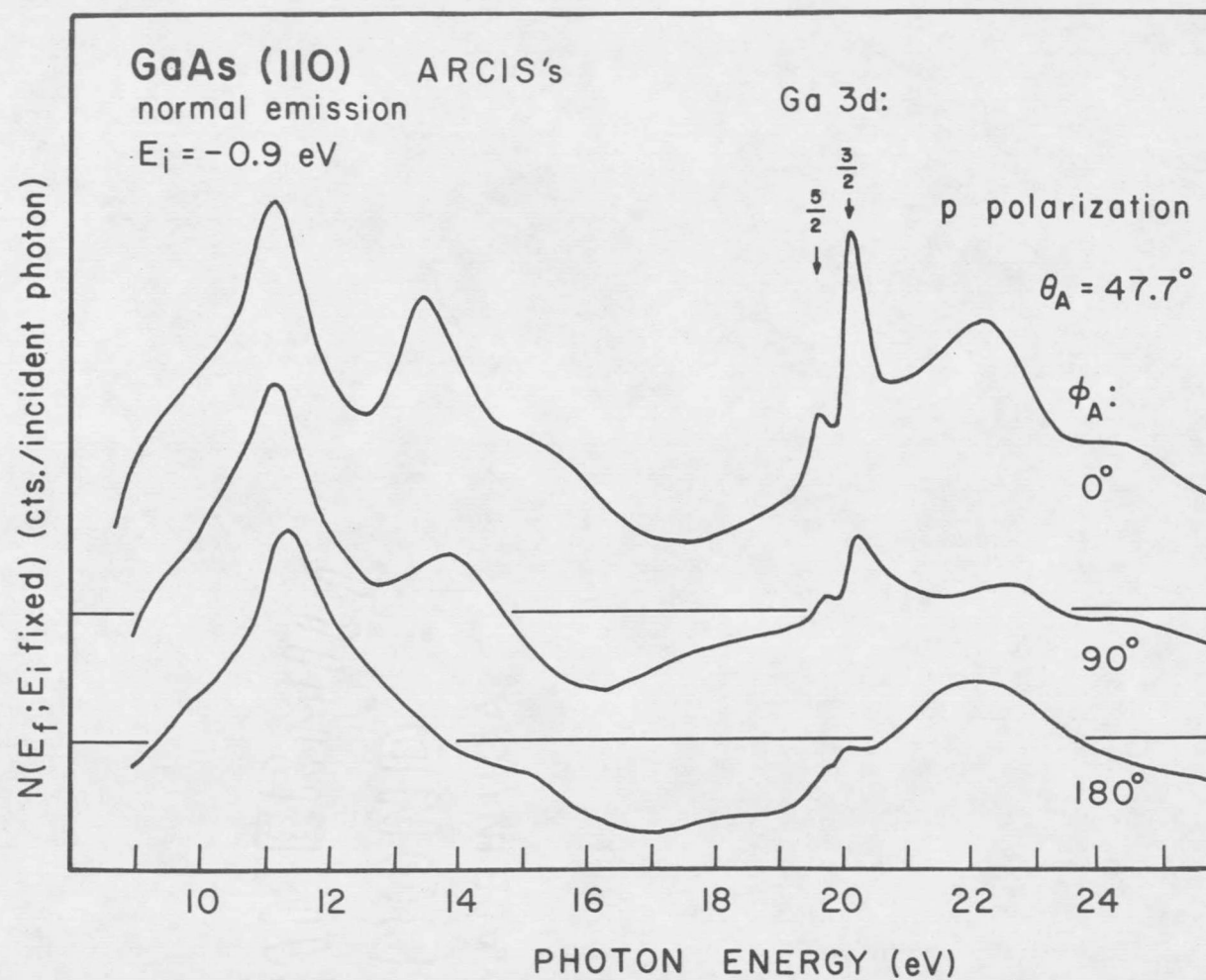


FIG. 37. Normal emission ARCIS's exhibiting surface exciton resonance emission.

to the photoemission is evident near $h\nu = 20$ eV for all three spectra. The resonance is a double-enhancement, corresponding to the spin-orbit splitting of the Ga 3d core level. The $j = 5/2$ contribution is at $h\nu = 19.65$ eV and the $j = 3/2$ contribution is at $h\nu = 20.2$ eV. All three ARCIS's in Fig. 37 were obtained for $E_i = -0.9$ eV, requiring that the DR process is important, as noted above and by LA. The resonance is also much stronger for $\vec{\epsilon}$ approximately parallel to the Ga dangling bond, suggesting that the feature is associated with the Ga ion, in agreement with LA's observations.

The effect of the resonant enhancement on an AREDC is shown in Fig. 38. These AREDC's were obtained at normal emission with p polarization, with $\vec{\epsilon}$ approximately parallel to the Ga dangling bond. The three spectra were obtained at photon energies at either side of the $j = 3/2$ resonance and on the resonance. The enhancement at $h\nu = 20.2$ eV is again clearly evident right up to the VBM, supporting the DR model.

3. Surface Contamination Sensitivity. The establishment of the exciton-like feature observed in the above spectra and by LA and others as a surface feature rests in its sensitivity to surface contamination. LA reported that a light Sb overlayer eliminated the resonance peaks.⁴⁵ Eastman and coworkers, however,

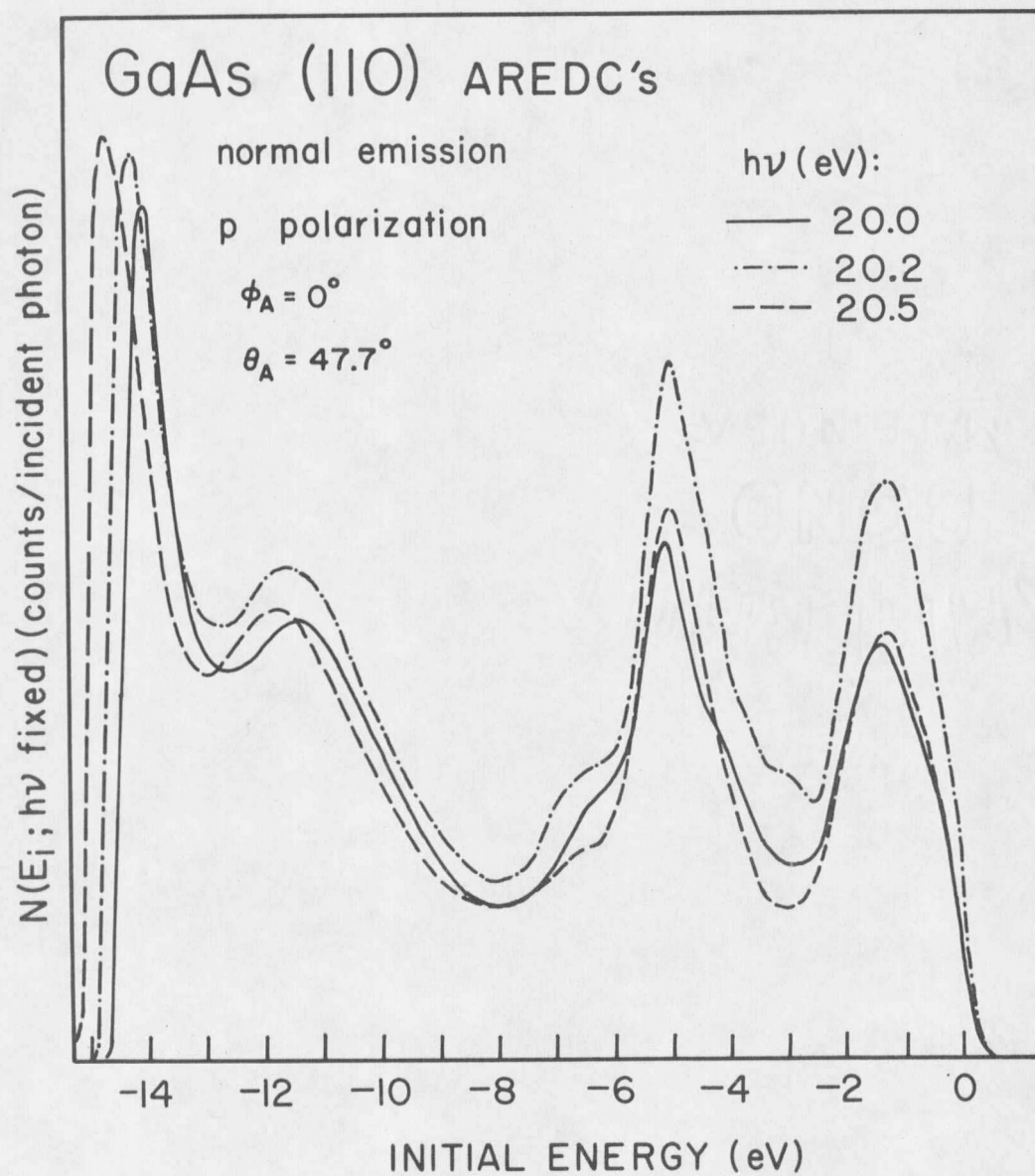


FIG. 38. Normal emission AREDC's obtained at either side of and on the surface exciton resonance at $h\nu = 20.2$ eV.

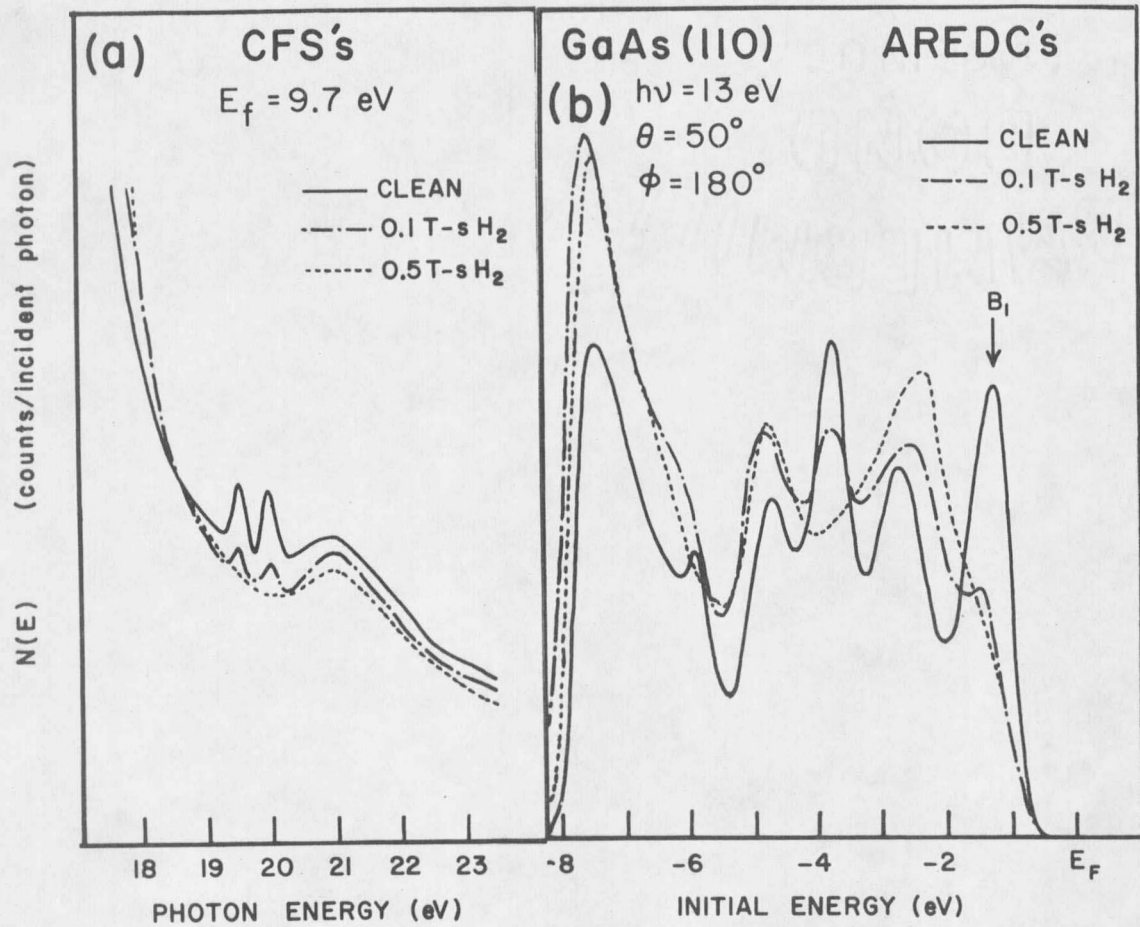


FIG. 39. (a) Contamination test CFS's for exciton resonance emission.

(b) Surface state B_1 for similar contaminations.

reported that certain contaminants, notably Pd, did not remove the resonance from the emission spectra.⁴⁹ More recent work has suggested this insensitivity to Pd may be an anomaly.⁵⁵ In our angle-resolved studies, the surface resonance peaks disappeared for sufficiently heavy exposures to O_2 or H_2 . Figure 39 demonstrates this sensitivity to H_2 exposure. Three angle-integrated CFS's taken at $E_f = 9.7$ eV are shown in Fig. 39a, one obtained from a clean (110) surface, the other two after increasing exposures to H_2 . These spectra were obtained using s polarization. After a 0.5 Torr-sec. exposure the resonance peaks from the surface exciton are no longer evident. Fig. 39b exhibits a contamination set of AREDC's for B_1 , with the same exposures of H_2 .

D. Bulk Band Structure Determination.

1. Normal Emission. Examination of the photoemission which exits the crystal perpendicular to the surface is very useful in attempting to "map out" bulk energy band levels. This normal emission consists of electrons for which $\vec{k}_{||} = 0$, both inside and outside the crystal. This condition, imposed by the conservation of $\vec{k}_{||}$ as discussed previously, implies that all wavevectors of the detected photoelectrons lie along a line in bulk $\vec{k}$ -space defined by $k_{||}$. For the (110) surface, $k_{||}$ at normal emission corresponds to the Σ symmetry line from Γ to X, repeated throughout $\vec{k}$ -space.

