



Angle resolved photoemission of single crystal SnO₂ using synchrotron radiation
by Peter Leland Gobby

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF philosophy
in Physics

Montana State University

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Abstract:

Polarization dependent angle-resolved ultraviolet photoemission (PARUPS) measurements have been performed on single crystal SnO₂(001) using synchrotron radiation. Using photon energies up to 40 eV angle-integrated data revealed a total valence band width of approximately 9 eV, with a large density of states centered about 1.5 eV below the valence band maximum due to oxygen 2p states. A core level and its associated excitons were also investigated and have been interpreted as due to tin 4d levels.

Angle-resolved measurements allowed certain lower valence band structures to be emphasized which also showed strong polarization dependences. These structures have also been interpreted as due to tin 4d states. A covalent model was proposed which allowed this tin 4d character in both the observed core and the lower valence bands, though the two were separated by about 15 eV. Another initial state feature just above the valence band maximum was studied and has been interpreted as due to a large concentration of oxygen vacancies near the surface. It was felt that these vacancies were induced by annealing the crystal in vacuum.

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ANGLE RESOLVED PHOTOEMISSION OF SINGLE CRYSTAL SnO_2
USING SYNCHROTRON RADIATION

by

PETER LELAND GOBBY

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

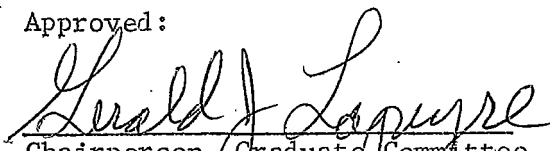
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ABSTRACT

Polarization dependent angle-resolved ultraviolet photoemission (PARUPS) measurements have been performed on single crystal $\text{SnO}_2(001)$ using synchrotron radiation. Using photon energies up to 40 eV² angle-integrated data revealed a total valence band width of approximately 9 eV, with a large density of states centered about 1.5 eV below the valence band maximum due to oxygen 2p states. A core level and its associated excitons were also investigated and have been interpreted as due to tin 4d levels.

Angle-resolved measurements allowed certain lower valence band structures to be emphasized which also showed strong polarization dependences. These structures have also been interpreted as due to tin 4d states. A covalent model was proposed which allowed this tin 4d character in both the observed core and the lower valence bands, though the two were separated by about 15 eV. Another initial state feature just above the valence band maximum was studied and has been interpreted as due to a large concentration of oxygen vacancies near the surface. It was felt that these vacancies were induced by annealing the crystal in vacuum.

I. INTRODUCTION

Since the pioneering work of Berglund and Spicer¹ less than 15 years ago, ultraviolet photoemission spectroscopy (UPS) has grown to be one of the leading tools of the solid-state physicist. Its appeal is two-fold. First the photon energy range of 1 - 50 eV used is in the range necessary to excite valence electrons and shallow core electrons into normally unoccupied states. It is these valence and shallow core electrons which contribute to molecular and crystal binding and are consequently of primary interest to the solid-state physicist. The second appeal lies in the fact that UPS is a double spectroscopy. That is, electron emission is determined as a function of the final energy of the electron as well as the photon energy. In contrast, a reflectance experiment, for example, is a single spectroscopy, since the reflectance is determined as a function of only the photon energy.

More recently, the availability of synchrotron radiation² with its intense continuum has made it practical to restrict the emission angle of the detected electron over a wide range of final energies. In effect, this allows one to measure the momentum as well as kinetic energy of the emitted electron. The polarized nature of the synchrotron radiation has also been utilized to help bring about polarization dependent angle-resolved photoemission. These studies have allowed

the determination of high densities of states in the electronic energy band structure of gallium arsenide³ and tungsten⁴ and, in the case of some two dimensional crystals⁵ and surface states^{6,7}, direct measurement of the total electronic energy bands.

Tin oxide provides an interesting challenge for this powerful tool. It is known to be a wide band gap ($E_g \sim 3.5$ eV) semiconductor crystallizing in the rutile structure. Naturally occurring crystals are known as cassiterite. It is chemically inert, with a high melting point, perhaps as high as 2000°C.⁸ Its most notable current use is as a transparent conducting film on airplane windows for purposes of defrosting.

Relatively little is known about the electronic structure of SnO_2 compared to, say, silicon, gallium arsenide, tungsten or even the alkali halides. Most experimental work has centered on electrical conductivity measurements^{9,10,11} and optical studies¹²⁻¹⁸ at or near the band gap. Conductivity experiments have particularly been hampered by a lack of good quality single crystals. Prior to this work, no photoemission work had been reported. Theoretical studies are few; this is due in part to the complicated rutile structure. There have been two band calculations reported in the literature, with values for the valence band widths of approximately 5 eV¹⁹ and more than 10 eV²⁰, respectively.

Furthering the understanding of SnO_2 - particularly its

electronic structure - can benefit two scientific groups: theoretical physicists and semiconductor device physicists. The benefits to the latter group are straightforward and uncomplicated. The search for rugged high temperature semiconductor devices remains in progress. Tin oxide, with its chemical inertness and wide band gap, definitely has potential in this regard. In a related vein, some work has been done on indium-tin oxide and antimony doped tin oxide films regarding selective surfaces for solar collectors.²¹ Pertinent data on the electronic structure of tin oxide will be necessary to maximize the probability of success in these two areas.

Tin oxide should be interesting to theoretical physicists because of its lack of simplicity. The more standard semiconductors - silicon, germanium and gallium arsenide - have two simplifying things in common: cubic symmetry and predominantly covalent bonding using atomic s and p orbitals. The electronic structures of these materials consequently have a number of similarities. The calculated energy band structures have been checked against much experimental data and have fared well.^{3,4} The band structure theorists have thus been able to check and adjust their calculation techniques for these materials and now can extend these techniques to similar materials with a high degree of confidence. But extension to tin oxide is not so straightforward. Evidence of this lies in the difference of the calculated band widths previously mentioned. The unit cell of tin oxide is

tetragonal instead of cubic, and the bonding is probably not well described as either covalent or ionic, but a strong mixture of the two. There is even evidence in this study of significant d as well as s and p atomic orbitals involved in the covalent aspect of the binding. Experimental data on more complicated systems such as tin oxide will allow the theoretical techniques to be advanced still further.

Pertinent data on the electronic structure of tin oxide have been acquired in this thesis project. Using photon energies up to 40 eV, the valence bands (VBs), lower conduction bands (CBs) and an atomic-like core level were studied. A structure lying just above the valence band maximum (VBM) was observed and has been interpreted as due to defects induced by sample preparation. Exclusion of this defect structure from the bulk VBs resulted in a total experimental VB width of ~9 eV. Angle-resolved measurements allowed some VB structures to be further emphasized, so that interpretation of their respective atomic origins was somewhat simplified. These data seem to indicate that bonding in SnO_2 has strong covalent as well as ionic character.

II. SnO_2 BACKGROUND DATA

A. Structure of Tin Oxide

Tin oxide crystallizes in the rutile structure with space group $D_{4h}^{14, 22}$. The unit cell shown in Fig. 1 is simple tetragonal and contains two tin atoms and four oxygen atoms. $a = b = 4.74 \text{ \AA}$, while $c = 3.19 \text{ \AA}$, and the nearest neighbor oxygen-oxygen distance is $2.54 \text{ \AA}$.²³ With these x-ray diffraction data, it is then straightforward to calculate the remaining pertinent parameters.

Each tin atom is surrounded by an irregular octahedron of oxygens. The Sn-O distance is $2.08 \text{ \AA}$ for those lying in an (001) plane and $2.04 \text{ \AA}$ for the remaining four. The O-Sn-O "dumbbell" in the (001) plane is perpendicular to the plane containing the tin atom and the other four oxygen atoms. The acute angle between two adjacent oxygens with the tin atom at the vertex is 77° .

Another perspective of the tin oxide structure can be attained with the help of Fig. 2, a view of the (001) face of the crystal looking down the $\vec{c}$ axis. The sizes of the tin and oxygen spheres correspond to their ionic radii - Sn^{4+} and O^{2-} , respectively.²⁴

For completeness the Brillouin zone (BZ) for stannic oxide is shown in Fig. 3. The irreducible 1/16 zone is labeled with symmetry points and lines following the notation of Koster.²⁵

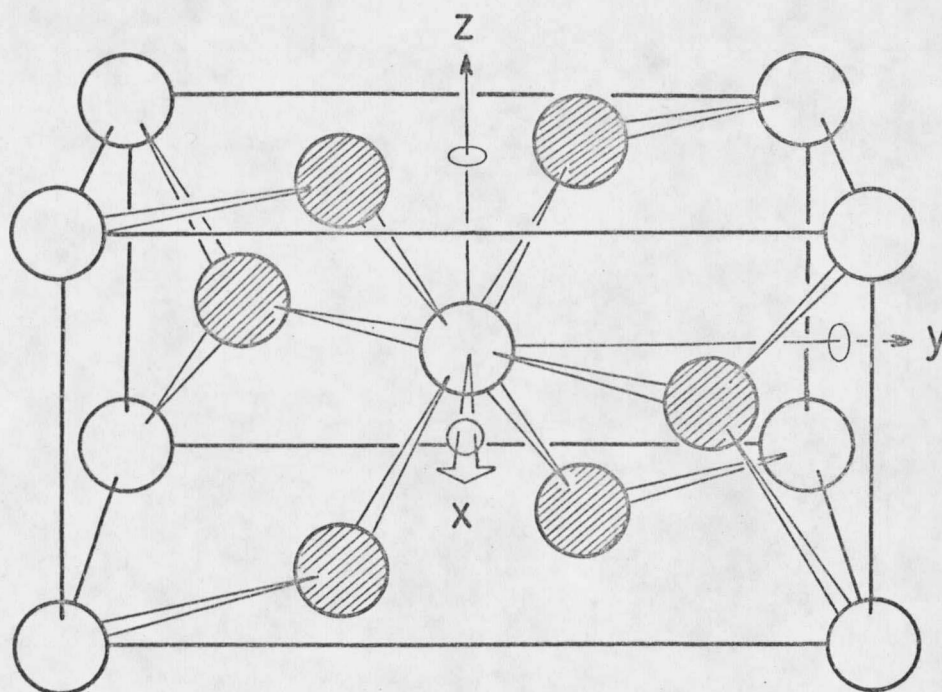


FIG. 1. SnO_2 unit cell. Shaded spheres represent the oxygen atoms.

