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

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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 ofGallium Arsenide was studied using synchrotron radiation. The 4° resolution, in conjunction with the wide photon energy continuum of synchrotron radiation (hv < 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 ~-I 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 ς 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.

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USING SYNCHROTRON RADIATION

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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 $\hbar \vec{k}_{\parallel}$ 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 $\vec{\varepsilon}$ 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 elec-
trons. 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 photo-electrons as a function of kinetic energy provides much useful information about the strength and energies of the optical trans-itions. 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, Gobeli, Allen, and Kane[2] demonstrated that a sub-stantial 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 aniso-tropic angular distribution.[3] Tentative experimental work proceeded at several laboratories, concentrating on the variation of emission

with polar angle[4-7] or on emission from several crystal faces.[8]
The first study of both polar and azimuthal dependence of photo-
emission 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 TaS_2[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 stand-
points. 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 bulk[18-20] 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
$\sim$ 1 eV and $\sim$ 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

$$\{(\frac{1}{2m}) \vec{p}^{\,2} + V(\vec{r})\}\psi = E\psi \tag{1}$$

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

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

where $U_k(\vec{r})$ 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

$$E = \hbar^2 k^2 / 2m \quad . \tag{3}$$

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

the potential arbitrarily weak, we can write

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

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 GaAs[20] 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 resolution[19] and will be neglected in the interpretation of the results.
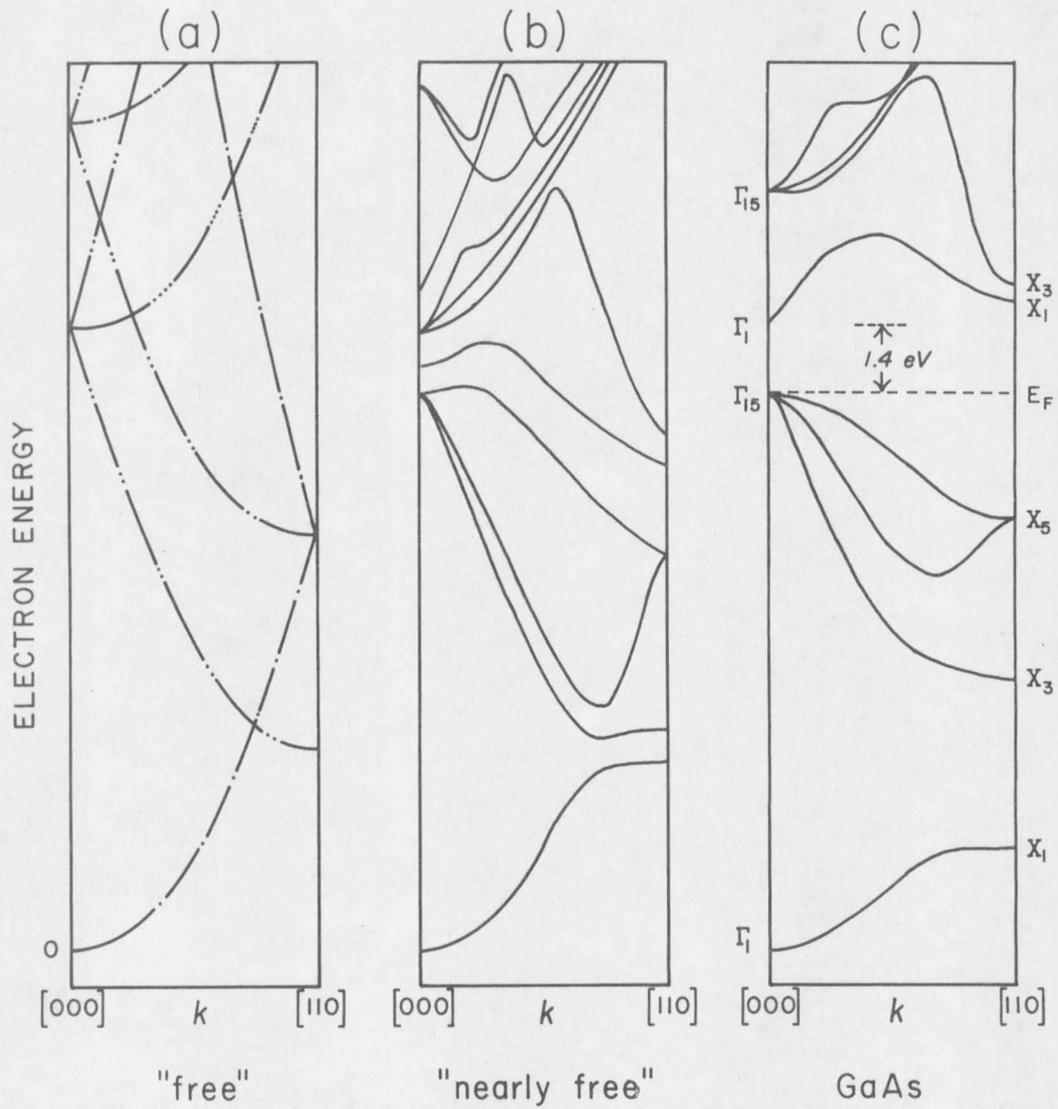
FIG. 1. Energy band structure along the (110) direction in k-space for three different crystal potentials.

2. <u>Repeated Zone Scheme.</u> 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

$$\vec{k}' = \vec{k} - \vec{G} \tag{5}$$

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

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

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

$$= \Psi(\vec{k},\vec{r}) \tag{6}$$

where

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

is periodic in the lattice as required. It follows that energy E_{k}
outside the first zone is equal to an $E_{k'}$ 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:

$$E_k = E_{k+G} \qquad . \qquad \qquad (8)$$

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 wave-
vector $\vec{k}$ 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 suffi-
cient 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

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

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

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

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

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

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

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

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 $|i>$ and $<f|$ 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

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

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"