The energy bands are commonly calculated along symmetry lines, including Σ , and thus calculations are available to compare to experiment, providing a guideline in interpretation. The Σ line, and hence the normal emission, is important for (110) GaAs because it is the only symmetry line for which constant $\vec{k}_{||}$ data may be collected that represents transitions only along the symmetry line. The symmetry points Γ and X which are included are also important points of high symmetry in the bulk BZ.

The energy bands along Σ , as shown in Fig. 23, consist of two symmetry types, Σ_1 and Σ_2 . Both designations are one-dimensional representations, with the identity E and the mirror plane reflection JC_2 as the only two symmetry operations. Σ_1 is even under reflection in the mirror plane and Σ_2 is odd under reflection. Transitions between these bands along Σ are then subject to the same arguments given earlier in section IVA about the effects of the orientation of the vector potential $\vec{A}$. That is, transitions between states of the same parity (under reflection JC_2) are forbidden when $\vec{A}$ is perpendicular to the mirror plane and transitions between states of opposite parity are forbidden when $\vec{A}$ is in the mirror plane.^{43,44} The transition is forbidden when its matrix element is not invariant under the symmetry operation. These selection rules may be used to help identify the symmetries of bands involved in observed transitions.

The details of the interaction of the surface with the normal components of wavevector $k_{\perp}$ are not known. All that is known is that the surface mixes together states of several values of $k_{\perp}'$ inside the sample to produce the observed outgoing electron state of wavevector $k_{\perp}$.³³ Thus an observed photoelectron may have had any of several values of $k_{\perp}'$ inside the crystal, subject only to the constraint that $k_{\perp}'$ is along Σ . The method of data analysis for the normal emission was to assume that an observed feature could be due to transitions at any value of $k_{\perp}$ along Σ , and then to search the calculated bands along Σ for critical points or parallel bands at the appropriate initial and final energies. In several cases this led to an unambiguous assignment of the bands involved in the transition.

Normal emission data was obtained for several orientations of $\vec{A}$ relative to the crystal symmetries, including both s and p polarization, using the polarization mount and the sample/analyzer configuration of Fig. 18. The condition $\vec{k}_{\parallel} = 0$ holds for all three modes of angle-resolved photoemission spectroscopy (AREDC, ARCIS, and ARCFs), such that all direct transitions in the observed spectra take place along Σ . Figures 40, 41, and 42 show sets of each of the three modes of spectroscopy, all taken at the same normal emission and polarization orientation. All spectra were obtained with p polarization, with $\theta_A = 47.7^\circ$ and $\phi_A = 0^\circ$. The

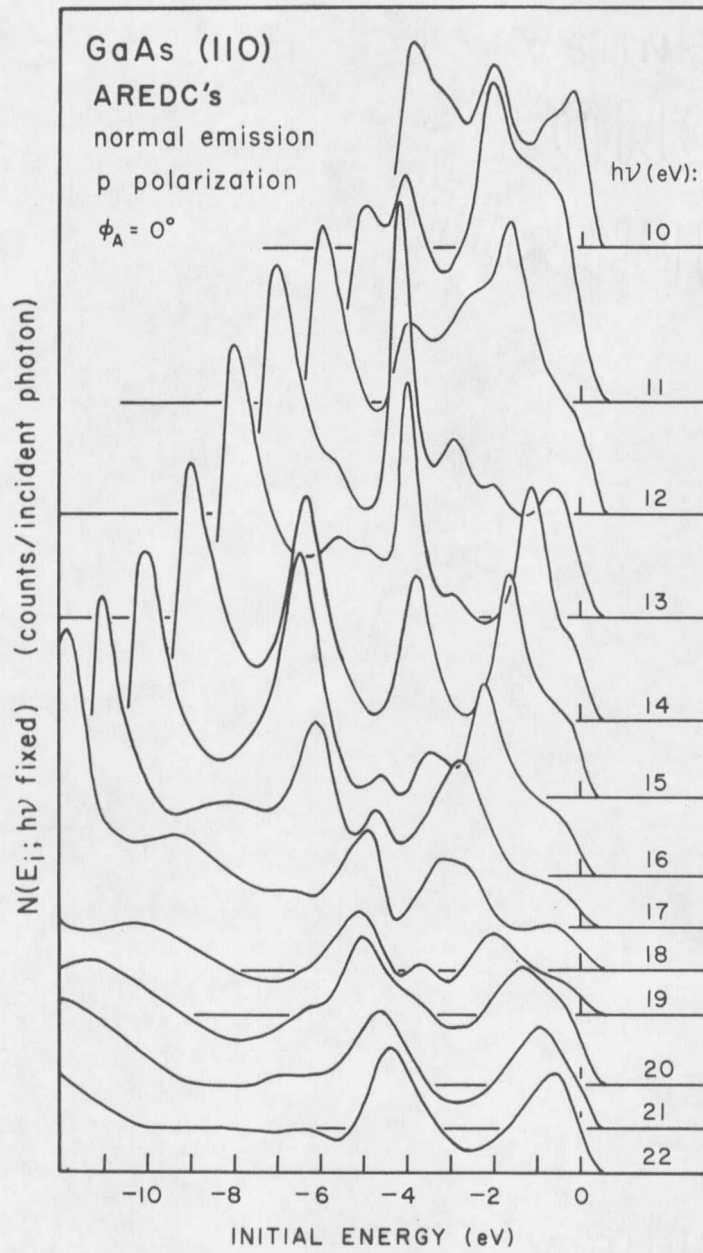


FIG. 40. Normal emission AREDC's obtained with $\vec{\epsilon}$ at $\theta_A = 47.7^\circ$ and $\phi_A = 0^\circ$.

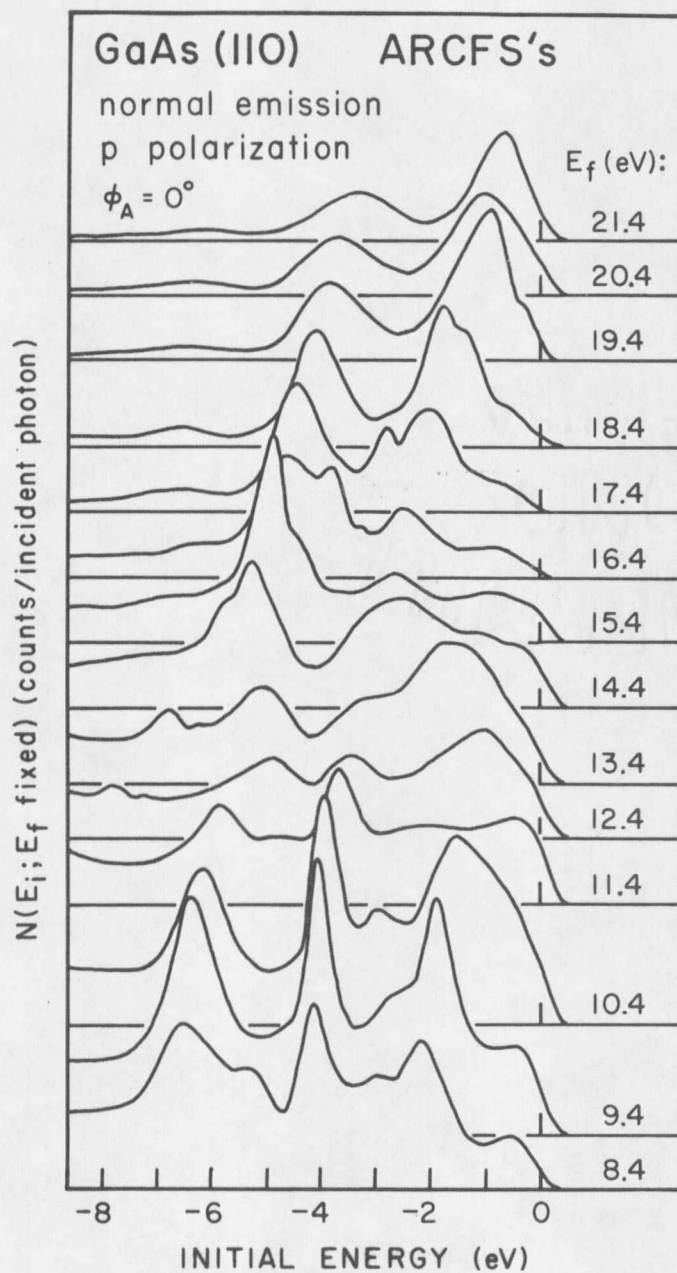


FIG. 41. Normal emission ARCFS's obtained with $\vec{\epsilon}$ at $\theta_A = 47.7^\circ$ and $\phi_A = 0^\circ$.

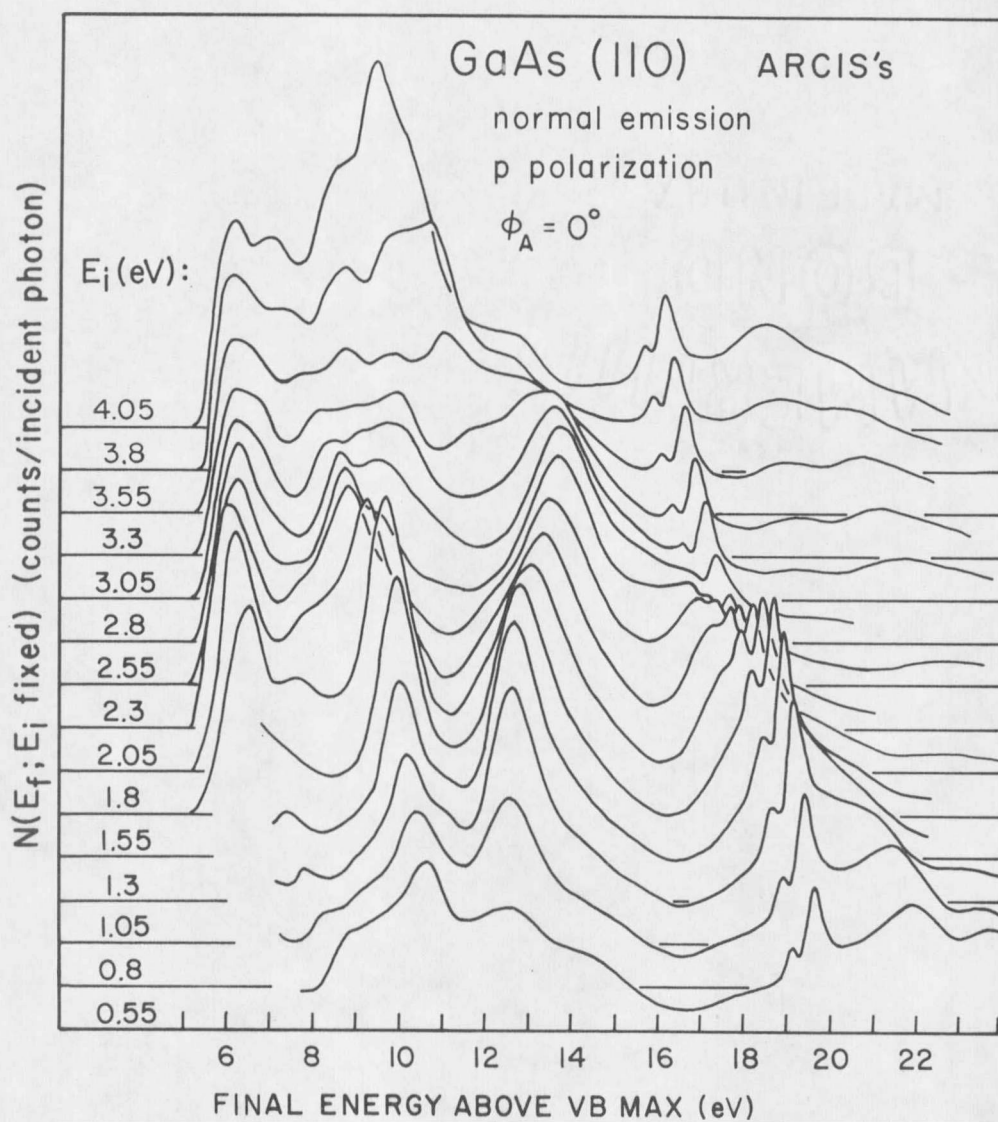


FIG. 42. Normal emission ARCIS's obtained with $\vec{\epsilon}$ at $\theta_A = 47.7^\circ$ and $\phi_A = 0^\circ$.

AREDC's of Fig. 40 illustrate the conventional approach, for which $h\nu$ is constant, but E_i and E_f are variables in each spectrum. These AREDC's are plotted versus E_i measured from the VBM. The energy position of the VBM at Γ_{15} was determined from a normal emission AREDC at $h\nu = 10.5$ eV, for which the transition $\Gamma_{15} \rightarrow \Gamma_{12}$ is prominent. Figure 41 shows a set of ARCFS's for the same emission, illustrating that initial band structure dominates in each curve, but varies from curve to curve as the final energy is changed. The ARCFS's are plotted versus the same initial energy scale as in Fig. 40. Figure 42, showing ARCIS's, illustrates how final band structure affects the emission, each curve representing how initial states at each different initial energy couple into final states over the same range of final energy.

2. Initial Band Critical Points. The theoretical calculations of energy bands may be expected to be most accurate for the valence bands, since the calculations are generally fitted to experimental valence band critical point energies. An experimental demonstration of valence band emission from a few of these critical points is therefore of interest, since the present experiment is capable of isolating photoemission due only to particular critical points. This capability increases the accuracy of energy level assignments over other photoemission techniques.

The valence band critical points which are accessible in the normal emission are illustrated in Fig. 43. The calculated valence bands along Σ are illustrated in the lower portion of the figure and an angle-resolved CFS (ARCFS) is in the upper part. The lowest valence band is omitted from the band diagram as it is not observed at the available photon energies. The ARCFS was obtained for the final states at 9.4 eV above the VBM, and is plotted with both photon energy and initial energy as horizontal energy scales. The final state energy was chosen so as to best display transitions from several initial critical points.