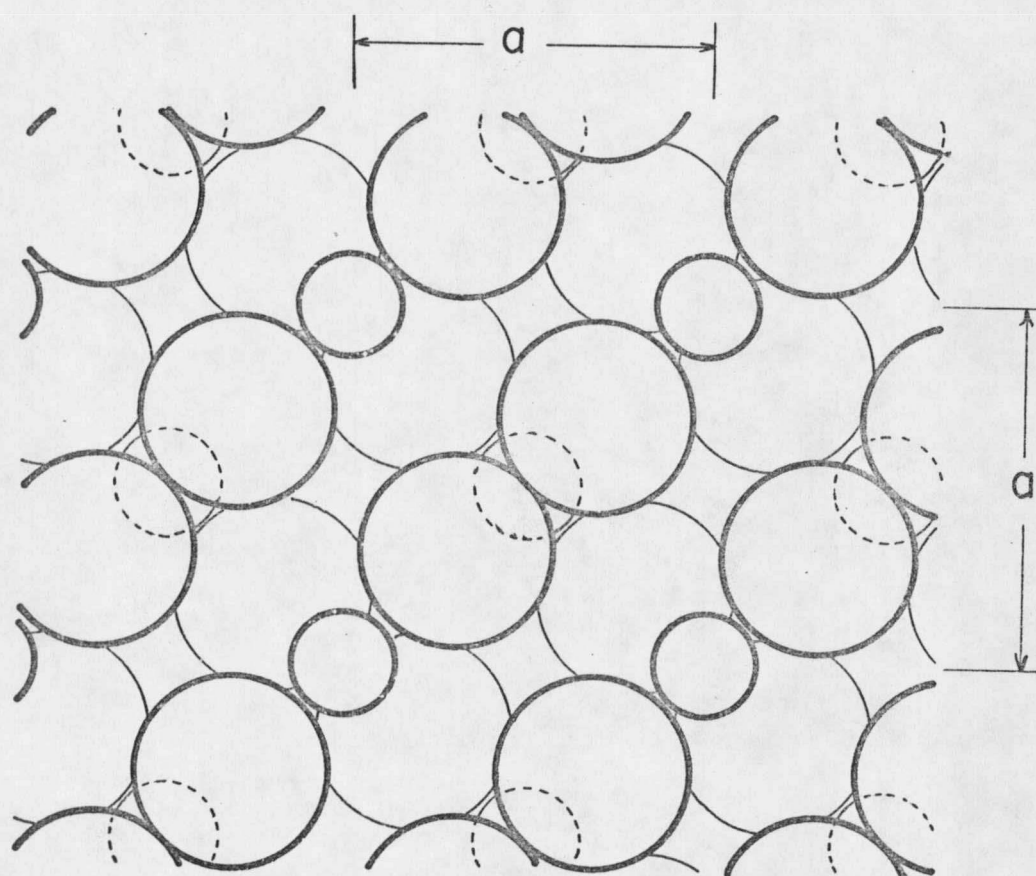


FIG. 2. Top view of SnO_2 (001) face.

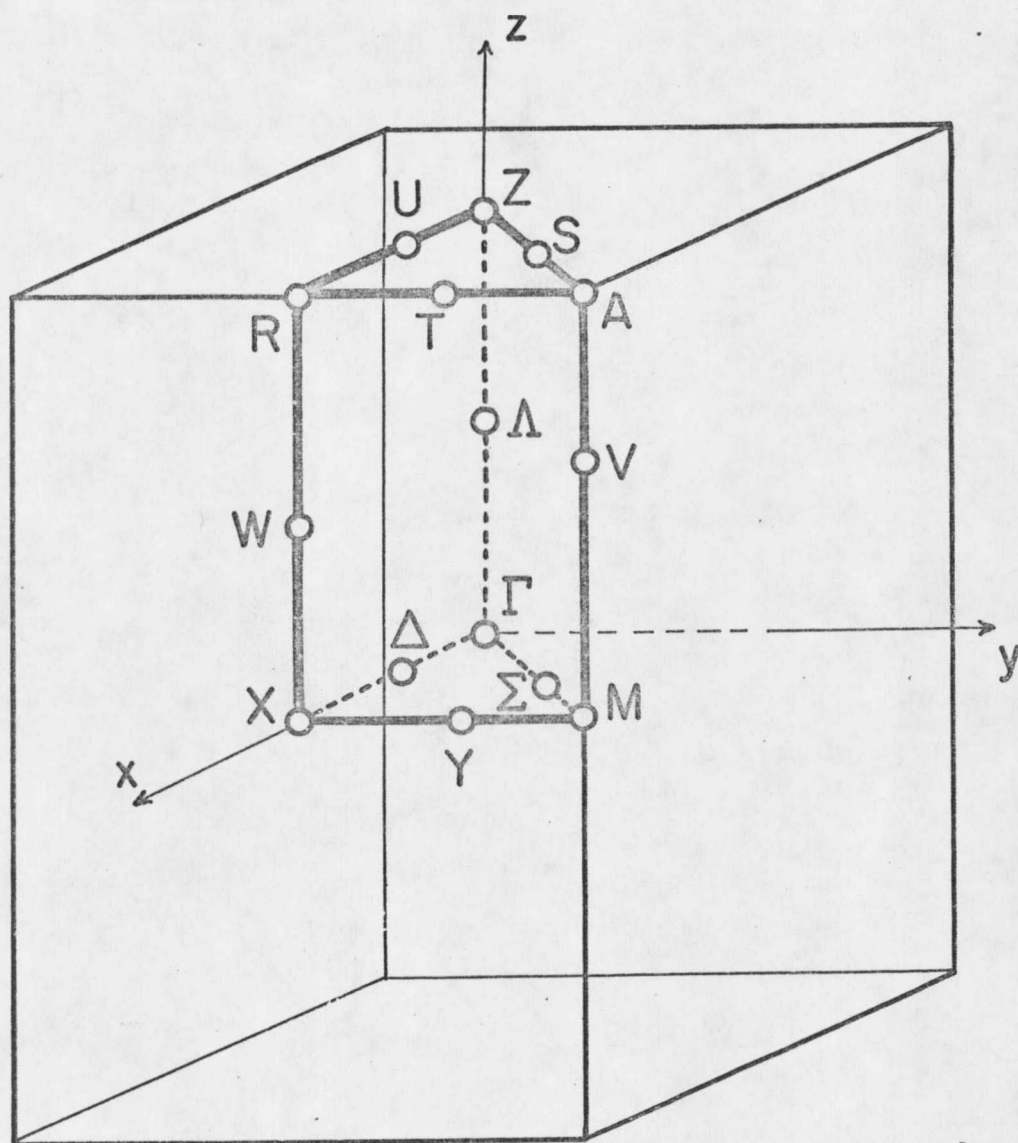


FIG. 3. SnO_2 Brillouin zone.

B. Survey of Tin Oxide Literature

Compared to the more traditional semiconductors, e.g., silicon, germanium and gallium arsenide, the available literature concerning tin oxide has been relatively sparse. Experimental work has been hampered by a lack of high quality crystals, and theoretical work by the complicated crystal structure. Of course progress in one area would spur interest in the other.

Two band calculations for tin oxide have been reported: a self-consistent augmented plane wave (APW) calculation by Arlinghaus¹⁹, and a Kohn-Korringa-Rostoker (KKR) calculation by Jacquemin and Bordure (JB)²⁰. The resulting bands are shown in Fig. 4 and Fig. 5. It should be noted that only the points of highest symmetry, that is, Γ , X, R, A, Z and M, were actually calculated in each case, with compatibility relations and other symmetry considerations being used for the actual plotting of the bands. As can be observed in the figures, each calculation was quite different. Arlinghaus predicted a minimum indirect bandgap of 2.6 eV, while JB chose a direct minimum 4.0 eV gap in their semi-empirical calculation. The total VB widths are about 5 eV for Arlinghaus, but more than 10 eV for JB. Moreover JB's calculation resulted in numerous degeneracies at zone boundaries, with only nominal splitting between many pairs of bands. Arlinghaus has much fewer degeneracies and no noticeable band pairings. The calculations



FIG. 4. APW band structure calculation of SnO_2 .

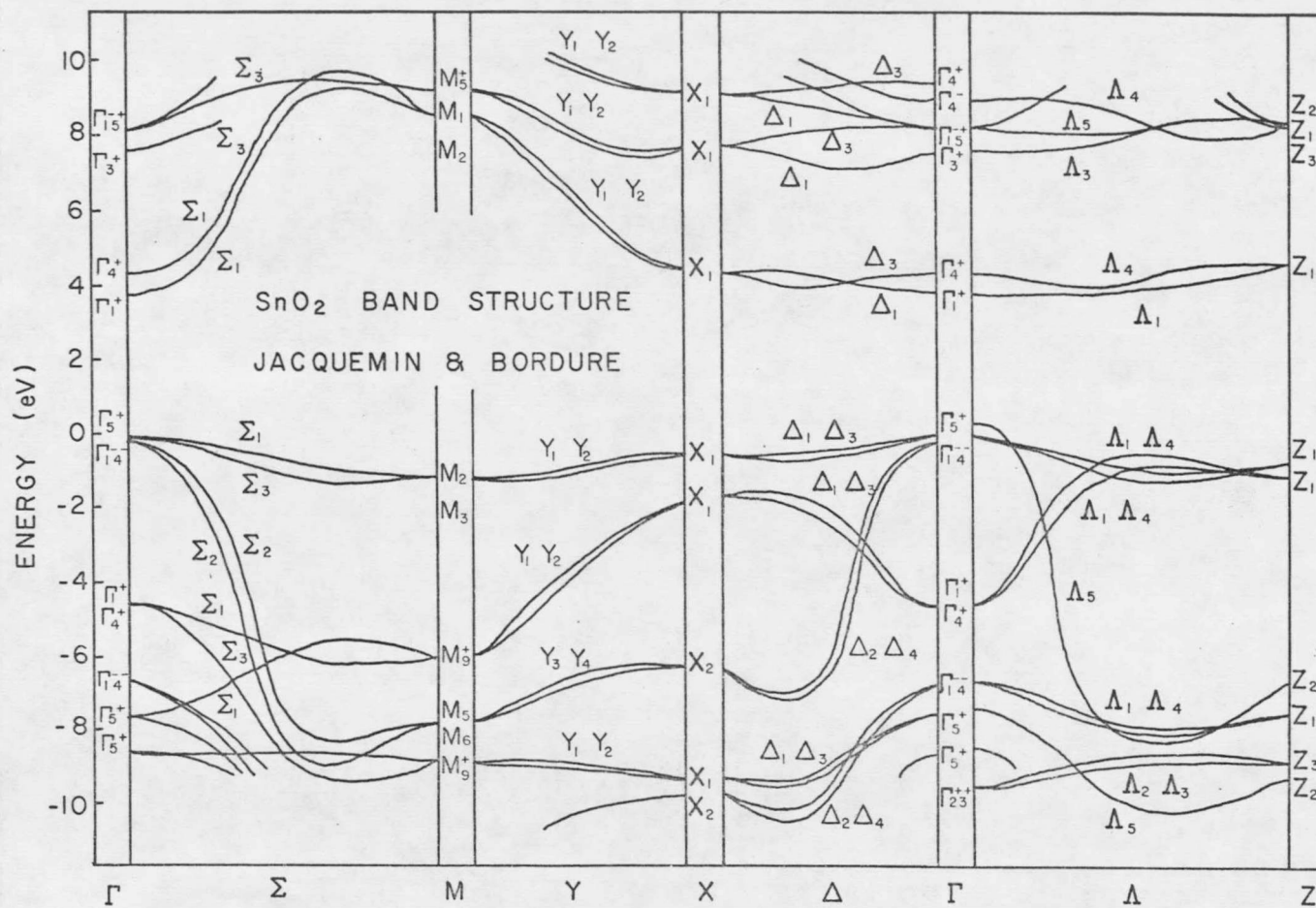


FIG. 5. KKR band structure calculation of SnO_2 .

do agree in that the lower CBs were determined as being derived from empty tin 5s states, while the VBs were primarily derived from filled oxygen 2p states.

Lower lying atomic states, namely oxygen 2s and tin 4d, have also been calculated. As part of his APW calculation, Arlinghaus also predicted tin 4d bands with a width of about 5.5 eV lying about 4 eV below the bottom of the oxygen derived VBs. In another calculation, Jacquemin has predicted tin 4d states at 17.6 eV below the CB minimum, with the oxygen 2s states somewhat below that.²⁶ No width to these levels was reported by Jacquemin.

The energy level diagram of Fig. 6 compares the calculations of Arlinghaus and JB (with the core levels due to Jacquemin added). It is interesting to note that in each calculation the tin 4d levels in SnO_2 lie quite close to the VBs, and the oxygen 2s states lie considerably below this. This is opposite to what one would expect from purely atomic energy levels. This fact may be merely due to the ionic model adopted as the basis for each of the calculations. That is, the ionic character tends to uniformly raise the energy of all the tin electrons, while depressing the energy of all the electrons on the oxygens. This is because each tin atom is surrounded by six negative ions, and each oxygen has three positive ions as its nearest neighbors. The band calculation, whether APW or KKR, then mostly serves to spread out these levels without causing any major shifts in energy.

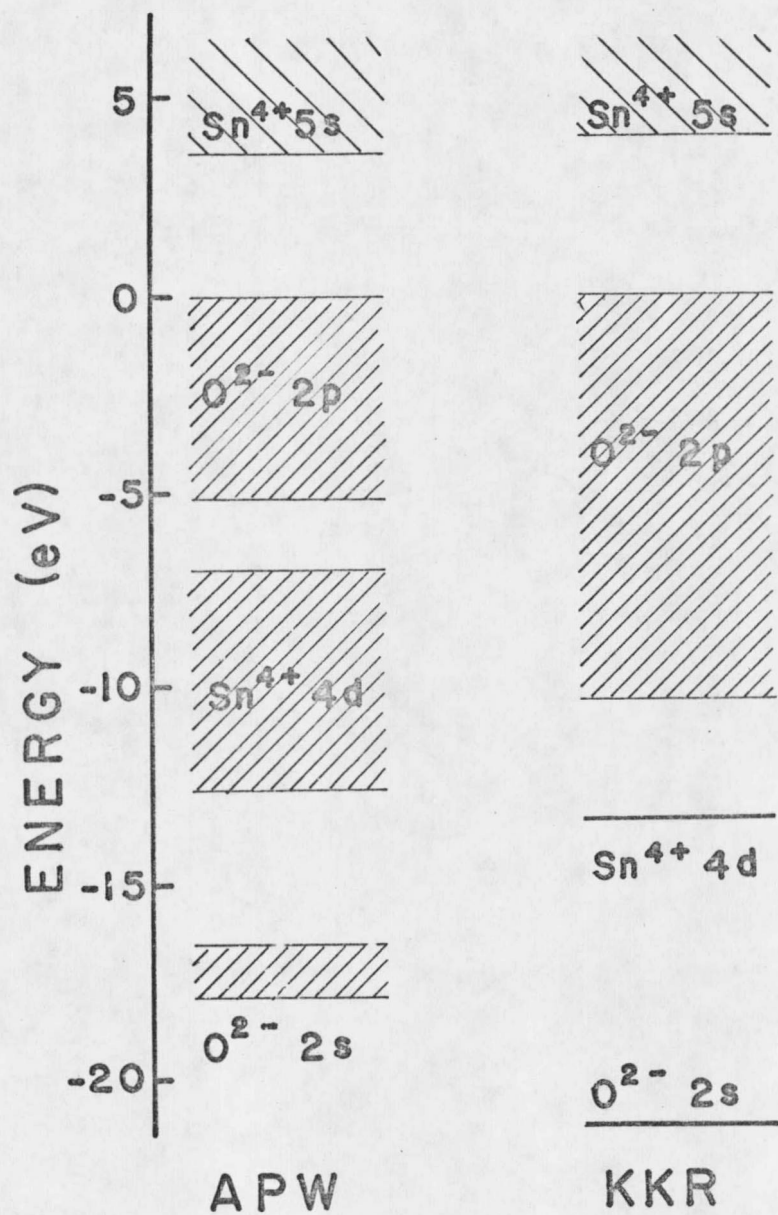


FIG. 6. Comparison of calculated SnO_2 energy levels.

A point about each band calculation should be mentioned at this time. The published bands of Arlinghaus did not indicate the W_1 band symmetries for the bands along W shown in Fig. 4. These were determined by application of the compatibility relations.²³ Secondly, the calculation of JB shows bands of identical symmetry crossing along the Λ line. This is, of course, not allowed. It can be easily remedied by flattening the upper Λ_1, Λ_4 bands somewhat to remove the crossing. This should cause no problem, since only the energies at the zone boundaries were calculated.

The predominance of experimental work with tin oxide has centered around its electrical properties and optical properties near the band gap. A number of workers^{9,10,11} have studied bulk electrical properties. From these studies tin oxide can be described as an n-type semiconductor with oxygen vacancies providing two donor levels in undoped crystals corresponding to two electrons trapped in each defect. Antimony works well as an n-type dopant, while no p-type dopant has been found.

Optical data have resulted in a wide range of minimum band gap values, 2.25 to 3.7 eV.¹²⁻¹⁸ Much of these earlier data were taken on natural crystals or polycrystalline films, which were defect laden, so interpretation of the spectra was difficult. For single crystals alone however, the best value for the minimum direct gap is about 3.6 eV.^{12,13} Still, it is not clear whether an indirect gap less than 3.6 eV exists.

Recently reflectivity measurements on an un-oriented single crystal of SnO_2 have been reported by Jacquemin, Raisin and Robin-Kandare (JRR) for photon energies well above the band gap, 4 - 28 eV.²⁷ Comparison was made between features of the reflectance spectrum and the band calculation of JB. Reasonable agreement was found for the lower photon energy range, that is, $h\nu \lesssim 10$ eV. Also available is the reflectance spectrum for the crystal used in this study taken by Olsen.²⁸ The two spectra are shown in Fig. 7. The scale shown applies directly to the spectrum of Olsen. However the JRR spectrum ordinate was labeled "reflecting power" and exceeded a value of "1" for a portion of the spectrum. Ten percent reflectivity on the scale shown corresponds to a value of "1" for the reflecting power of JRR. The spectra agree within a few tenths of an eV on the onset of interband transitions at $E_g = 3.6$ eV. Furthermore each spectrum shows the general decrease in reflectivity in the 20 eV range after the broad structure around 15 - 16 eV. Other structure differences were probably due to differences in orientation. Rieck²⁹ has also performed reflectivity measurements on single crystal SnO_2 in which the electric vector of the light was perpendicular to the $\vec{c}$ axis ($\vec{E} \perp \vec{c}$) which qualitatively agree with the work of Olsen. The structures were similarly shaped and at the same photon energies, but the amplitude of the reflectivity was about a factor of two larger for the work of Rieck.