The first critical point, Γ_{15} , is of course very interesting because it is the maximum valence band position throughout the BZ. This critical point is indicated as the leading edge of the ARCFS. The strong peak at $E_i = -1.8$ eV is due to a high density of states in the conduction band, as will be demonstrated shortly. The second critical point, X_5 , is not sharply delineated, being represented by only a weak feature at $E_i = -2.8$ eV. The third critical point at $\Sigma_1^{\min}$ is perhaps most interesting as it is only present as a trailing shoulder in angle-integrated UPS spectra.⁵⁷ Here in the angle-resolved spectra, the emission is a dramatic feature which is nearly as sharp as the instrumental resolution allows. The energy position is clearly in very good agreement with the calculated bands. The final peak in the ARCFS corresponds to X_3 , or more

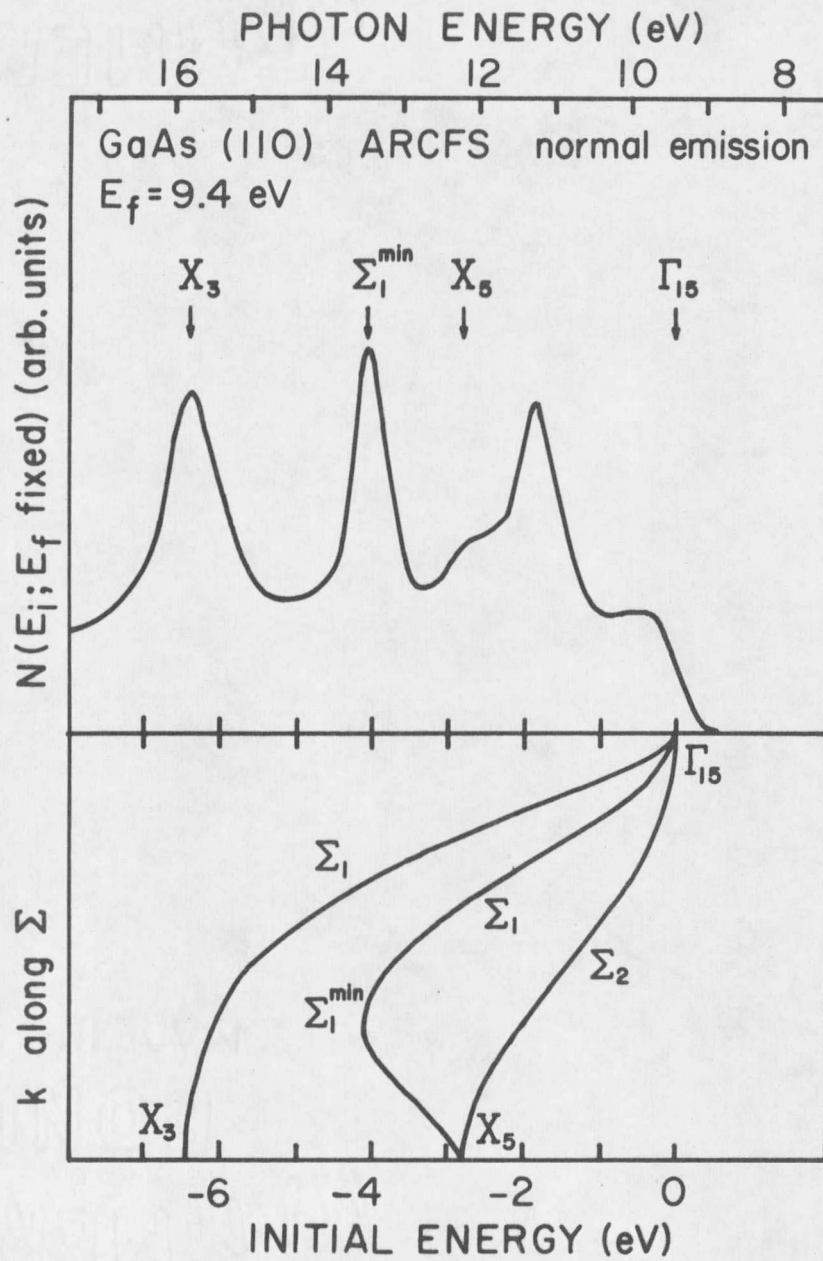


FIG. 43. ARCFS obtained at normal emission, exhibiting critical points in the valence bands along Σ .

properly to band 2 near K, since no final bands exist at the X point at this final energy, but final bands are available near K. The calculated position of X_3 is perhaps ~ 0.2 eV higher than observed in these data.²⁰

Another symmetry point which is accessible in emission from the (110) face is the L point. Figure 44 displays an ARCFs which is obtained for $E_f = 12.3$ eV, $\theta_p = 44.5^\circ$, and $\phi_p = 306^\circ$. At these parameters $k_{||}$ is fixed at $0.95 \text{ \AA}^{-1}$ and the bulk emission originates along a line in k -space which passes along the hexagonal side of the BZ, through W and L. This line, parallel to $k_{\perp}$, is designated the Q line. The Q line for GaAs has no higher symmetry than an arbitrary point in the zone, and so bands are not generally calculated along it. The bands along the Q line sketched in the lower part of Fig. 44 are based on limited information. The values for L_3 and L_1 are from the pseudopotential calculation of Pandey and Phillips,²⁰ while the W points are from Chelikowsky, Chadi, and Cohen.¹⁸

The bands in Fig. 44 illustrate that the maximum valence band position along the Q line is at L_3 , rather than at Γ_{15} . L_3 has been placed in the various calculations at energy positions varying from 0.9 eV^{18} to 1.3 eV^{19} below the VBM at Γ_{15} . The ARCFs of Fig. 44, obtained at a final energy for which there are expected to be final bands at the L point,²⁰ clearly indicates strong emission which extends to $E_i = -1.15$ eV. This emission is interpreted as direct

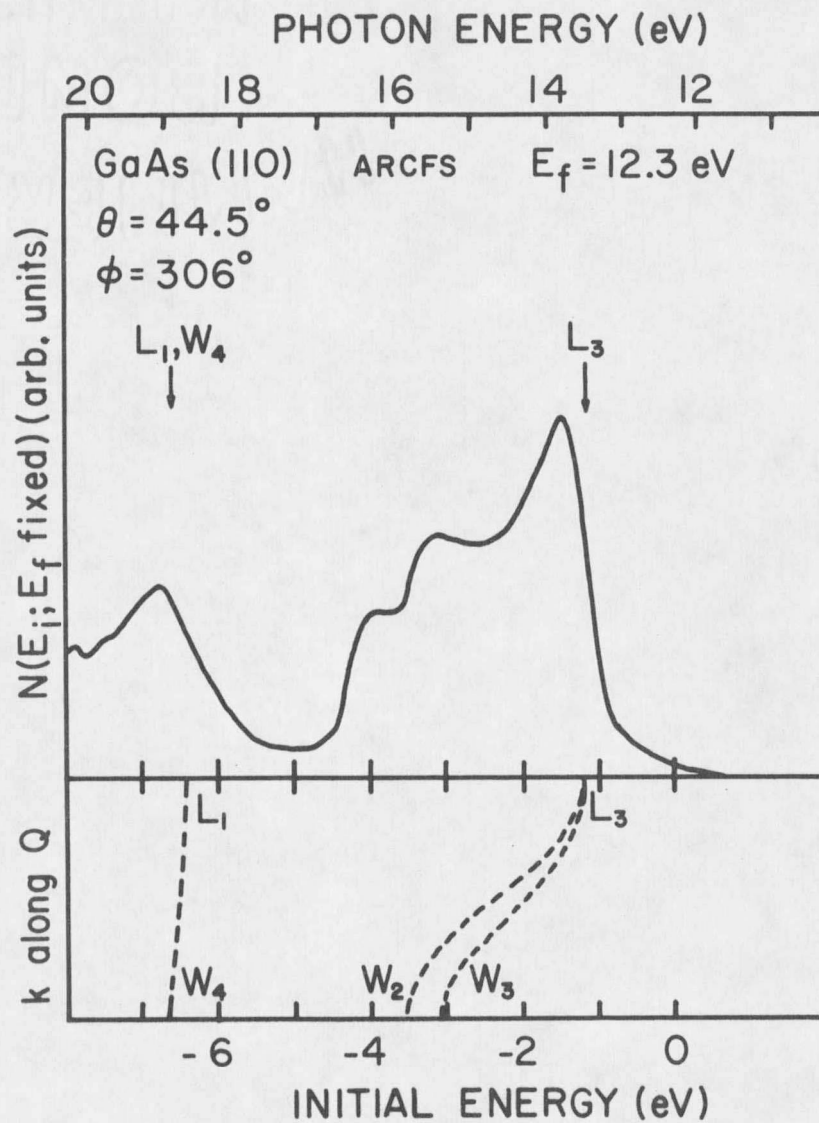


FIG. 44. ARCFs exhibiting emission from valence bands along $L \rightarrow W$.

Table I. Energies (in eV) of selected initial band critical points in GaAs relative to the VBM.

Critical point	EXPERIMENTAL		THEORETICAL	
	This work	UPS(ref. 57)	(ref. 18)	(ref. 20)
L_3	$- 1.15 \pm 0.1$	$- 0.8 \pm 0.2$	$- 0.9$	$- 1.20$
X_5	$- 2.9 \pm 0.2$	...	$- 2.5$	$- 2.83$
$\Sigma_1^{\min}$	$- 4.1 \pm 0.1$	$- 4.1 \pm 0.2$	$- 3.9$	$- 4.10$
X_3	$- 6.8 \pm 0.2$	$- 6.8 \pm 0.2$	$- 6.8$	$- 6.44$

transitions from L_3 and is labelled as such in the figure. The maximum energy position is in good agreement with the plotted band position of L_3 at $E_1 = -1.2$ eV. Note that a small tail of emission extends up to the VBM. This tail is probably due to phonon-scattered electrons which originated at the center of the BZ. Because of the uncertainty in the band structure away from L, no interpretation is assigned to the features in the ARCFs at 3-4 eV below the VBM. The features are very suggestive of a correspondence with the W_2 and W_3 critical points; but we have no assurance that they are not due to critical points in the conduction bands.

The accuracy of the energy level assignments in the calculated valence bands by Pandey and Phillips is seen to be quite good. The observed energy positions of several valence band critical points is summarized in Table I, together with the assignments made by three theoretical calculations and those made by an angle-integrated UPS experiment.

3. Final Band Structure. Having established the accuracy of the calculated valence bands, the next step is to identify structure in the conduction bands, referenced to initial band critical points. The ARCIS mode of data collection is especially suited for application to this problem in studying the normal emission. Unfortunately the ARCIS and AREDC modes are difficult to analyze for

$\theta_p \neq 0^\circ$ since $\vec{k}_{||}$ is not a constant for such spectra, resulting in the sampling of a plane in bulk $\vec{k}$ -space, rather than a line.

The use of the ARCIS mode to help identify final band structure is perhaps best explained by examination of Fig. 45. The figure consists of three parts, all plotted versus a common energy scale measured relative to the VBM. Diagrammed in the lower part of the figure are the calculated bands along the symmetry line Σ , with the lowest valence band once again deleted. A portion of the lower conduction bands is also deleted for convenience. The bands are labeled by their symmetry designations at Γ and X and by the band numbers of Fig. 23. In the upper part of the figure are two experimental spectra, an AREDC taken at $h\nu = 10.5$ eV and an ARCIS obtained for $E_i = -0.05$ eV. Both spectra were taken at normal emission with s polarization. The initial energy window of the ARCIS, $E_i = -0.05$ eV is indicated in the band diagram as well as on the AREDC. The 0.5 eV width of the analyzer energy window is shown by dotted lines. This initial energy window includes all three valence bands very close to Γ_{15} , the VBM. By selecting these states, one restricts the final states (in a direct-transition model) to states with $\vec{k}$ very close to Γ . Several possible direct transitions are indicated in the band diagram. The transitions

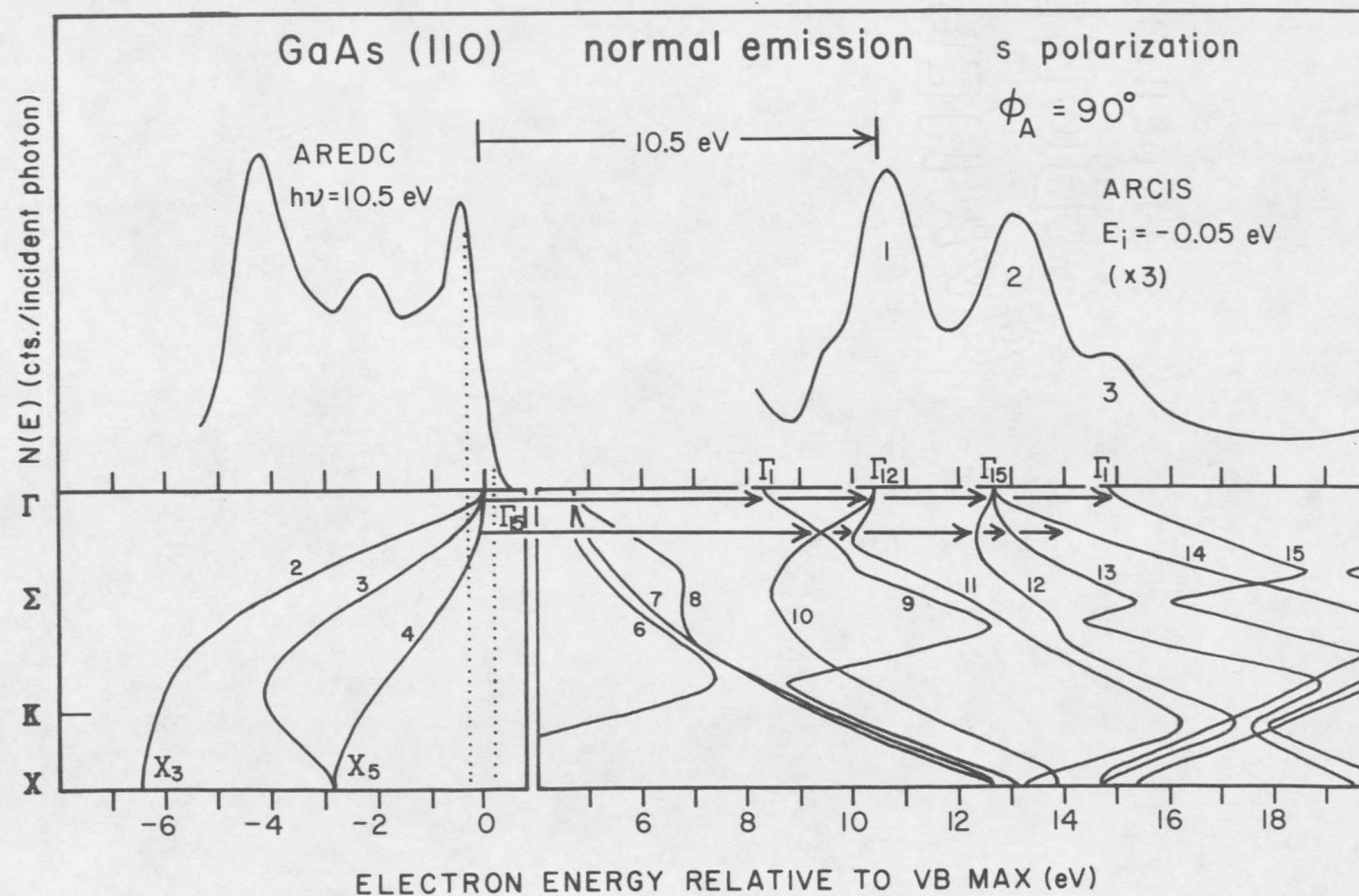


FIG. 45. ARCIS showing transitions from near Γ_{15} along Σ .