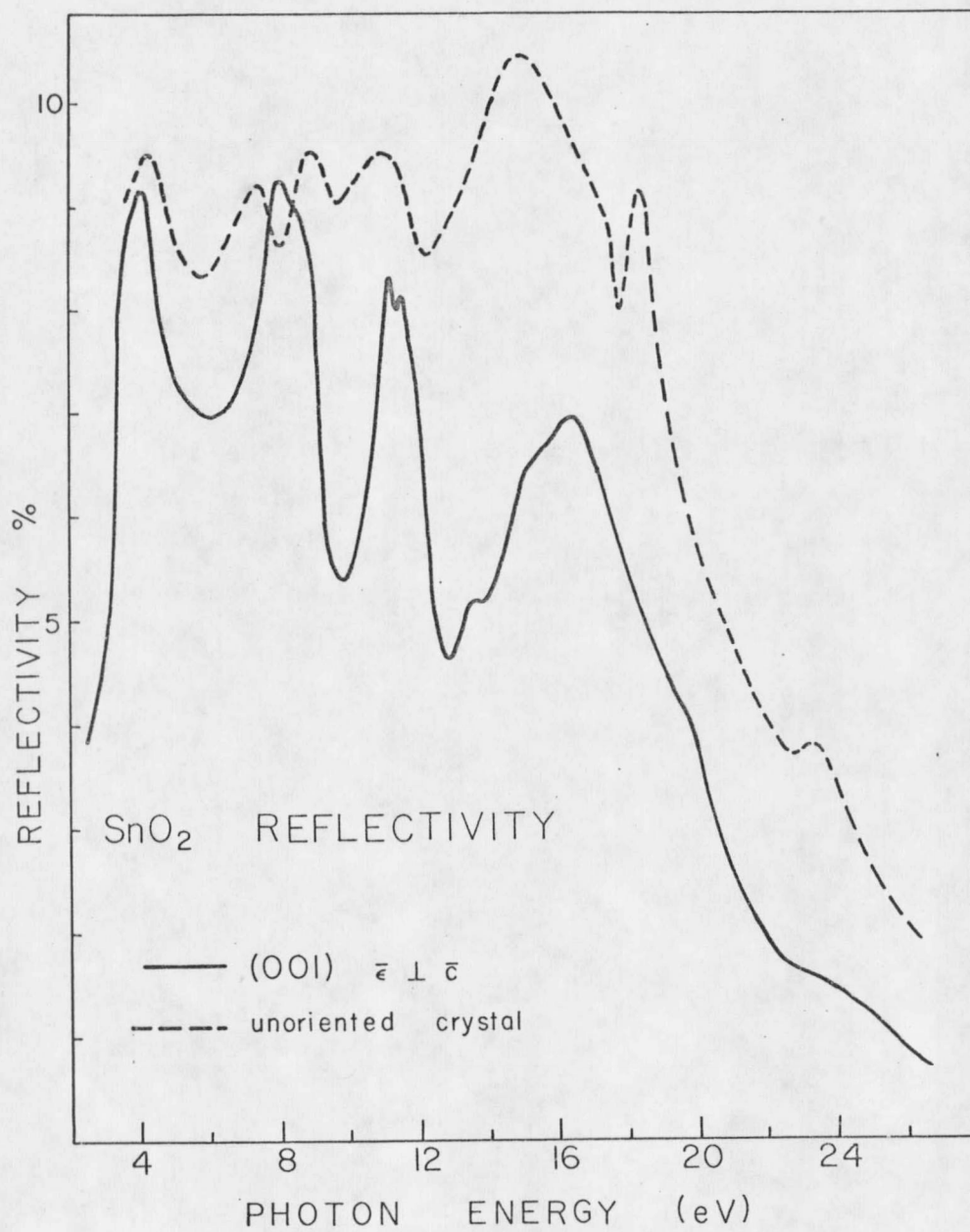


FIG. 7. SnO_2 reflectivity spectra.

Although no previous UPS experiments have been performed on single crystal SnO_2 , Powell and Spicer (PS) have reported some UPS data on oxidized tin films.³⁰ Even with heavy oxidation, emission at the Fermi level (E_F) was still observed, indicating incomplete oxidation. Two structures at -3.0 eV and -5.0 eV, where $E_F = 0$, were identified as due to SnO_2 . The total width of the structures identified as due to tin oxide was about 5.3 eV which was compared to the band calculation of Arlinghaus. The leading edge of the interpreted tin oxide emission corresponded to a valence band maximum at -1.7 eV which is consistent with a 3.4 eV bandgap for stoichiometric SnO_2 . These findings will be considered again in the later sections, when they will be compared to the current data.

C. Tin Oxide - Ionic or Covalent?

The nature of the bonding in SnO_2 is not obvious and, as such, demands some discussion. Though usually termed ionic, SnO_2 bonding must possess covalent character as well. This is evident when one attempts to interpret the tin oxide UPS data. Some features of the data seem to suggest ionic character, while others demand at least some covalent character. In fact Arlinghaus¹⁹ claims that bonding in tin oxide must be predominantly covalent, even though he uses Sn^{+4} and O^{-2} spheres as the basis for his energy band calculation.

No heteronuclear bond can be without ionic character. There must be some charge transfer between bound dissimilar atoms. Only homonuclear bonds such as the tetrahedral carbon-carbon bonds in diamond can be said to be without ionic character. Crystals such as gallium arsenide and silicon carbide, though termed covalent, must involve some charge separation.

On the other hand, compounds consisting of spherical positive and negative charge distributions, that is, purely ionic compounds, do not exist either. Even the alkali-fluorides, with the greatest electronegativity differences of any bonds, must possess at least some covalent character. The reasons are simple enough. Each ion is surrounded by a number, usually four or six, of oppositely charged ions. The electrostatic field thus imposed on the negative ion, for instance, is non-spherical, and its charge distribution will be distorted in the directions of those nearest neighbor positive ions. This distortion of the charge distributions results in overlap of the electron clouds and subsequent covalent bonding.

So where does tin oxide fit in the ionic-covalent spectrum? With an electronegativity difference of 1.75 (3.45 for oxygen and 1.7 for tin), it would seem that it should be strongly ionic. Ionicity definitions vary, but on Pauling's²⁴ scale tin oxide would be only 50% ionic, compared to 65% for sodium chloride and only 9%

for gallium arsenide. A more recent and elaborate ionicity scale has been developed by Phillips^{31,32} and extended to complex materials by Levine³³. On this scale, ionicities of 32%, 78% and 96% are calculated for GaAs³¹, SnO₂³³ and NaCl³¹, respectively. But even with this larger ionicity, tin oxide bonding would have a substantial 22% covalent character. It may well be that for the purpose of band calculations, tin oxide is not adequately described by either an ionic or covalent model exclusively.

The existing band calculations for tin oxide utilize an ionic model.^{19,20} As such the four 5s and 5p electrons of tin are assumed transferred to the two oxygens, filling their 2p shells. The valence bands are then primarily derived from these filled oxygen 2p levels, with the tin 4d and oxygen 2s levels only slightly perturbed from their atomic configurations. This leaves the 5s and 5p levels of tin unoccupied, from which the lowest conduction bands are derived.

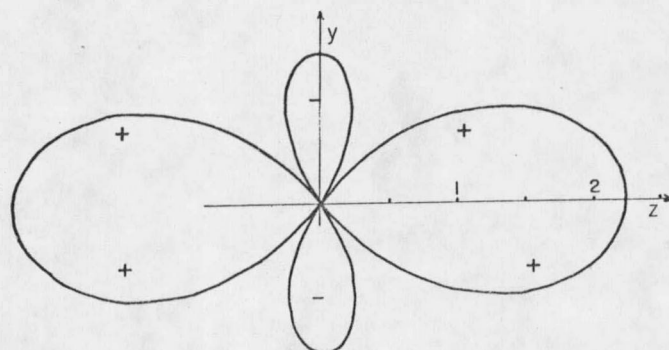
A covalent bonding model for tin oxide would result in more complicated band symmetries. Referring again to Fig. 1, one notes that each tin atom is surrounded by an octahedron of nearly equidistant oxygen atoms, and each oxygen has three co-planar tins as its nearest neighbors. To form covalent bonds, each atom must have one orbital for each nearest neighbor.^{24,34} With atomic orbitals used as basis functions, six orthogonal tin orbitals cannot be

formed from only the 5s function and the three 5p functions. Some other symmetries are necessary. In analogy with the transition metal complexes, d-like symmetry is the most likely.^{24,34} Two tin d orbitals along with the aforementioned s and p orbitals allow the construction of so-called d^2sp^3 hybrid orbitals.

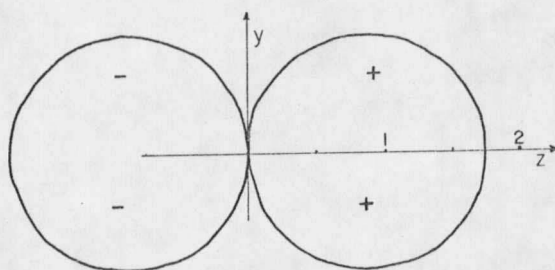
Fig. 8 shows the component orbitals used in forming one of the six equivalent d^2sp^3 hybrid orbitals, also shown as Ψ . The s function is not shown, since it is merely a constant. The other d^2sp^3 hybrids utilize p_x , p_y and $d_{x^2-y^2}$, as well as the s, p_z and d_{z^2} functions.²⁴ The + and - signs indicate the algebraic sign of the function in each area.

The scales on the positive z-axes demonstrate another fact about these hybrids that makes them appealing for use in covalent bonds. For the particular hybrid shown, the increased amplitude in the +z direction results in an increased overlap with the wavefunctions of the nearest neighbor atom in that direction. This further enhances the covalent character of the bond.

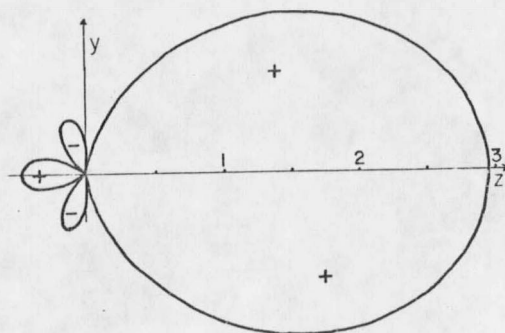
The three orbitals centered on each oxygen also present a non-trivial case. Referring again to Fig. 1 and focusing attention on either of the two oxygens totally within the unit cells, one notes that the three nearest neighbor tin atoms all are co-planar with the oxygen. Three mutually orthogonal orbitals which all lie in this



$$d_{z^2} = \sqrt{\frac{5}{4}} (3 \cos^2 \theta - 1)$$



$$p_z = \sqrt{3} \cos \theta$$



$$\Psi = \sqrt{\frac{1}{6}} + \sqrt{\frac{1}{2}} p_z + \sqrt{\frac{1}{3}} d_{z^2}$$

FIG. 8. A d^2sp^3 hybrid orbital and its components.

plane cannot be constructed from just the three oxygen 2p functions.

In order to get the necessary trigonal orbitals, an s function must be used along with two of the p orbitals, say p_x and p_y , to hybridize into the sp^2 orbitals. Along the x-axis the pertinent sp^2 orbital would be

$$\psi_{sp^2} = 1/\sqrt{3} + \sqrt{2/3} p_x = 1/\sqrt{3} + \sqrt{2} \sin\theta \cos\phi, \quad (1)$$

where θ and ϕ are the polar and azimuthal angles, respectively.

This same scheme utilizing d^2sp^3 and sp^2 hybrid orbitals has to be used to explain the bonding in TiO_2 , which also crystallizes in the rutile structure.³⁵ The ionicity of TiO_s would even be greater than that of SnO_2 , since the electronegativity of titanium is 1.6, while that of tin is 1.7. Still, the covalent model seems appropriate for TiO_2 . To account for the large ionicity the hybrids are allowed to be greatly distorted towards the oxygens.