are clustered near conduction band critical points at Γ , which are Γ_1 , Γ_{12} , Γ_{15} , and Γ_1 . The ARCIS reflects these transitions in two peaks and a shoulder, all in very reasonable agreement with the band diagram. Peak 1 in the ARCIS can clearly be associated with transitions at or near Γ_{12} , peak 2 with Γ_{15} , and peak 3 with Γ_1 . The indicated positions of Γ_{12} , Γ_{15} , and Γ_1 are given in Table II along with calculated values and values obtained by other experiments.

The usefulness of the ARCIS in studying conduction band structure lies in displaying in one spectrum the strength of transitions to a range of final energies. The initial energy involved in the transitions is kept constant and may be selected to include a critical point in the valence bands. One caution needs to be observed in interpreting the results. Examination of a single spectra of any of the three modes may lead to errors in assigning peaks to direct transitions. For example, for some initial energies, inelastic scattering from states at another initial energy may lead to peaks in the ARCIS at certain photon energies which are not due to direct transitions at all. Thus, one needs to study the AREDC data in conjunction with the ARCIS's or a complete set of adjacent ARCIS's in order to preclude mistaken peak identifications. An example is a part of Fig. 45. The AREDC at the left of the figure shows that the peak at $h\nu = 10.5$ eV in the ARCIS

is indeed due to a strong transition probability from states near the VBM, and not due to scattered electrons from a completely different initial energy.

It should also be noted that the photoemission spectra are expected to show transitions involving critical points (transitions between parallel bands). A transition between initial and final bands whose slopes are of different sign is not expected to be dominant in the spectra. Peak 3 in Fig. 45 may be weak for this reason.

The analysis presented in conjunction with Fig. 45 can be repeated for a number of different initial energies. We shall present four other important examples. Another set of initial states is responsible for the ARCIS of Fig. 46. The bands are diagrammed as in Fig. 45, but the AREDC is taken at $h\nu = 11.5$ eV and the ARCIS at $E_i = -1.8$ eV. These spectra were obtained using p polarization, with $\vec{\epsilon}$ at $\phi_A = 0^\circ$ and $\theta_A = 47.7^\circ$. The initial energy window again includes all three valence bands, but at values of $\vec{k}$ well away from Γ . Several possible direct transitions are indicated in the band diagram. Since the transitions are not clustered near Γ , the identification of structure in the ARCIS is not quite so straightforward. The most prominent structure in the ARCIS, peak 3, is most probably due to the two critical points in bands 9 and 11. This prominent structure is also the

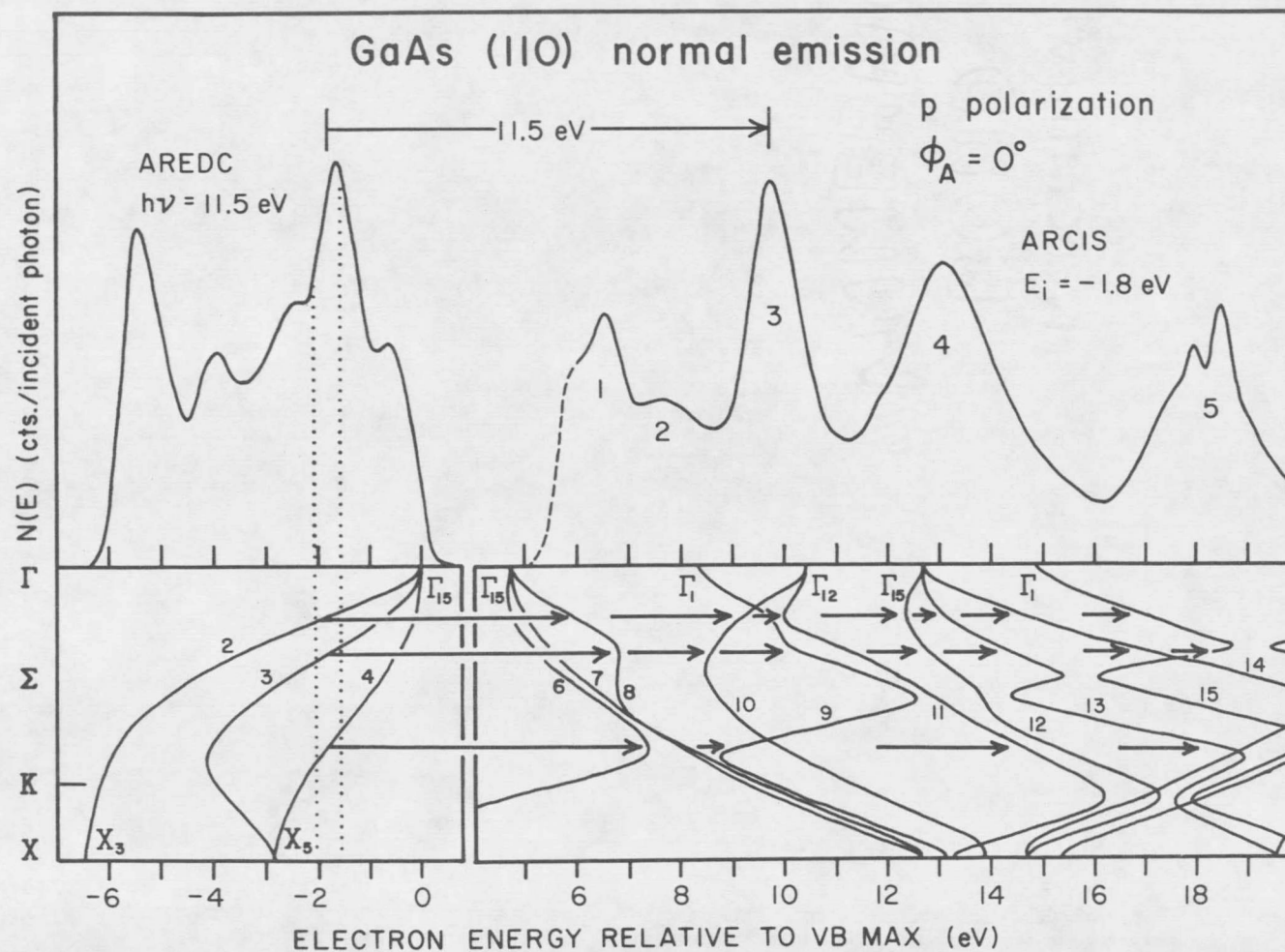


FIG. 46. ARCIS showing transitions from initial bands at $E_i = -1.8 \text{ eV}$.

source of the peak at $E_i = -1.8$ eV in the ARCFs of Fig. 43. As can be seen in Fig. 46, the calculated position of these critical points is ~ 0.3 eV too high. Peak 4, centered at $E_f = 13$ eV, is due to transitions to bands 12 and 13, which are somewhat low in energy in the calculation, along with Γ_{15} . The final large structure, peak 5, which has the surface-exciton decay superimposed over it, is probably due to several final bands close to the K point at $E_f \sim 18$ eV.

In the next example, Fig. 47, the initial energy window includes the valence band critical point X_5 . The AREDC was obtained at $h\nu = 16$ eV and the ARCIS at $E_i = -2.8$ eV, both with p polarization with $\phi_A = 180^\circ$. The ARCIS in Fig. 47 extends down to the vacuum level. Peak 1 may be due in part to the indicated transitions at band 8, but is also composed of scattered electrons near threshold. Peak 2 is identified as transitions from bands 2 and 3 to band 10, while bands 9 and 11 are apparently responsible for the broad peak 3. Peak 4, for which the AREDC is illustrative at $h\nu = 16$ eV, is of the most interest since it appears to be due to transitions from X_5 to the several X critical points near $E_f = 13$ eV. However, transitions to bands near the center of Σ may also contribute substantially to this feature, as its magnitude is sensitive to the polarization orientation in such a way as to indicate a preponderance of $\Sigma_1 \rightarrow \Sigma_1$ transitions. The transitions

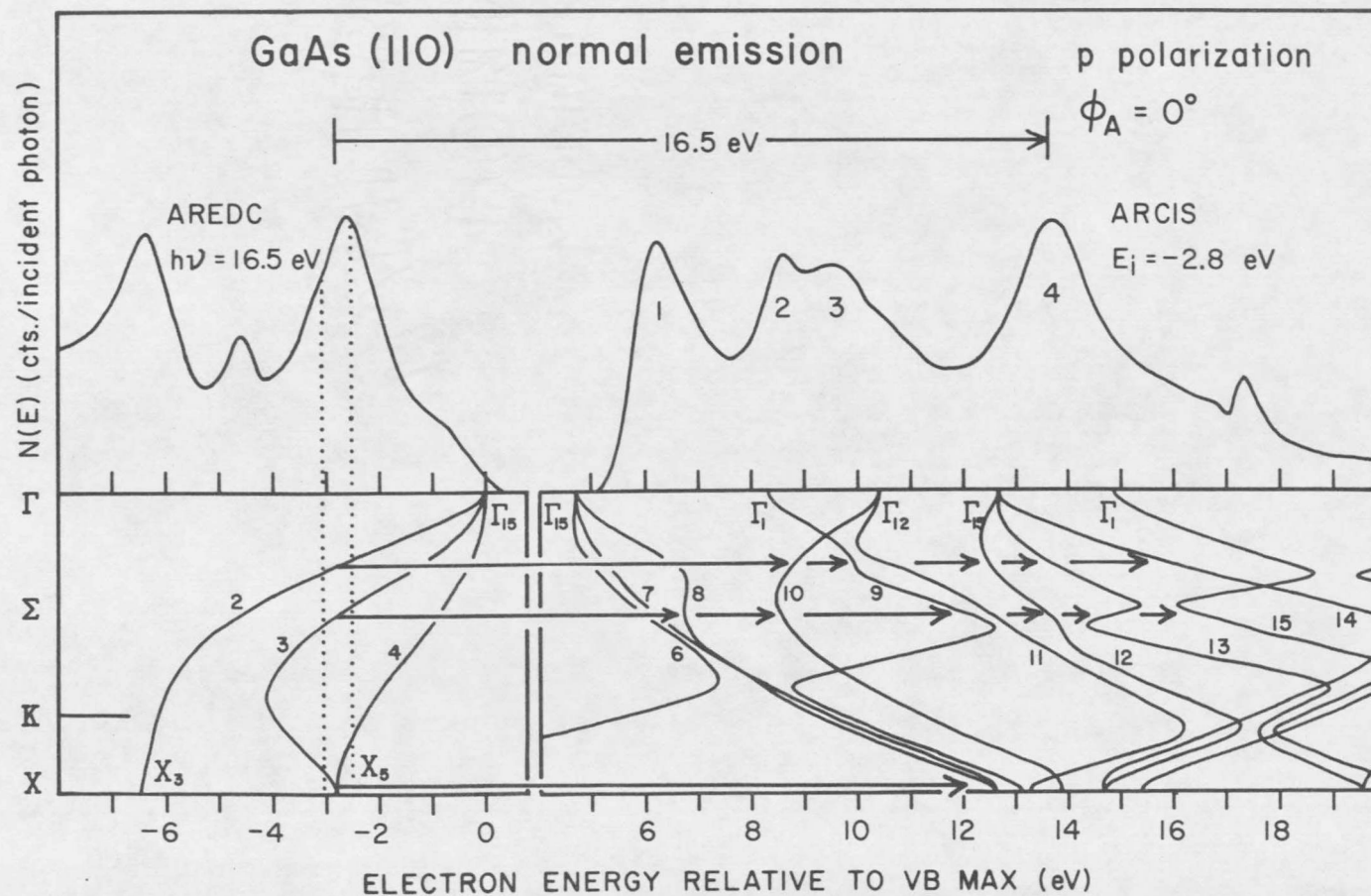


FIG. 47. ARCIS showing transitions from initial bands at $E_i = -2.8$ eV.

near the center of Σ at these final energies are all of this type.

A significant valence band critical point, $\Sigma_1^{\min}$, is included in the initial energy window of the ARCIS of Fig. 48. The AREDC of this figure was taken at $h\nu = 18.5$ eV and the ARCIS at $E_i = -4.05$ eV. These spectra were obtained with the polarization vector in the p position at $\phi_A = 0^\circ$. As indicated in the band diagram, the initial energy window of the ARCIS includes two Σ_1 bands, band 2 near the center of the Σ line, and band 3 on either side of $\Sigma_1^{\min}$. Since the energy resolution of the CMA is ~ 0.5 eV, $\Sigma_1^{\min}$ is included. The ARCIS is dominated by peaks 3 and 4, at $E_f = 8.6$ eV and 9.4 eV. Peak 3 may contain a contribution from a transition of band 2 to the minimum in band 10 in addition to transitions from the region of $\Sigma_1^{\min}$. Peak 4, on the other hand, almost certainly is due to transitions from band 3, including $\Sigma_1^{\min}$, to the region of the minimum in band 9. The AREDC at $h\nu = 13.5$ eV illustrates that the peak in the ARCIS is due to the sharp initial band DOS at $\Sigma_1^{\min}$. The theoretically calculated position of the minimum in band 9 is too low by ~ 0.3 eV. Of the other features in Fig. 48, peak 1 is due to scattered electrons, peak 2 may be assigned to $\Sigma_1^{\min}$ band 2, peak 5 reflects elastic scattering from another initial energy, and peak 6 may be transitions to the several bands near K at $E_f = 18.5$ eV. The double peak at $E_f = 16$ eV is due to core-surface exciton decay.

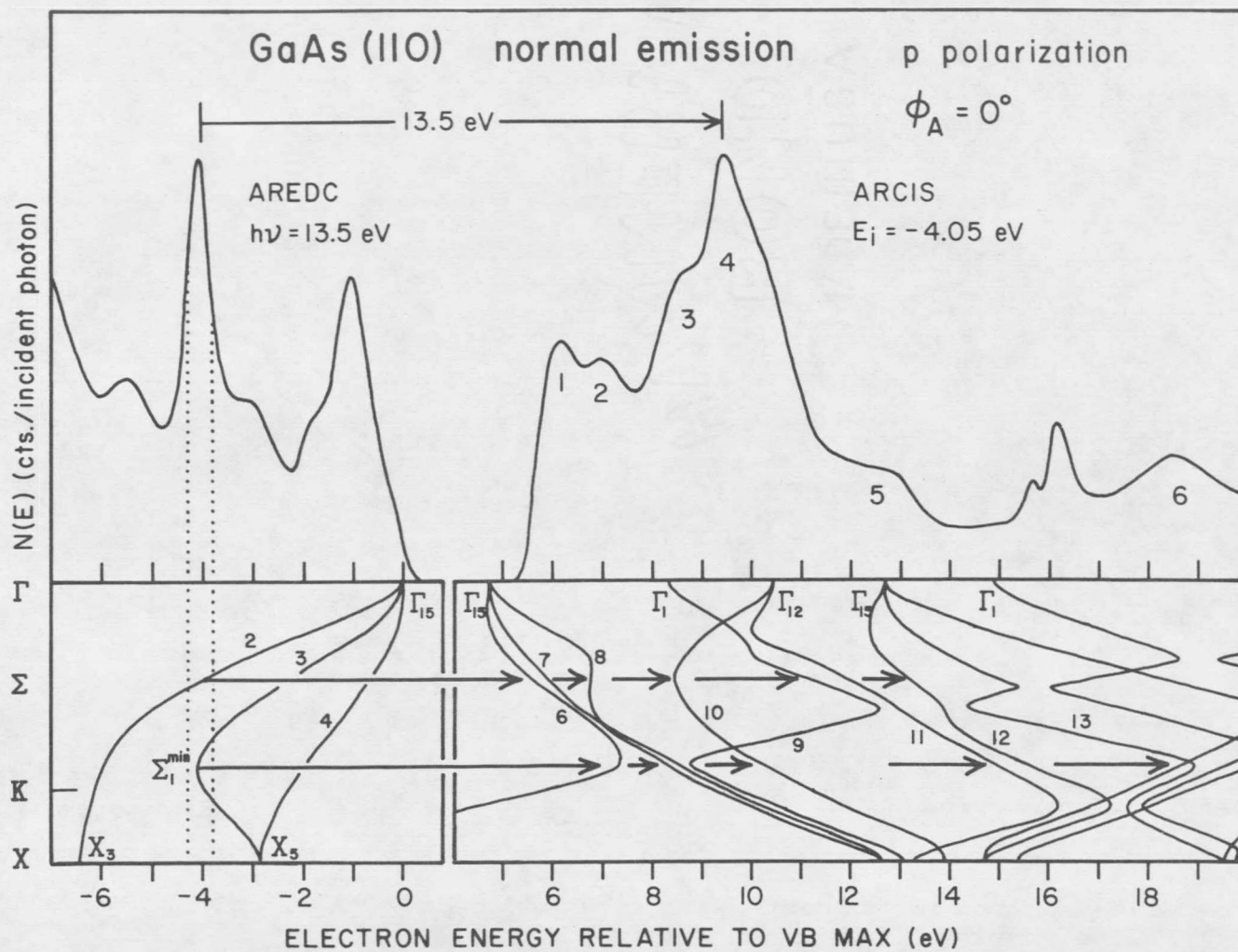


FIG. 48. ARCIS showing transitions from initial bands at $E_i = -4.05$ eV.

The final example of this technique is for an initial energy window which includes only one valence band. Figure 49 shows an AREDC obtained at $h\nu = 15.5$ eV, and an ARCIS taken for $E_i = -6.55$ eV. As indicated in the previous section, the calculated position of X_3 is ~ 0.3 eV too high, so the initial energy window intersects band 2 close to K, rather than at X_3 . This correction to the band diagram is indicated in the figure with dashed lines. The 0.5 eV energy window thus includes band 2 both at X_3 and near K. The ARCIS has two features of interest. (Peak 1 is due to scattered electrons at threshold.) The major peak, labeled peak 2, is apparently due to final bands near K and including the minimum of band 9. Again, the position of this latter critical point is seen to be ~ 0.3 eV too low in the calculation, in agreement with Fig. 48. The second feature, peak 3, with the core-surface exciton decay superimposed, is identified as transitions from X_3 to the several critical points at X between 12 and 16 eV above the VBM.

In each of the examples above, the polarization condition of the spectra was chosen so as to best display several important transitions. The energy positions of conduction band critical points relative to the VBM at Γ_{15} as determined from the above and other spectra are summarized in Table II. The calculated energies of Pandey and Phillips²⁰ are also shown, along with Electromerectance measurements by Aspnes, Olson, and Lynch.⁵⁸

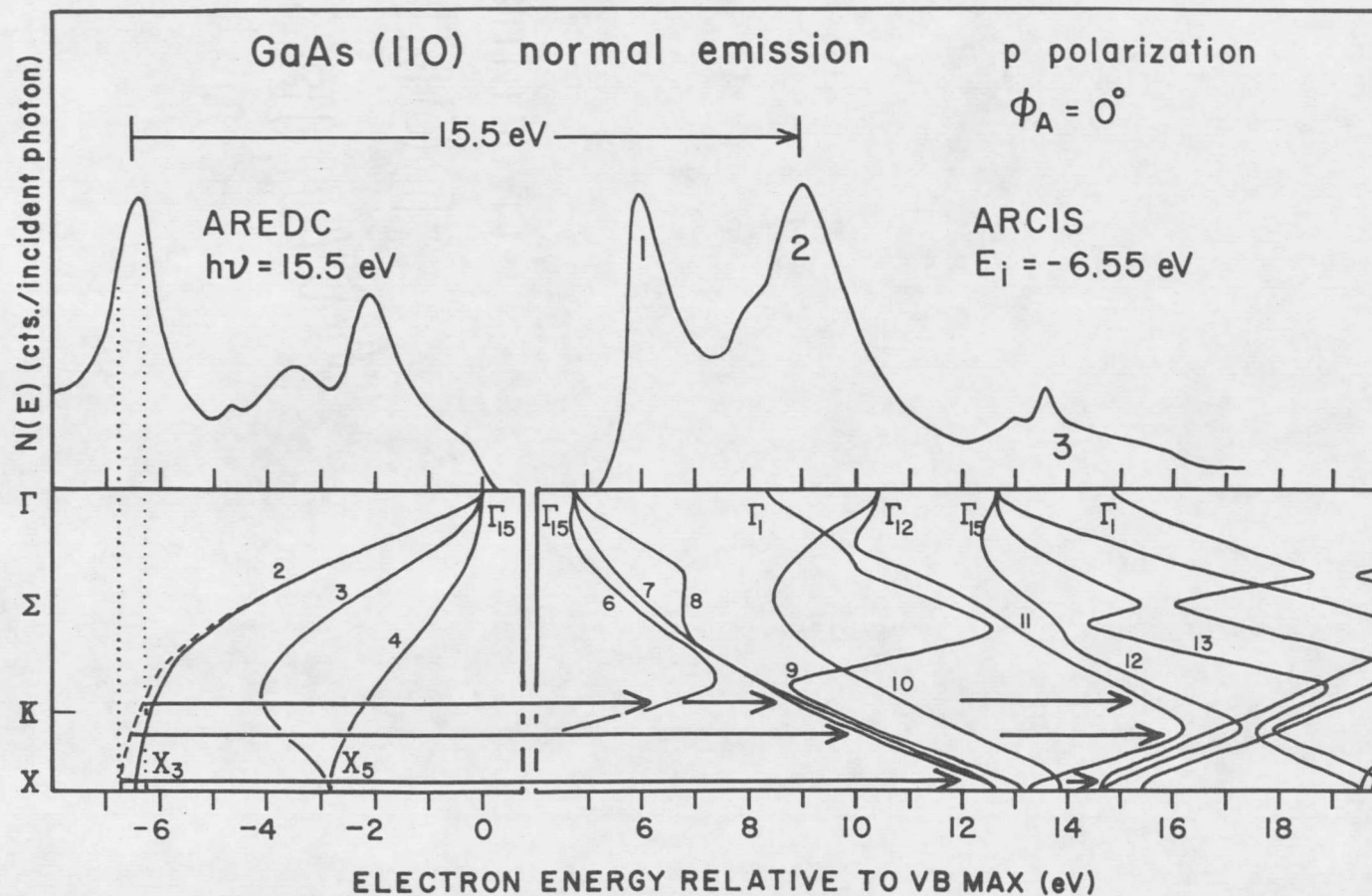


FIG. 49. ARCIS showing transitions from initial bands at $E_i = -6.55 \text{ eV}$.

Table II. Energies (in eV) of selected final band critical points in GaAs relative to the VBM.

Critical point	EXPERIMENTAL		THEORETICAL
	This work	ER(ref. 58)	(ref. 20)
Γ_{12}	10.6 ± 0.3	10.53	10.4
Γ_{15}	12.8 ± 0.3	...	12.6
Γ_1	14.9 ± 0.3	...	14.9
$\Sigma_1^{c8}(\text{min})$	7.0 ± 0.3	...	6.7
$\Sigma_1^{c9}(\text{min})$	9.2 ± 0.3	...	8.8
$\Sigma_2^{c10}(\text{min})$	8.6 ± 0.3	...	8.4
$\Sigma_1^{c12}(\text{min})$	9.8 ± 0.3	...	9.9

4. Polarization Dependence. The effects of changing the orientation of the electric polarization vector $\vec{\epsilon}$ relative to crystal symmetries have been demonstrated to be substantial for certain transitions. This is certainly true for the normal emission as well. The AREDC's of Fig. 50 demonstrate polarization dependence for normal emission at $h\nu = 17$ eV. Both curves were obtained with s polarization, the solid curve with $\vec{A}$ parallel to the surface mirror plane and the dashed curve with $\vec{A}$ perpendicular to the mirror plane. (The vector potential $\vec{A}$ is parallel to $\vec{\epsilon}$.) Three major features are affected by the change. A peak centered at $E_i = -0.5$ eV is "turned on" for $\vec{A}$ perpendicular to the mirror plane, and peaks at $E_i = -3.0$ eV and -6.0 eV are "turned off" for the same orientation. Examination of the band structure along Σ shows that the high energy peak contains transitions from band 4 of symmetry Σ_2 , while the other two peaks can contain only transitions from bands 2 and 3, which are of symmetry Σ_1 . Most final bands along Σ at $10 < E_f < 18$ eV are of symmetry Σ_1 , particularly away from Γ or X. Since Σ_1 is even under reflection in the mirror plane and Σ_2 is odd, the arguments of section IV-A apply. If the final bands are indeed of symmetry Σ_1 , then the peak at $E_i = -0.5$ eV should be much weaker for $\vec{A}$ parallel to the mirror plane, and the peaks at $E_i = -3.0$ and -6.0 eV should be minimized for $\vec{A}$ perpendicular to the mirror plane. This, of course, is precisely what Fig. 50

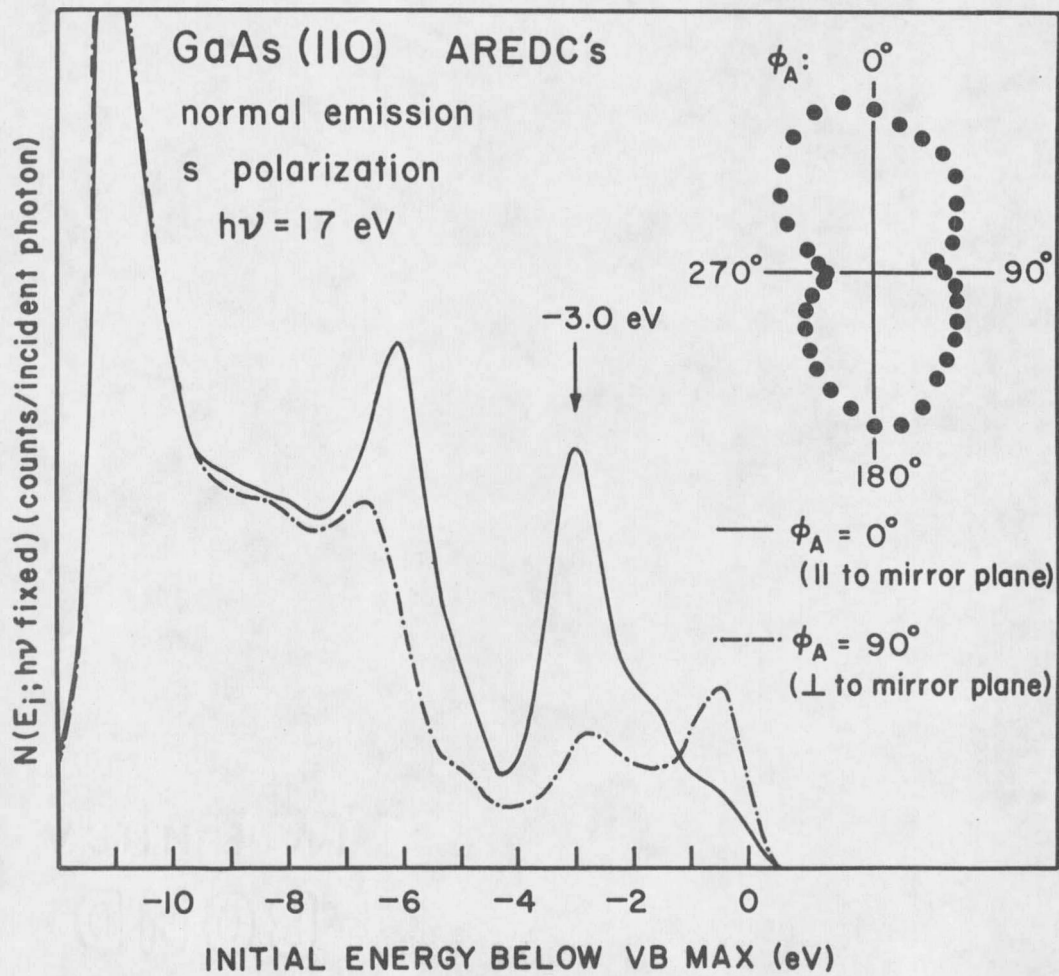


FIG. 50. AREDC's obtained at normal emission exhibiting s polarization dependence of transitions along Σ .

exhibits.