Use of the d orbitals is much clearer in TiO_2 than in SnO_2 . For Ti the 3d levels are only partially filled and lie within a few eV of the 4s level. The small energy difference between these levels allows the hybrid interpretation to be easily rationalized. Atomic tin, on the other hand, has filled 4d levels lying more than 20 eV below the 5s level, while the empty 5d levels are more than 12 eV above the 5s level. Whether 4d or 5d tin levels are used for the hybrids for tin oxide, the large energy separation of

these levels tends to make the covalent hybrid picture for SnO_2 not so appealing as for TiO_2 . Still the two compounds do demonstrate the same crystal structure, which seems to indicate similar binding mechanisms. Moreover, the tin-oxygen distance of about two $\text{\AA}$ is quite small and would be expected to result in a very strong perturbation of the atomic wave functions.

Fig. 9 shows the radial functions³⁶ of the tin 4d and oxygen 2p with their centers separated by 2.08 $\text{\AA}$. The large overlap could possibly result in the necessary perturbation to account for the formation of the d^2sp^3 and sp^2 hybrids. Further discussion of possible d character in the bonding electrons of tin oxide is left until later.

HERMAN & SKILLMAN
RADIAL WAVEFUNCTION
OVERLAP

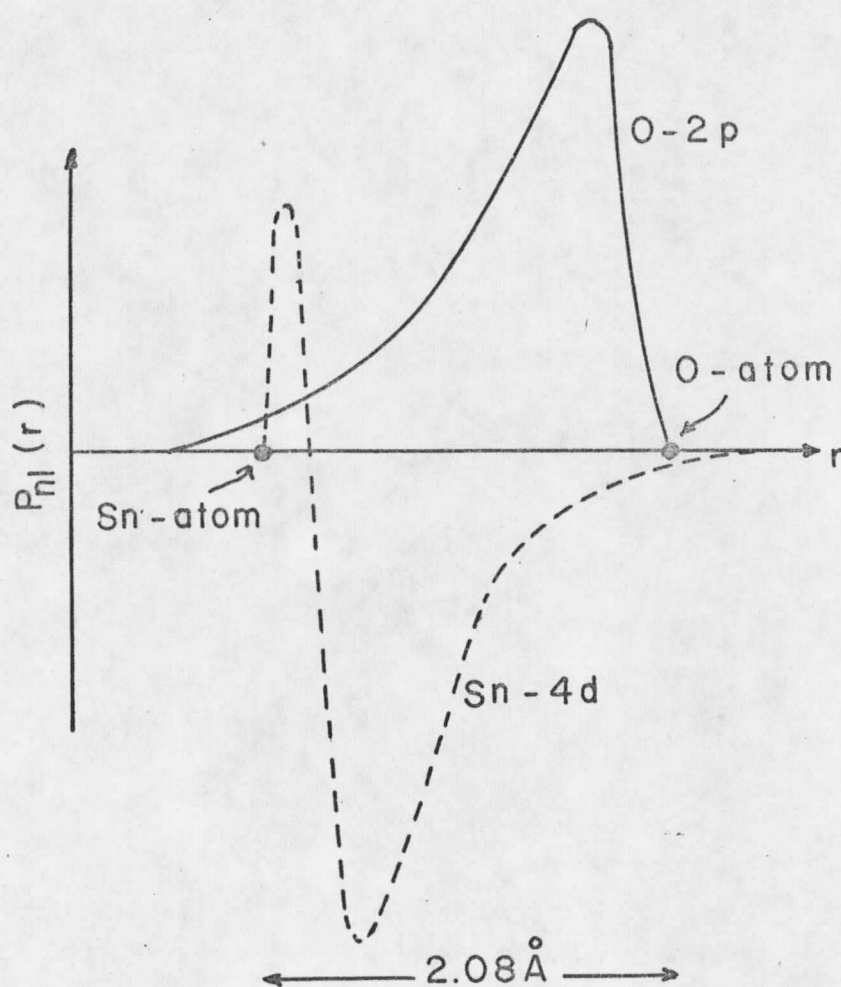


FIG. 9. Overlap of tin 4d and oxygen 2p radial wavefunctions.

III. GENERAL THEORY

A. Solid State Energy Levels

The bulk of photoemission data can be understood with application of the one-electron approximation where energy levels are determined for only one electron in a periodic potential produced by the ion cores and the remaining electrons. The Schroedinger equation,

$$(\nabla^2/2m + V) \Psi = E\Psi, \quad (2)$$

can, in principle, be solved to determine the various values of E for which the equation is satisfied.

The solutions are the so-called Bloch states,³⁷

$$\Psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) \cdot e^{i\vec{k} \cdot \vec{r}}, \quad (3)$$

where $u_{\vec{k}}(\vec{r})$ is a function with the periodicity of the lattice. The quantum number $\vec{k}$ takes on closely spaced discrete values for a macroscopic crystal which become continuous for the infinite crystal.

The allowed energy levels are plotted as a function of $\vec{k}$, i.e., $E = E(\vec{k})$. $E(\vec{k})$ is a multi-valued periodic function, with period $\vec{G}$, where $\vec{G}$ is a reciprocal lattice vector. Usually only the smallest irreducible portion of $\vec{k}$ -space, known as the first Brillouin Zone (BZ), is considered. This view of electronic energy bands is called the reduced zone scheme.

All of the bands for a material are usually not shown. Only the valence bands and lower conduction bands, which are of the greatest interest to the solid state physicist, are normally shown. This is a reasonable omission, however, since deep lying core levels will tend to replicate atomic levels, that is, no band-like character, and high lying conduction bands will tend to depend only on general crystalline form and lattice constants and be void of atomic character. For example, the silicon derived 2s bands in silicon and quartz (SiO_2) would be similar, while the high energy conduction bands in silicon, germanium and diamond would qualitatively agree since these three all crystallize in the diamond structure.

B. Photoabsorption

Light incident on the crystal changes the Schroedinger equation since $\vec{p}$ must be replaced with $\vec{p} - q\vec{A}/c$ ³⁸, where $\vec{A}$ is the vector potential of the electromagnetic field, q is the charge, and c is the speed of light. Making this substitution and disregarding terms involving A^2 , the Hamiltonian becomes

$$H = p^2/2m + V - (q/mc)\vec{A} \cdot \vec{p}. \quad (4)$$

The latter term is then treated as a time dependent perturbation. Choosing z as the propagation direction of the incident light, with

$\vec{A}$ in the x -direction, it can be shown that the matrix element for insertion into the Golden Rule is

$$H_{if} = \langle f | e^{ikz} p_x | i \rangle (qA/mc) \quad (5)$$

where here k is the wavevector of the light, and $\langle f |$ and $| i \rangle$ are the final and initial states of the electron, respectively. By expanding the exponential as

$$e^{ikz} = 1 + ikz + (ikz)^2/2 + \dots \quad (6)$$

and retaining only the first term yields the dipole approximation, in which

$$H_{if} = (qA/mc) \langle f | p_x | i \rangle. \quad (7)$$

Upon utilization of $p_x = m\dot{x}$ and $\dot{x} = (i/\hbar)[H, x]$, the matrix element becomes

$$(iqA/\hbar c)(E_f - E_i)\langle f | x | i \rangle, \quad (8)$$

where E_f and E_i are the final and initial energies of the electron, respectively.

Using the Bloch function for $\langle f |$ and $| i \rangle$, one gets

$$\langle f | x | i \rangle = \int_{\text{crystal}} e^{i\vec{k}' \cdot \vec{r}} u_{\vec{k}'}(\vec{r}) x e^{i\vec{k}'' \cdot \vec{r}} u_{\vec{k}''}(\vec{r}) dV \quad (9)$$

Since the $u_{\vec{k}}(\vec{r})$ are periodic with $\vec{R}_n$, the periodicity of the lattice, this becomes

$$\sum_{\text{all cells}} \int_{\text{one cell}} \exp \left\{ -i\vec{k}' \cdot (\vec{r} + \vec{R}_n) \right\} u_{\vec{k}'}(\vec{r}) \times \exp \left\{ i\vec{k}'' \cdot (\vec{r} + \vec{R}_n) \right\} u_{\vec{k}''}(\vec{r}) dV \quad (10)$$

Interchanging the sum and integral, this becomes

$$\int_{\text{one cell}} u_{\vec{k}'}(\vec{r}) \times u_{\vec{k}''}(\vec{r}) dV \sum_{\text{all cells}} \exp [i(\vec{r} + \vec{R}_n) \cdot (\vec{k}'' - \vec{k}')] \quad (11)$$

Since the sum is over the whole crystal, it vanishes unless

$\vec{R}_n \cdot (\vec{k}'' - \vec{k}')$ is an integral multiple of 2π . This is equivalent to

$$\vec{k}' - \vec{k}'' = \Delta\vec{k} = \vec{G}, \quad (12)$$

and is the basis for the $\vec{k}$ -conserving direct transitions.

C. Selection Rules

The treatment just given for the infinite crystal results in the so-called direct transition model. Since $\Delta\vec{k} = \vec{G}$ and $E(\vec{k}+\vec{G}) = E(\vec{k})$, it is said that $\vec{k}$ is conserved in the reduced zone scheme. Other models have been proposed which, in some cases, provide a more accurate description of observed phenomena.

For completeness one should mention the basically phenomenological non-direct model of Spicer.^{1,39,40} The essence of the model was that $\vec{k}$ was not a good quantum number for solids, and that $\vec{k}$ conservation therefore was not considered important in the optical transition. However, the non-direct model has received less serious application in recent years.

Two other models should be considered, one which has gained acceptance and the other having just recently been suggested, but both of which are compatible with the direct transition model. The first of these is the indirect or phonon-assisted model. The phonon is the quantum of energy involved in lattice vibrations. As such its momentum $\hbar\vec{k}$ is large while its energy $\hbar\Omega$ is negligible -- usually on the order of tens of meV. This can be compared to the photon, for which the energy is large and the momentum negligible, and the electron, for which neither the energy nor momentum are

negligible. An indirect transition is then considered as photon absorption concurrent with phonon absorption or creation. The direct transition model is then modified to

$$\Delta \vec{k} = \vec{G} + \vec{k} \quad (13)$$

for the indirect case.