The insert in the upper right hand corner of Fig. 50 is a "polarization" ϕ -pattern. The energy window was fixed at $E_i = -3.0$ eV for $h\nu = 17$ eV (such that the initial energy includes bands 2 and 3) and the crystal was rotated. Since the analyzer is accepting normal emission, the only parameter which changes is the orientation of $\vec{A}$ relative to the crystal. The scale of the resulting polar plot is labeled as ϕ_A . The ϕ_A values of 0° and 180° correspond to $\vec{A}$ being parallel to the mirror plane, while the ϕ_A values of 90° and 270° correspond to $\vec{A}$ perpendicular to the mirror plane. The ϕ -pattern, corresponding to the second peak in the AREDC's, shows minima for $\vec{A}$ perpendicular to the mirror plane and maxima for $\vec{A}$ parallel to the mirror plane, in agreement with the discussion above.

Polarization effects for p polarization have not been as simple in interpretation as for s polarization. The preceding arguments about the parity of $\vec{A}$ under reflection in the mirror plane may still be applied, since $\vec{A}$ now has a vertical component which always remains in the mirror plane and a horizontal component which just corresponds to s polarization. However, this procedure predicts no difference between spectra obtained for $\vec{A}$ aligned with one "dangling bond" and for $\vec{A}$ aligned with the opposite "dangling bond". In practice, there are substantial differences. The

directions, taken from the ideal surface geometry, are used for reference purposes only, and should not be taken to imply that the observed effects are necessarily associated only with the surface.

At least two arguments may be appealed to in an attempt to explain the discrepancy. One, surface effects are certainly nontrivial, even though we have deliberately neglected the surface thus far in this section in an attempt to make a "first approximation" interpretation of the observations. The asymmetry of the surface would certainly lead to different results for $\vec{A}$ aligned with one dangling bond as opposed to the other dangling bond. Photoemission which originates at the first layer of atoms would then be expected to show polarization effects such as are observed. This dependence would in turn exhibit itself to some extent in the observed spectra since photoemission spectroscopy probes at most only several layers of atoms.^{30,31}

The second argument applies to photoemission from bulk states. The two positions of $\vec{A}$ in question are: (1) $\vec{A}$ approximately parallel to the Ga dangling bond, and (2) $\vec{A}$ approximately parallel to the As dangling bond. In the bulk lattice structure, both of these orientations correspond to $\vec{A}$ being parallel to a Ga-As bond. This is why the previous arguments predict no emission differences between the two; $\vec{A}$ is in the same orientation relative

to the bulk crystal symmetries in each case. However, the fact that the photoemitted electrons are detected in only the [110] direction introduces an asymmetry in the system which may lead to emission differences between the two cases. Although $\vec{A}$ is along a Ga-As bond in each case, in one case the Ga is nearer the surface and in the other the As is nearer. Rotating $\vec{A}$ from position (1) to position (2) is then equivalent to moving the observation point from one side of the crystal to the opposite side. The same transitions are excited, but the resulting photoemission spectra are collected in opposite directions. Differences will appear if the final momentum distribution of the excited electrons is weighted more heavily in one direction than in the other. The observed polarization effects would then correspond to variations in momentum distribution rather than variations in the strength of the transitions.

An example of AREDC's collected with $\vec{A}$ in each of the two positions described above is given in Fig. 51. These spectra were obtained at normal emission for $h\nu = 18.5$ eV and p polarization. For the solid curve, $\vec{A}$ was approximately parallel to the Ga dangling bond at $\phi_A = 0^\circ$, and for the dashed curve $\vec{A}$ was aligned with the As dangling bond at $\phi_A = 180^\circ$. There are obviously substantial differences in the two spectra, notably in structure at $E_i = -2.2$ eV and at $E_i = -5.1$ eV. The initial energy of -2.2 eV includes

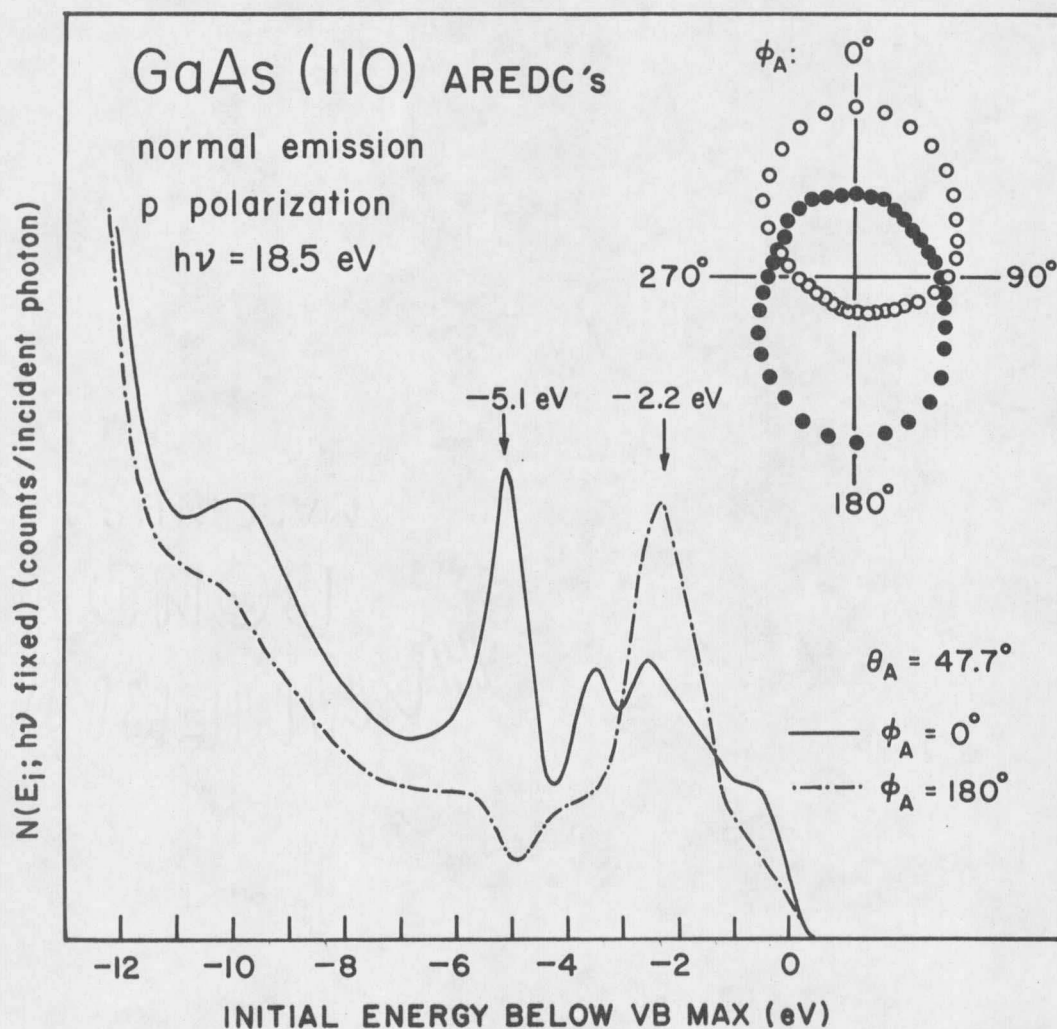


FIG. 51. AREDC's obtained at normal emission exhibiting p polarization dependence of transitions along Σ .

bands 2,3, and 4 while - 5.1 eV includes only band 2. For the curve taken at $\phi_A = 180^\circ$, the first structure is dominant while the second is absent. At $\phi_A = 0^\circ$, the strength of the first peak is considerably reduced, while the second is now very strong. The insert in Fig. 51 shows polarization ϕ -patterns for each of these peaks. The solid dots represent the emission at $E_i = - 2.2$ eV as $\vec{A}$ is rotated around the normal to the surface. The open dots represent the emission at $E_i = - 5.1$ eV for the same process. $\vec{A}$ remains at $\theta_A = 47.7^\circ$ as it rotates. The two structures are seen to have opposite dependences on the orientation of $\vec{A}$. The first structure has a maximum at $\phi_A = 180^\circ$ and the second a maximum at $\phi_A = 0^\circ$.

A detailed explanation of this type of polarization dependence in terms of the surface or of momentum distributions as discussed above is not possible at this time. First, a more detailed knowledge of the local electronic structure at the surface layer is needed before contributions from the surface can be estimated. Second, analyzing the dependence due to variations in the momentum distributions requires more exact forms for the bulk wavefunctions than are presently available.

V. SUMMARY

Angle-resolved photoemission spectroscopy has emerged within the last few years as a very promising new experimental technique for studying the electronic structure of solids.²⁻¹⁴ By measuring the direction as well as the kinetic energy of photoemitted electrons, the experimenter directly obtains momentum information about the optical excitation that has been hitherto inaccessible. Within certain limitations, the electron "band structure" of two-dimensional systems such as surface states may be mapped out directly from experiment. The band structure of three-dimensional bulk systems may also be explored, with somewhat greater limitations.

Concurrently with the development of angle-resolved photoemission spectroscopy, increasing attention has been given to the use of synchrotron radiation sources for such experiments.¹⁵ The continuum of synchrotron radiation provides a very intense, stable source of polarized radiation over a range of wavelengths including many energies not available from any other source. In application to photoemission spectroscopy, synchrotron radiation permits the acquisition of spectra for which photon energy is scanned while collecting electrons at either constant "initial" or "final" energy. In this way, enhancements or resonances which occur at a constant photon energy are easily studied. The high photon energies which

are available in synchrotron radiation permit excitation to final states which had been previously inaccessible. In application to angle-resolved photoemission spectroscopy, these higher photon energies also translate to access to a larger region of momentum space.

The goal of this research project has been twofold. The first aspect was to develop equipment and techniques for doing angle-resolved photoemission spectroscopy in an existing experimental chamber maintained at the University of Wisconsin's Synchrotron Radiation Center. The second aspect was to refine and demonstrate the utility of the techniques in a careful study of a typical semiconductor. Gallium arsenide was chosen as the subject of the investigation for several reasons. First, it is currently of great interest in device applications. Second, many theoretical calculations of GaAs bands, both in the bulk¹⁸⁻²⁰ and at the surface,²¹⁻²⁵ have been made with which the experimental results could be compared. Third, clean (110) GaAs surfaces could be easily prepared in situ by cleaving in the vacuum, surfaces which were inert enough to study for several days before noticeable contamination set in.

An angle-resolving electron energy analyzer was achieved by modifying an existing cylindrical mirror electron energy analyzer (CMA). The CMA normally accepts electrons in a flux cone of half-

angle 42.3° and thickness 12° . The modification consisted of an internally mounted, rotatable drum with a small aperture in the side. When in position, the drum blocks all of the flux normally accepted by the analyzer except that passed through the aperture. By rotating the drum, any segment of the flux cone may be selected and passed through the analyzer to be detected. Linear translation of the drum selects either 4° or 12° angular resolution, or removes the drum entirely from the flux cone, restoring the CMA to its original function. These movements of the drum are performed through a rotary/linear motion feedthrough in the base flange of the CMA.

Sample holders and manipulators were devised such that a variety of sample/analyzer configurations could be used, permitting the study of emission at any azimuthal angle and at polar angles from 0° to 84.6° . In certain configurations the electric polarization vector $\vec{\epsilon}$ of the incident radiation could be rotated relative to crystal symmetries while collecting the same emission, either at $\theta = 0^\circ$ or at $\theta = 42.3^\circ$. For $\theta = 0^\circ$ (normal emission) $\vec{\epsilon}$ could also be rotated up out of the surface by 42.3° , providing a substantial component of p polarization.

The important experimental observations of (110) GaAs fell essentially into two groups. The first was the identification of emission due to two occupied surface states which are energetically degenerate with the bulk valence bands. Two separate surface

bands were identified and portions of their band structure mapped out. The first of these states, centered at approximately 1 eV below the valence band maximum, has a dispersion width of more than 1 eV, with the maximum initial energy occurring at the center of the surface Brillouin zone. The second surface state lies 6 eV below the valence band maximum and is localized near the zone corners. The initial energy of this state increases as one moves away from the zone corner in any direction. These two surface state bands are in excellent agreement with bands which are predicted in theoretical calculations of the (110) surface,²¹⁻²⁵ but which have not been previously observed in experiment.