The final model takes into account the fact that photoemission experiments are performed on essentially semi-infinite crystals. The light is incident on a surface, and the emitted electrons emanate from that same surface. Even if the photoabsorption occurs well within the bulk, the photoelectrons must cross the surface if they are to be detected. As the electrons near the surface, they "see" the termination of periodicity in the normal direction. The normal component of $\vec{k}$ ($\vec{k}_{\perp}$) will cease to be a good quantum number; i.e., the surface will mix states of different $\vec{k}_{\perp}$. Though the original value of $\vec{k}_{\perp}$ is lost, the parallel component $\vec{k}_{\parallel}$ will be preserved. These "cross" transitions then have the less restrictive selection rule

$$\Delta \vec{k}_{\parallel} = \vec{G}_{\parallel}, \quad (14)$$

where $\vec{G}$ is a surface reciprocal lattice vector.

Fig. 10 is used to illustrate the selection rules. Transitions are shown schematically in each case for the same photon energy and the same hypothetical band structure. Direct transitions are shown

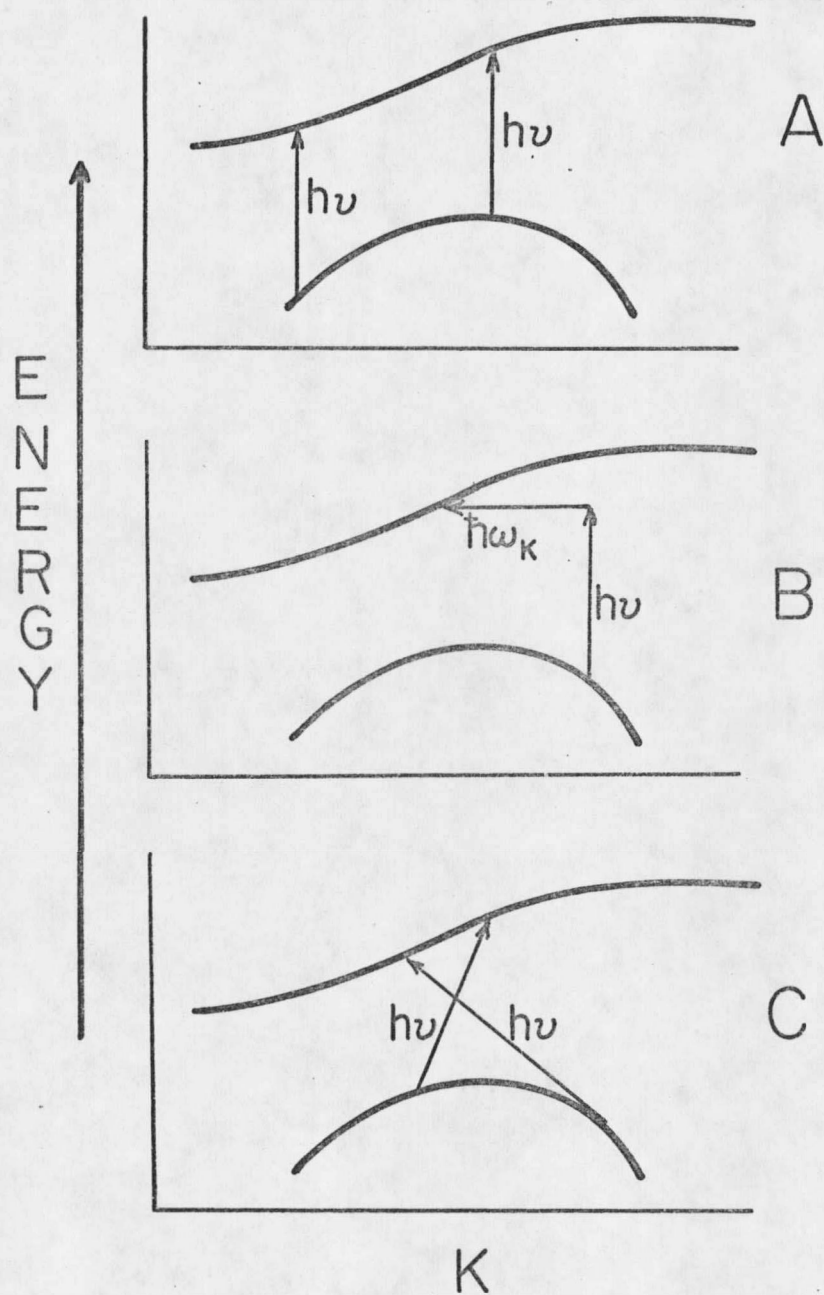


FIG. 10. Schematic of selection rules.

in A and indirect in B. Cross transitions are a combination of A and C; A for $\vec{k} = \vec{k}_{||}$ and C for $\vec{k} - \vec{k}_{\perp}$.

D. Inelastic Scattering

As the excited electron moves through the crystal, it encounters many other electrons, the preponderance of which are below the valence band maximum (VBM). Inelastic scattering, resulting in two excited electrons, can occur only if the energy of the first electron, E_f , is large enough so that it can give up some energy to the second electron, and both will end up in the conduction bands. Concisely stated, this condition is

$$h\nu > E_f - E_{VB} > 2E_g \quad (15)$$

where $h\nu$ is the photon energy, E_{VB} is the energy at the valence band maximum, and E_g is the band gap. For tin oxide, $E_g \approx 3.6$ eV and the threshold for emission (minimum value of $E_f - E_{VB}$ for electrons to escape from the surface) is ~ 7 eV, so essentially all emitted electrons were potential victims of inelastic scattering. On the other hand, this inelastic (pair production) scattering is energetically forbidden for small photon energies, that is, $h\nu < 2E_g$. This lack of inelastic scattering has been observed in some large band gap insulators.⁴¹

Besides energy transfer, inelastic scattering also includes momentum transfer. Not surprisingly this results in another selection rule on $\vec{k}$. However, since two electrons are involved, it is the total wavevector which must be conserved; i.e.,

$$\vec{k}_{1i}^* + \vec{k}_{2i} = \vec{k}_{1f}^* + \vec{k}_{2f}^* \quad (16)$$

where $\vec{k}_{1i}^*$ denotes $\vec{k}$ for the first (1) electron in its initial (i) excited (*) state.

This inelastic scattering results in the lower lying conduction band state of energy $E_f(\vec{k}_f)$ being filled even with no initial state available such that $h\nu = E_f - E_i$ and $\vec{k}_f - \vec{k}_i = \vec{G}$. The emission due to these secondaries is generally assumed to merely replicate the conduction band density of states.

E. Into The Vacuum

If the energy of the excited electron is greater than the threshold energy, E_T , the electron may escape the crystal and proceed in the vacuum. It is straightforward to show (see Appendix A) that $\vec{k}_\parallel$ is conserved as the electron crosses the surface. This is not intuitively obvious, since $\vec{k}$ in vacuum is simply related to the electron's physical momentum, $\hbar\vec{k} = m\vec{v}$; however, $\hbar\vec{k}$ is not synonymous with $m\vec{v}$ within the crystal.

It is, however, this fact which makes angle-resolved photo-emission valuable. Both the angle of emission and kinetic energy (K.E.) of the photoelectrons are measured. These are simply related to $k_{\parallel}^2$ via

$$k_{\parallel}^2 = \frac{2m(\text{K.E.})}{\hbar^2} \sin^2 \theta, \quad (17)$$

where θ is the polar angle. The azimuthal angle ϕ is also measured so that $\vec{k}_{\parallel}$ is easily determined.

Assuming either direct or cross transitions then allows determination of E_i and $\vec{k}_{i\parallel}$, the energy and parallel component of wavevector for the initial state. Information concerning the normal component of wavevector is unfortunately lost in cross transition; however, this component sometimes can be inferred from an accurate energy band calculation.

IV. EXPERIMENTAL APPARATUS AND PROCEDURE

A. Storage Ring Facility and Spectrometer

The photoemission spectrometer was designed for use at the University of Wisconsin Synchrotron Radiation Center storage ring facility of Fig. 11. Due to the highly relativistic nature of the electrons in the storage ring, the radiation emitted during the radial acceleration at the bending magnets is primarily in the forward tangential direction. This synchrotron radiation is passed through the light ports to various experiments. The port used for the spectrometer described herein was followed by a focusing mirror and normal incidence monochromator to disperse the light, all of which was provided by the Synchrotron Radiation Center.

The spectrometer is shown in Fig. 12. Light diverging from the monochromator was refocused by an elliptical mirror at a point in the center of the sample chamber. Upon entering the sample chamber, the light passed through a portion of the electron energy analyzer prior to reaching its focus. The light focus and center of the chamber were also coincident with the sample and the source point of the electron energy analyzer - a modified co-cylindrical mirror analyzer (CMA). Fig. 13 shows the light path and subsequent electron paths.

The spectral dependence of the light reaching the sample is shown in Fig. 14. The spectrum was acquired using sodium salicylate