The second group of observations were of bulk transitions. The restriction of momentum space permitted by angle-resolved photoemission enabled the examination of bulk band transitions along lines in k-space rather than over a volume. This in turn permitted comparison to calculated bands along those lines and identification of the bands involved in several of the observed transitions. A simple, direct-transition model proved sufficient to explain much of the observed phenomena. Certain polarization sensitive features in the emission were amenable to the explanation that a reorientation of the radiation vector potential $\vec{A}$ relative to crystal symmetries may "turn off" some interband transitions.

The observations of the surface states show the power of angle-resolved photoemission spectroscopy in studying two-dimensional surface phenomena, demonstrating the separation and study of broad surface emission that is degenerate with bulk valence band emission and thus inaccessible by any other existing experimental technique. The identification of the bulk transitions, on the other hand, demonstrates the utility of the technique in the study of bulk band structure, providing energy levels of specific band symmetry points that may in turn be used for fitting and improving theoretical band calculations. The equipment and techniques demonstrated here on GaAs are expected to be very useful in studies of the electronic structure of a wide variety of crystalline materials, both at the surface and in the bulk.

APPENDIX

APPENDIX

For the interested reader, the following figures summarize much of the data taken at normal emission with the four polarization conditions discussed in section IV D. Figures 52 and 53 exhibit AREDC's and ARCIS's obtained with p polarization, with $\vec{\epsilon}$ at $\phi_A = 180^\circ$ and $\theta_A = 47.7^\circ$. These spectra were obtained from the same cleave as those of Figs. 40 and 42, but with $\vec{\epsilon}$ approximately aligned with the As dangling bond instead of the Ga dangling bond. Figures 54 and 55 show AREDC's and ARCIS's obtained in s polarization, with $\vec{\epsilon}$ parallel to the mirror plane at $\phi_A = 0^\circ$. The final two figures, 56 and 57, exhibit AREDC's and ARCIS's taken in s polarization with $\vec{\epsilon}$ perpendicular to the mirror plane at $\phi_A = 90^\circ$. Both sets of s polarization data were obtained from the same cleave.

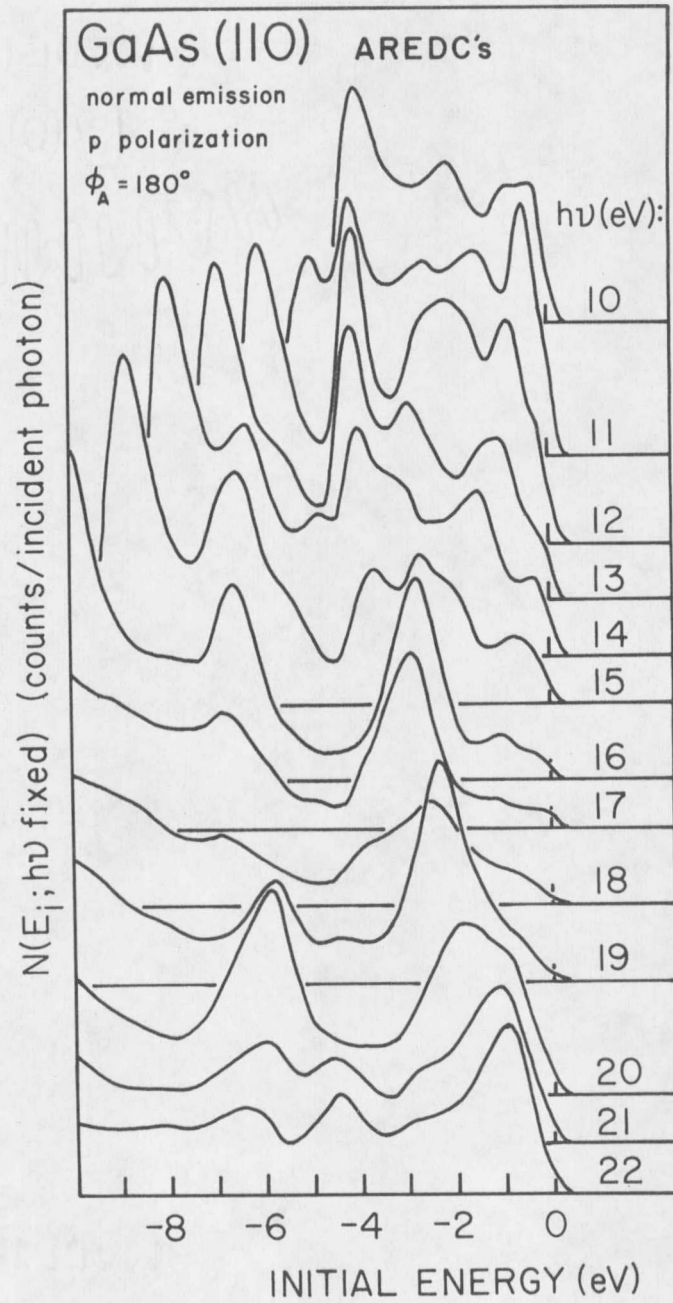


FIG. 52. Normal emission AREDC's obtained with $\vec{\epsilon}$ at $\theta_A = 47.7^\circ$ and $\phi_A = 180^\circ$.

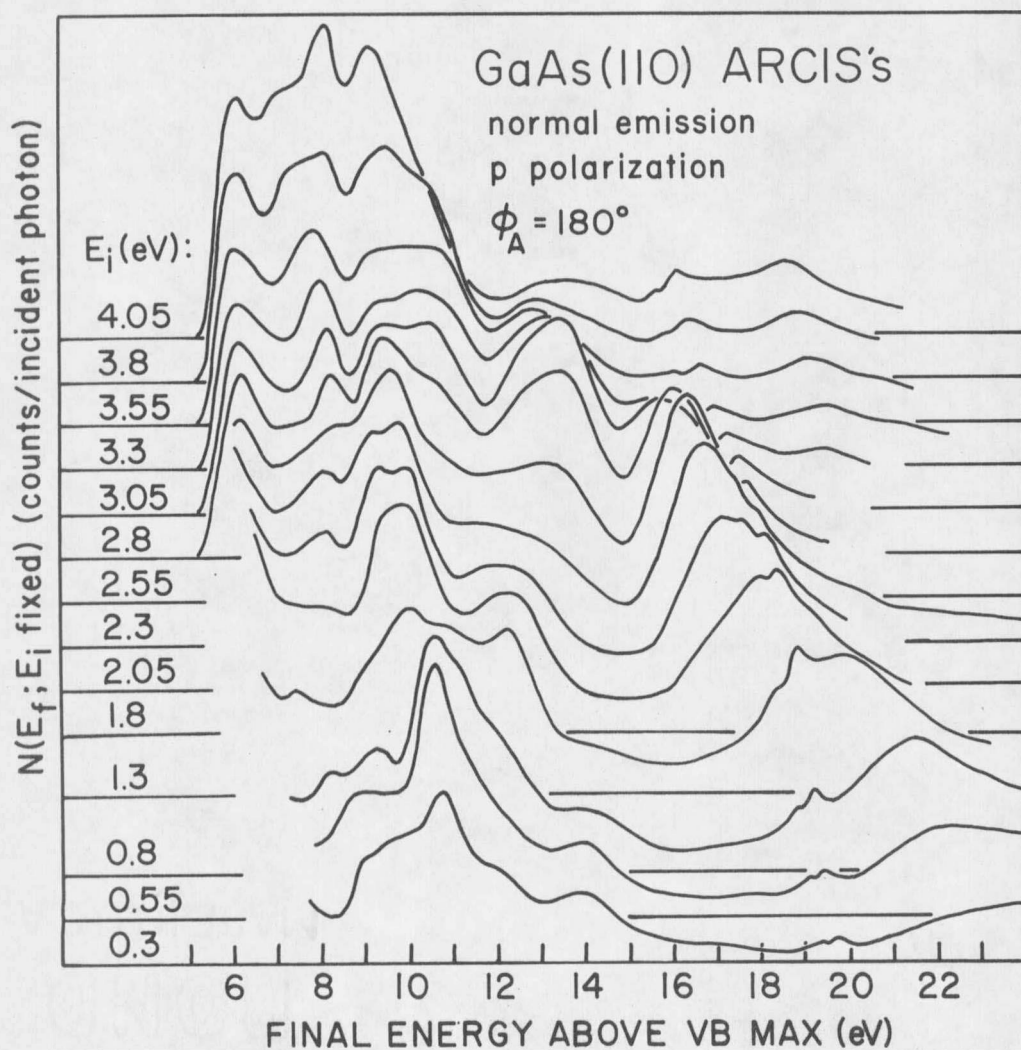


FIG. 53. Normal emission ARCIS's obtained with $\vec{\epsilon}$ at $\theta_A = 47.7^\circ$ and $\phi_A = 180^\circ$.

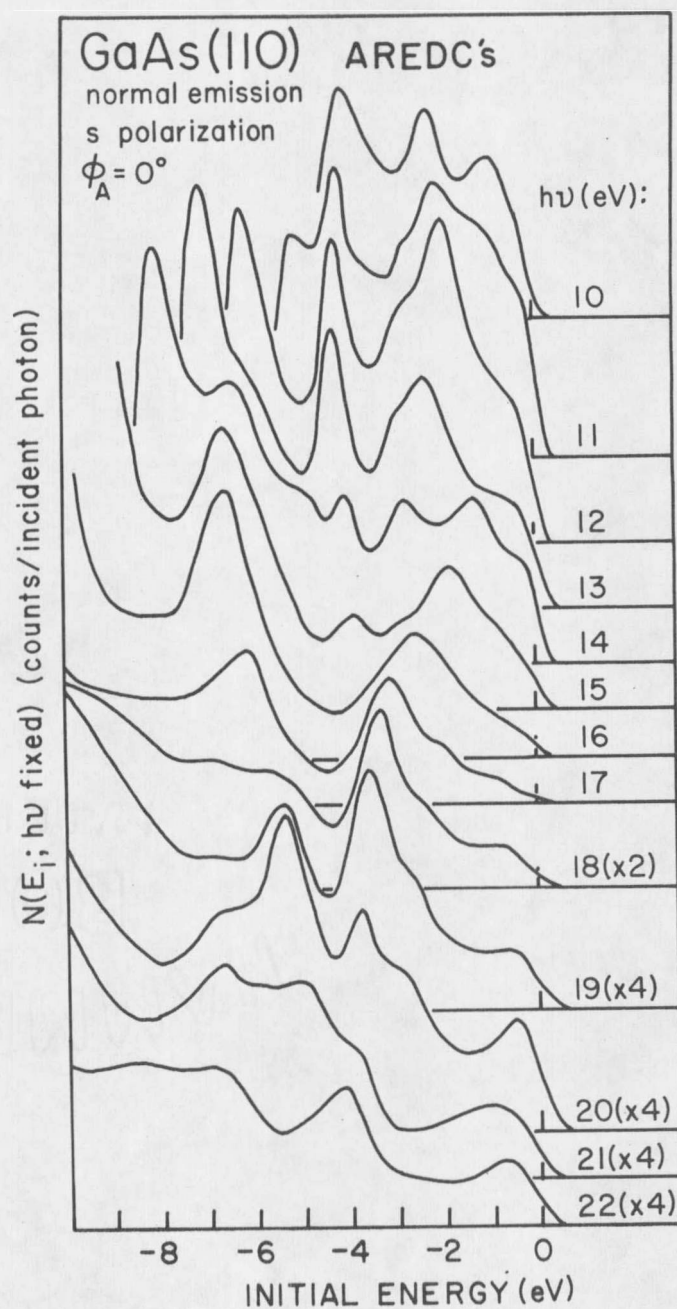


FIG. 54. Normal emission AREDC's obtained with $\vec{\epsilon}$ at $\phi_A = 0^\circ$ in s polarization.

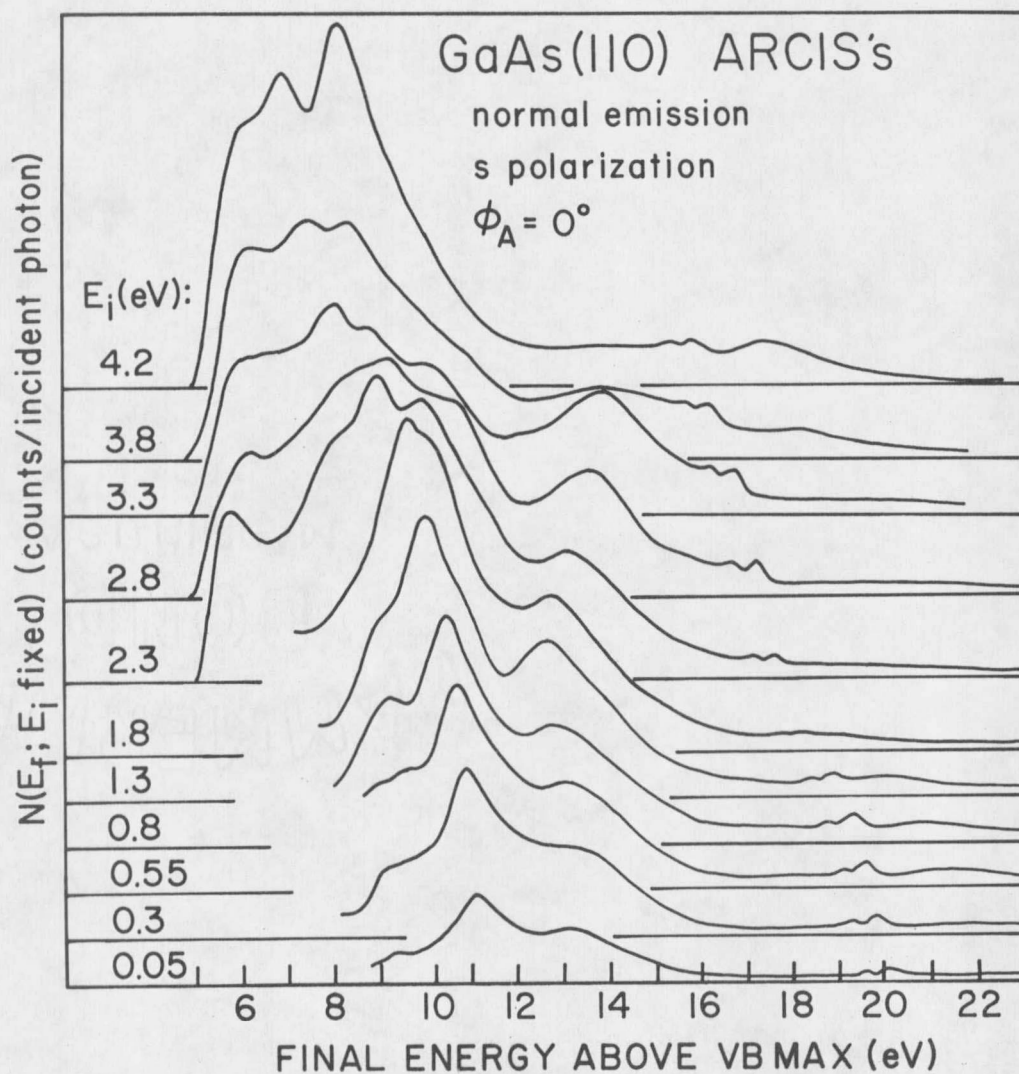


FIG. 55. Normal emission ARCIS's obtained with $\vec{\epsilon}$ at $\phi_A = 0^\circ$
in s polarization.

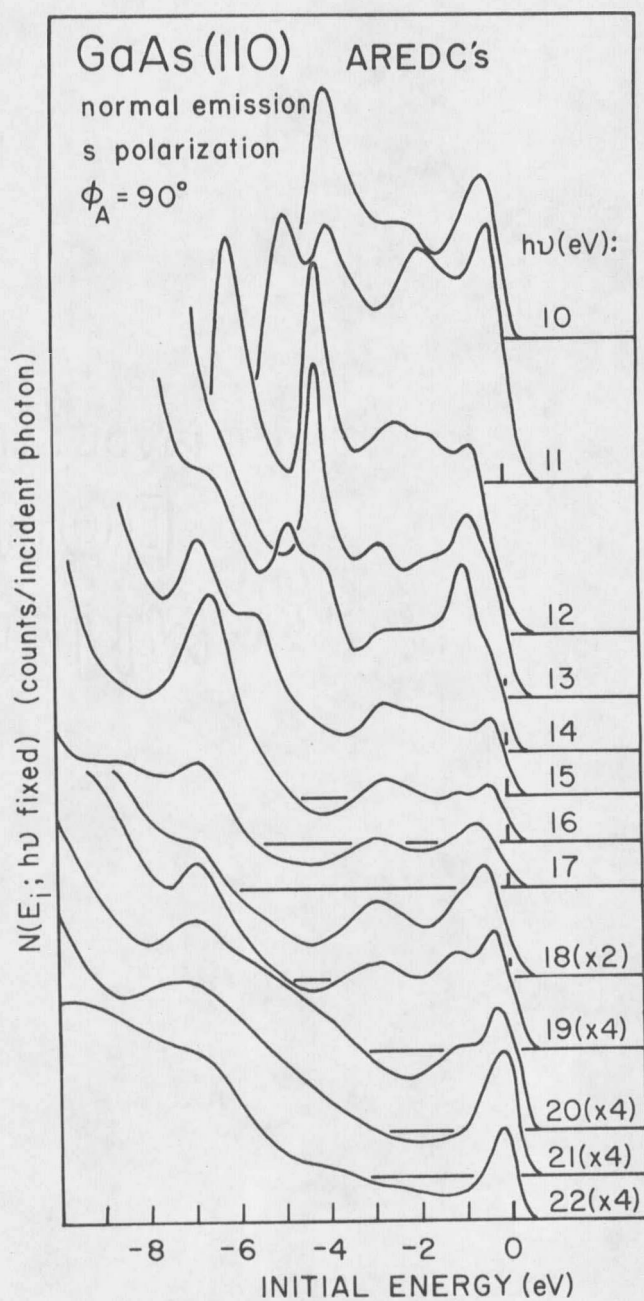


FIG. 56. Normal emission AREDC's obtained with $\vec{\epsilon}$ at $\phi_A = 90^\circ$ in s polarization.

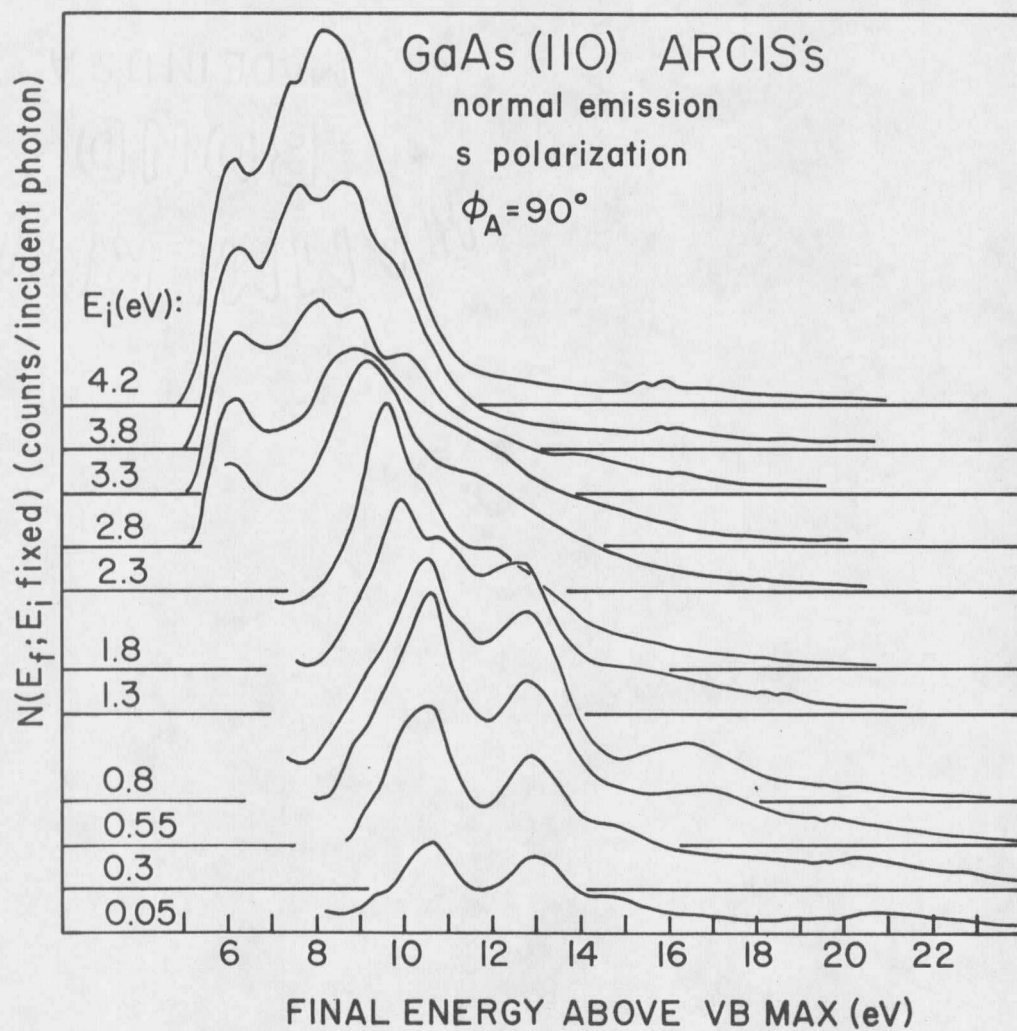


FIG. 57. Normal emission ARCIS's obtained with $\vec{\epsilon}$ at $\phi_A = 90^\circ$ in s polarization.

REFERENCES

REFERENCES

- ¹Frederick Wooten, Optical Properties of Solids (Academic Press, New York, 1972), Chap. 1.
- ²G. W. Gobeli, F. G. Allen, and E. O. Kane, Phys. Rev. Lett. 12, 94 (1964).
- ³G. D. Mahan, Phys. Rev. Lett. 24, 1068 (1970); and Phys. Rev. B2, 4334 (1970).
- ⁴U. Gerhardt and E. Dietz, Phys. Rev. Lett. 26, 1477 (1971).
- ⁵T. Gustafsson, P. O. Nilsson, and L. Wallden, Phys. Lett. 37A, 121 (1971).
- ⁶R. Y. Koyama and L. R. Hughey, Phys. Rev. Lett. 29, 1518 (1972).
- ⁷R. H. Williams, J. M. Thomas, M. Barber, and N. Alford, Chem. Phys. Lett. 17, 142 (1972).
- ⁸B. Feuerbacher and B. Fitton, Phys. Rev. Lett. 30, 923 (1973).
- ⁹N. V. Smith and M. M. Traum, Phys. Rev. Lett. 31, 1247 (1973).
- ¹⁰D. L. Rogers and C. Y. Fong, Phys. Rev. Lett. 34, 660 (1975).
- ¹¹M. M. Traum, N. V. Smith, and F. J. Di Salvo, Phys. Rev. Lett. 32, 1241 (1974).
- ¹²N. V. Smith, M. M. Traum, and F. J. Di Salvo, Solid State Commun. 15, 211 (1974).
- ¹³J. E. Rowe, M. M. Traum, and N. V. Smith, Phys. Rev. Lett. 33, 1333 (1974).
- ¹⁴M. M. Traum, J. E. Rowe, and N. V. Smith, J. Vac. Sci. Technol. 12, 298 (1975).
- ¹⁵M. L. Perlman, E. M. Rowe and R. E. Watson, Phys. Today 27, no. 7, 30 (1974).

- ¹⁶N. V. Smith, M. M. Traum, J. A. Knapp, J. Anderson, and G. J. Lapeyre, Phys. Rev. B13, 4462 (1976).
- ¹⁷R. Y. Koyama and L. R. Hughey (ref. 6) have reported angle-resolved photoemission of evaporated Au using synchrotron radiation.
- ¹⁸J. Chelikowsky, D. J. Chadi, and M. L. Cohen, Phys. Rev. B8, 2786 (1973).
- ¹⁹J. R. Chelikowsky and M. L. Cohen, Phys. Rev. Lett. 32, 674 (1974), and Phys. Rev. B14, 556 (1976).
- ²⁰K. C. Pandey and J. C. Phillips, Phys. Rev. B9, 1552 (1974).
- ²¹W. A. Harrison and S. Ciraci, Phys. Rev. B10, 1516 (1974).
- ²²J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B10, 5075 (1974).
- ²³C. Calandra and G. Santoro, J. Phys. C: Solid State Phys. 8, L86 (1975).
- ²⁴J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B13, 826 (1976).
- ²⁵J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, (to be published).
- ²⁶P. E. Gregory and W. E. Spicer, Phys. Rev. B13, 725 (1976).
- ²⁷E. Merzbacher, Quantum Mechanics (John Wiley and Sons, New York, 1961), Chap. 19, pp. 447-451.
- ²⁸Frederick Wooten, Optical Properties of Solids (Academic Press, New York, 1972), Chap. 5, pp. 110-116.
- ²⁹G. J. Lapeyre, A. D. Baer, J. Hermanson, J. Anderson, J. A. Knapp, and P. L. Gobby, Solid State Commun. 15, 1601 (1974).
- ³⁰C. J. Powell, Surface Sci. 44, 29 (1974).
- ³¹D. E. Eastman, Solid State Comm. 8, 41 (1970).
- ³²E. O. Kane, Phys. Rev. Lett. 12, 97 (1964).

- ³³P. J. Feibelman and D. E. Eastman, Phys. Rev. B10, 4932 (1974).
- ³⁴G. B. Duke, A. R. Lubinsky, B. W. Lee and P. Mark, J. Vac. Sci. Technol. 13, 761 (1976).
- ³⁵R. O. Jones, Phys. Rev. Lett. 20, 992 (1968).
- ³⁶G. Oster and Y. Nishijima, Sci. Amer. 209, No. 5, 54 (1963).
- ³⁷G. J. Lapeyre, P. L. Gobby, A. D. Baer, and C. Badgley, to be published.
- ³⁸R. Dorn, H. Luth, and G. J. Russell, Phys. Rev. B10, 5049 (1974).
- ³⁹O. W. Ranke and K. Jacobi, Solid State Communications 13, 705 (1973).
- ⁴⁰M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).
- ⁴¹R. H. Parmenter, Phys. Rev. 100, 573 (1955).
- ⁴²F.-J. Himpsel and W. Steinmann, Phys. Rev. Lett. 35, 1025 (1975).
- ⁴³H. Becker, E. Dietz, J. Gerhardt, and H. Angermuller, Phys. Rev. B12, 2084 (1975).
- ⁴⁴E. Dietz, H. Becker, and J. Gerhardt, Phys. Rev. Lett. 36, 1397 (1976).
- ⁴⁵G. J. Lapeyre and J. Anderson, Phys. Rev. Letters 35, 117 (1975).
- ⁴⁶R. Ludeke and A. Koma, Phys. Rev. Letters 34, 817 (1975).
- ⁴⁷D. E. Eastman and J. L. Freeouf, Phys. Rev. Letters 33, 1601 (1974).
- ⁴⁸J. H. Dinan, L. K. Galbraith, and T. E. Fischer, Surf. Sci. 26, 587 (1971).

⁴⁹D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 34, 1624 (1975).

⁵⁰J. R. Chelikowsky, Private communication.

⁵¹D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972).

⁵²Band bending changes were the same as seen by other workers in O₂ exposure; see W. E. Spicer and P. E. Gregory, CRC Crit. Rev. in Solid State Sciences, 5, 231 (1975).

⁵³J. Hermanson, private communication.

⁵⁴A. Huijser and J. van Laar, Surf. Sci. 52, 202 (1975).

⁵⁵W. Gudat and D. E. Eastman, J. Vac. Sci. Technol. 13, 831 (1976).

⁵⁶W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta, and P. W. Chye, J. Vac. Sci. Technol. 13, 780 (1976).

⁵⁷W. D. Grobman and D. E. Eastman, Phys. Rev. Lett. 29, 1508 (1972).

⁵⁸D. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. B 12, 2527 (1975).

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