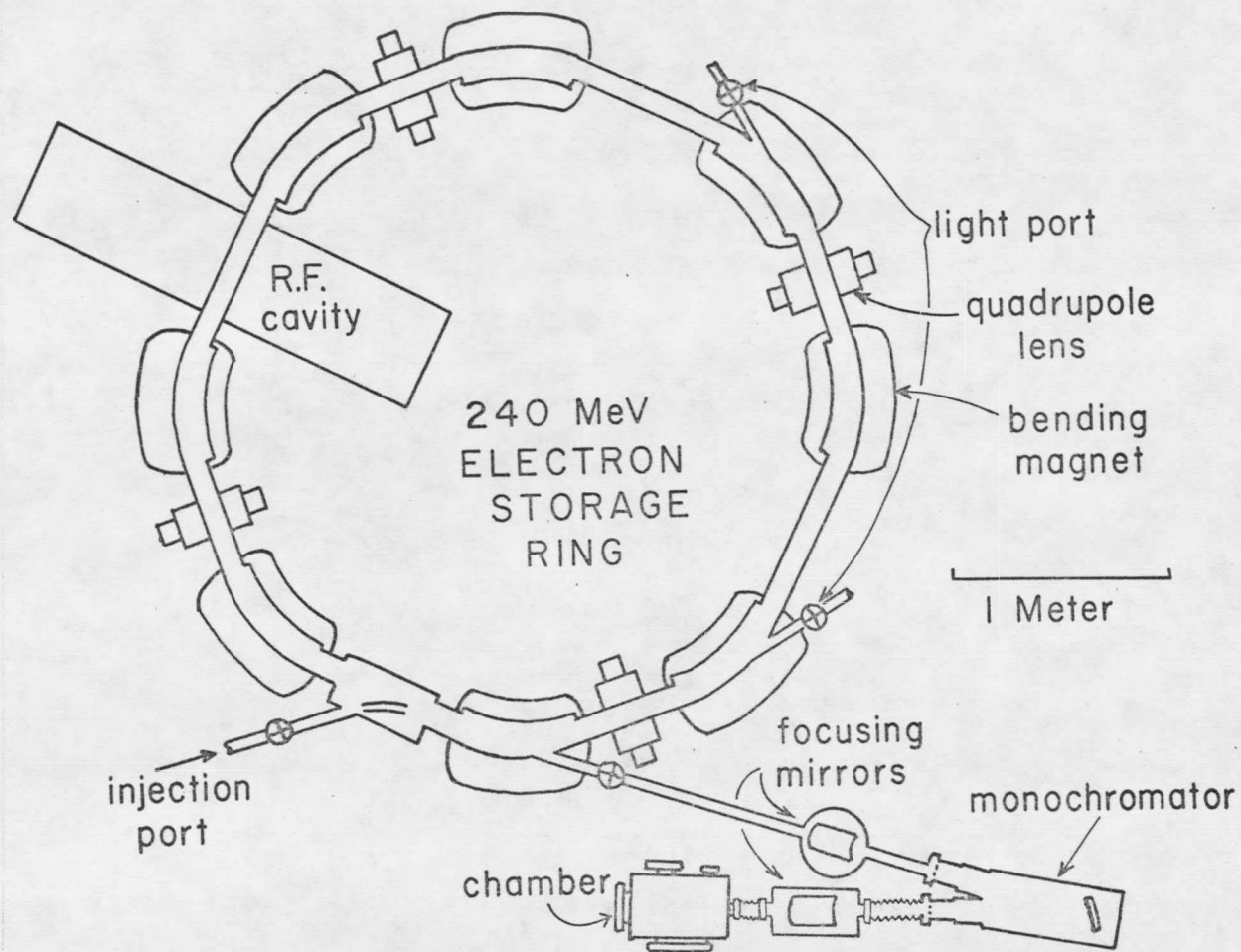


FIG. 11. Storage ring schematic.

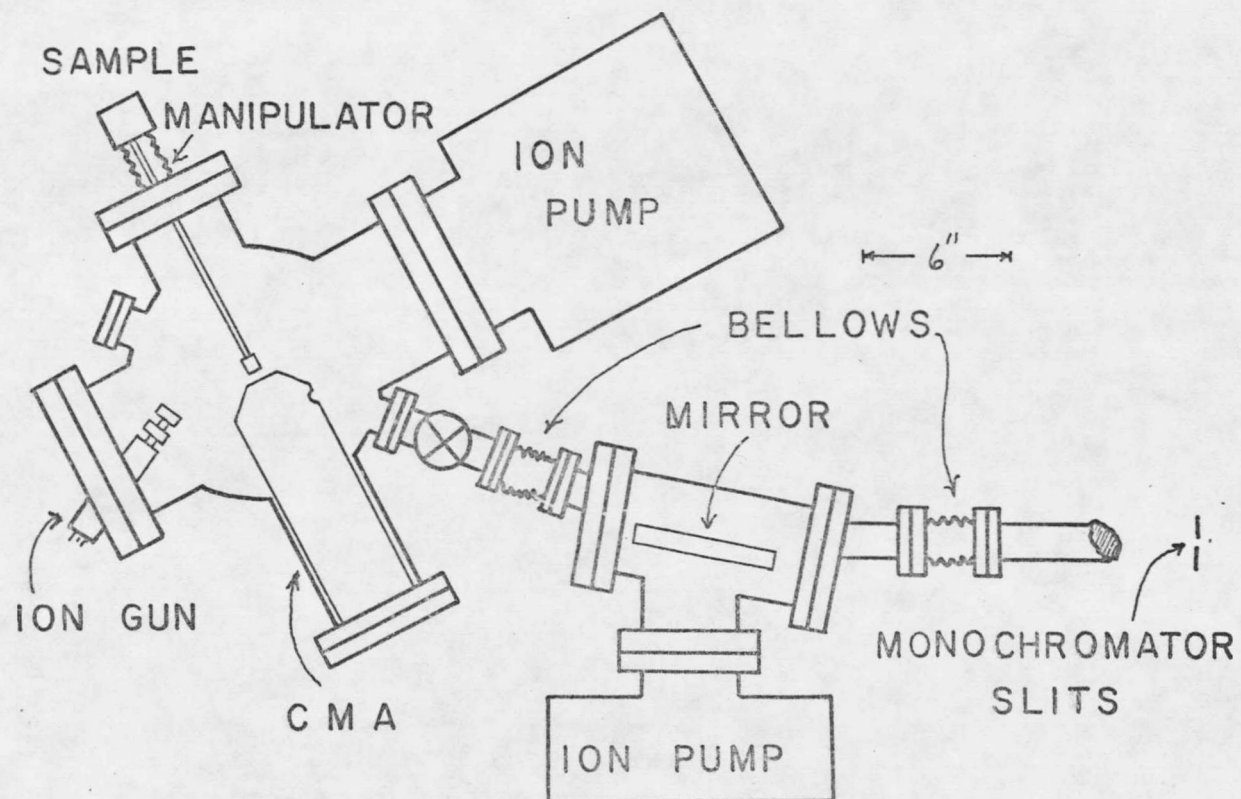


FIG. 12. Schematic of experimental chamber.

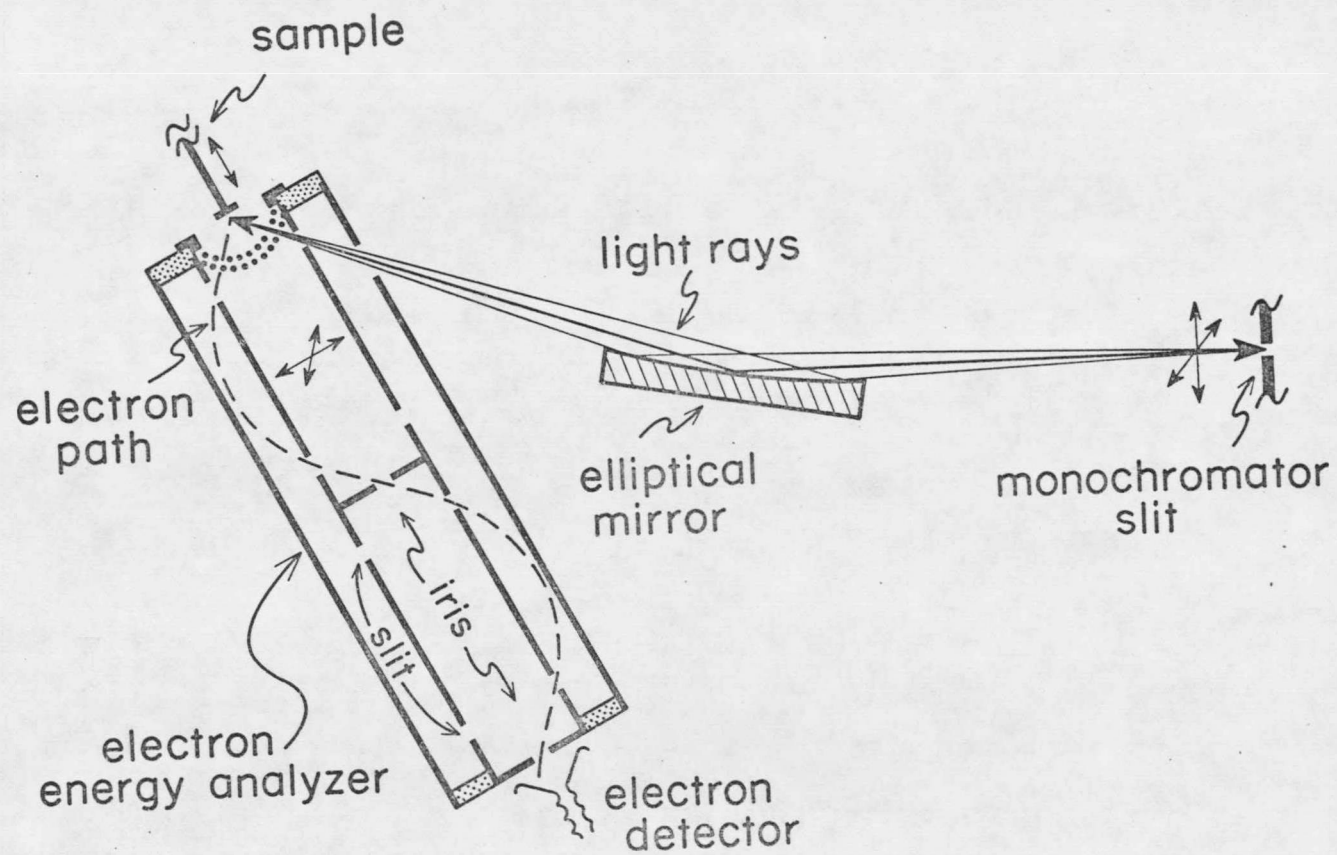


FIG. 13. Light and subsequent electron optics systems.

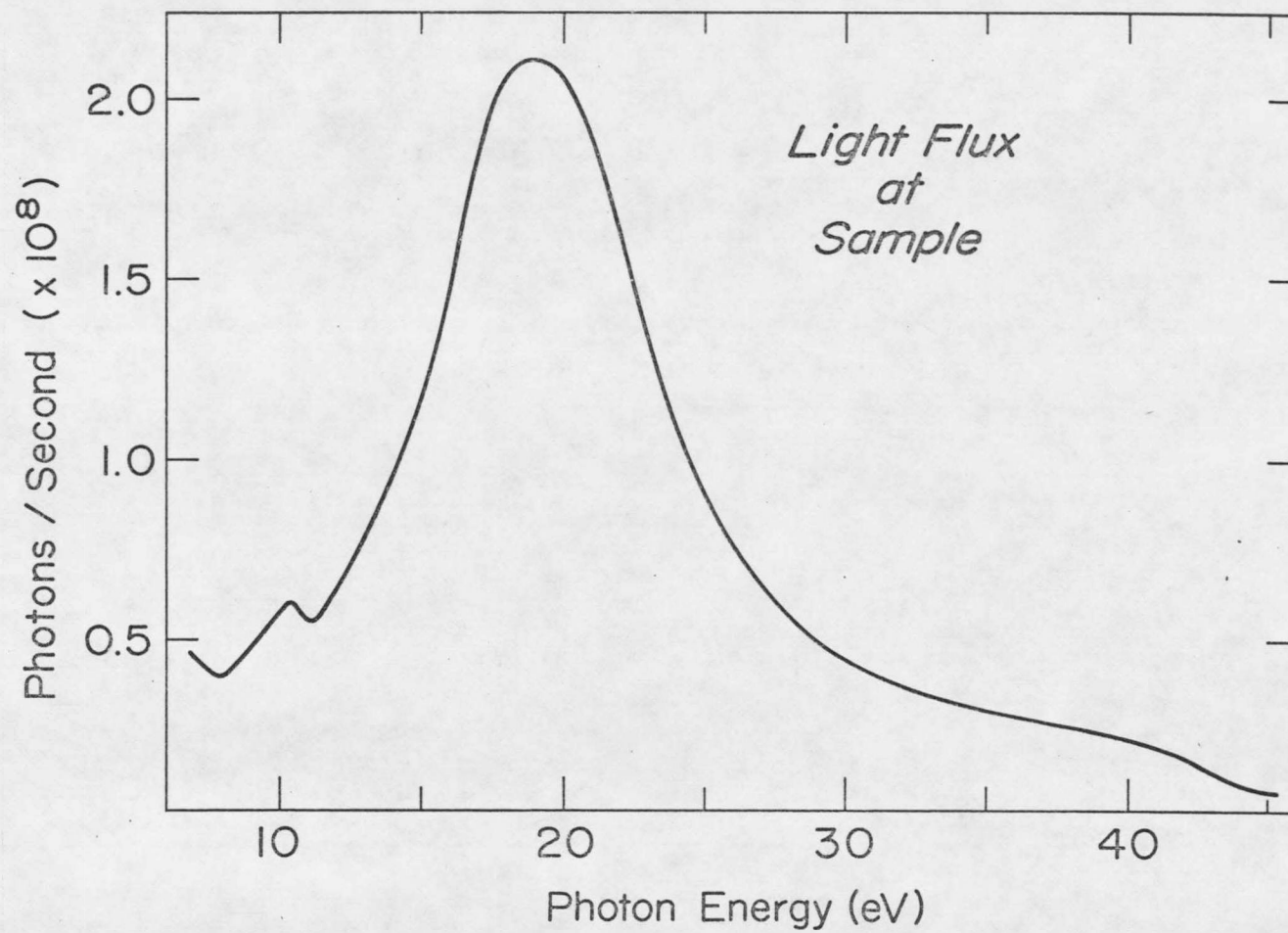


FIG. 14. Light curve.

as a phosphor and assuming its quantum efficiency to be independent of photon energy. The general shape of this light curve was determined to a large degree by the light optics system. Grazing reflections from the quartz mirrors and near normal reflection from the gold coated grating all tended to quench the flux at the higher photon energies. The actual curve shown was taken with a relatively new grating in place. Due to both radiation damage and contamination, the reflectivity of the grating would degrade to the point that the flux at 35 - 40 eV could be down by a factor of ten from the value shown in the figure. Still, over a two-week period, the light curve was considered as a constant. During that time the flux at a certain energy was assumed to vary only with the monochromator slit width and the electron current in the storage ring. Since both of these parameters were accurately determined, each UPS spectrum could be easily normalized to the incident photon flux.

B. Electron Energy Analyzer

The co-cylindrical mirror analyzer (CMA) has received thorough study which will not be repeated here.⁴² Some modifications, however, will be summarized. A cross section of the CMA is shown schematically in Fig. 15. The CMA accepts electrons whose trajectories lie between two cones of angle $42.3 \pm 6^\circ$. Accelerating/retarding grids were added to the first stage of the CMA, arranged

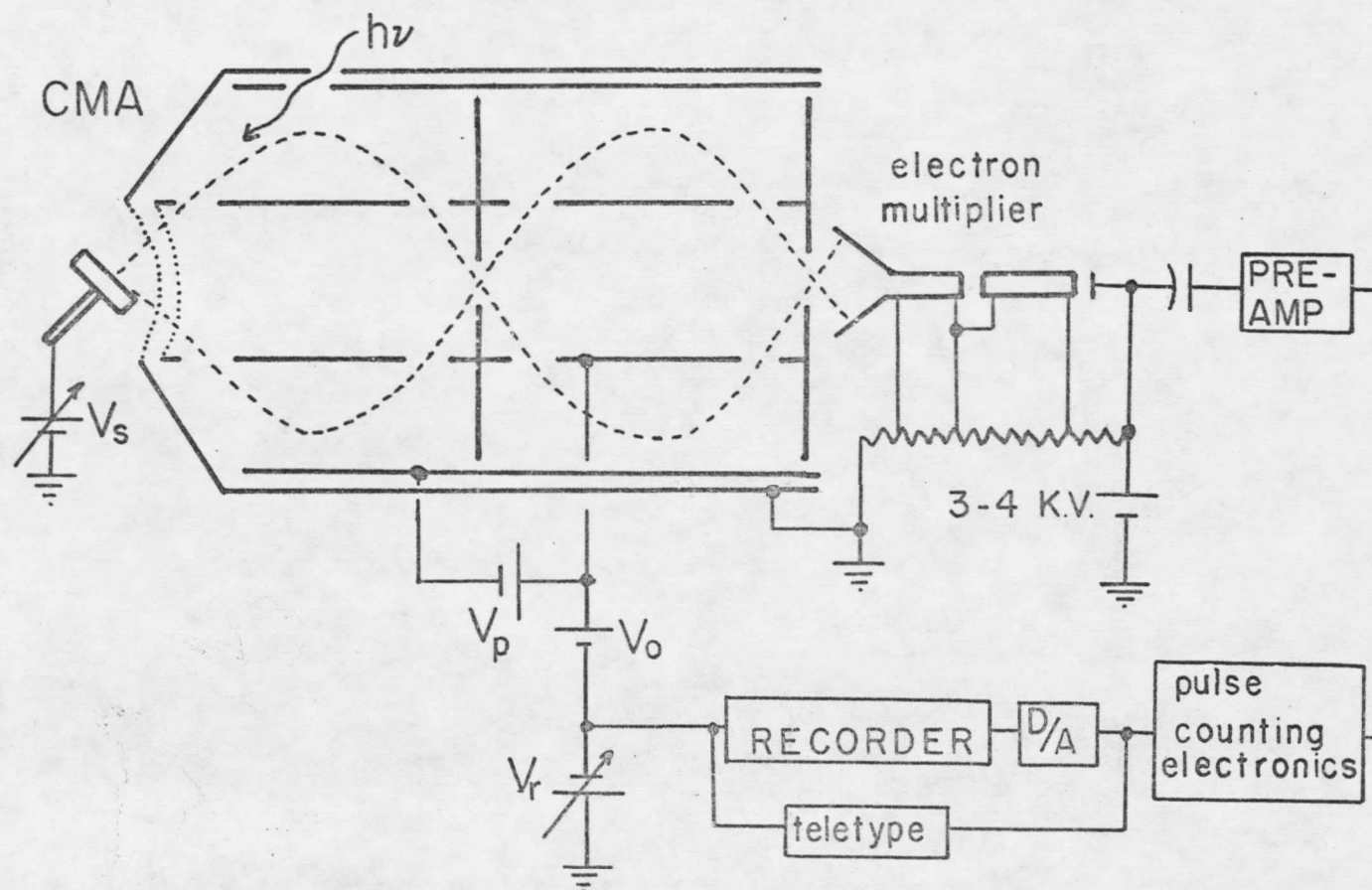


FIG. 15. CMA electronics and data acquisition electronics.

concentrically about the source point. With the first, smaller radius, screen grounded, the emitted electrons could be accelerated (or retarded) by application of the appropriate bias on the second, larger radius, screen. This preacceleration (-retardation) allowed the pass energy of the CMA to be held constant while spectra were taken. The pass energy was normally chosen as 20 eV. This in turn allowed for constant transmission of $\sim 4\%$ and energy resolution of .035 eV FWHM for the CMA. The bias arrangement for the sample and energy analyzer is shown in Fig. 15. With the first screen grounded, contact potentials between it and the sample were nulled out via adjustment of V_s . V_r provided the accelerating/retarding bias and was either held constant or ramped, depending on the type of spectrum being taken, while V_0 determined the starting condition. If the kinetic energy of the electron was equal to the pass energy of the CMA, $E_p = 1.76 V_p$, then it could be passed to the detector.

Fig. 15 also shows the data acquisition system. Pulses from the Spiraltron electron multiplier were amplified and then counted by a digital ratemeter. The three most significant figures of these data were then converted to an analog signal which drove the vertical axis of a servo x-y recorder. All digital data were simultaneously transferred to a paper tape for subsequent analysis. The x-axis of the recorder was driven by the ramp voltage, which was also recorded on the paper tape.

The angle-resolving feature of the analyzer was obtained by the placement of a drum mounted coaxially within the inner cylinder of the second stage of the CMA.⁴³ (See Fig. 16). The drum contains two small apertures, of 4° and 12° angular acceptance, respectively, whose location is determined by moving the drum in situ. The normal cone of electrons accepted by the CMA for energy analysis is thus further reduced to a ray of small divergence. The drum is retractable so that the analyzer could be readily switched from the angle-resolved to the CMA angle-integrated mode. With the sample face oriented towards a portion of the acceptance cone of the CMA as is Fig. 16, the variation of emission angle with the aperture setting is a complex function of the geometry. The emission direction is measured by the polar angle θ and the azimuthal angle ϕ . The $\theta = 0$ direction corresponds to emission perpendicular to the (001) surface, while $\phi = 0$ was chosen for convenience to lie in the $\langle 100 \rangle$ direction of the crystal. The relation of θ and ϕ to the drum position ϕ_D is described in Appendix B.

The transmission of the angle-resolving analyzer was highly anisotropic. Evidence of this is demonstrated in Fig. 17. Most of the structure in the transmission curve is due to Moire patterns⁴⁴ which resulted from the shadowing effects of the six screens along

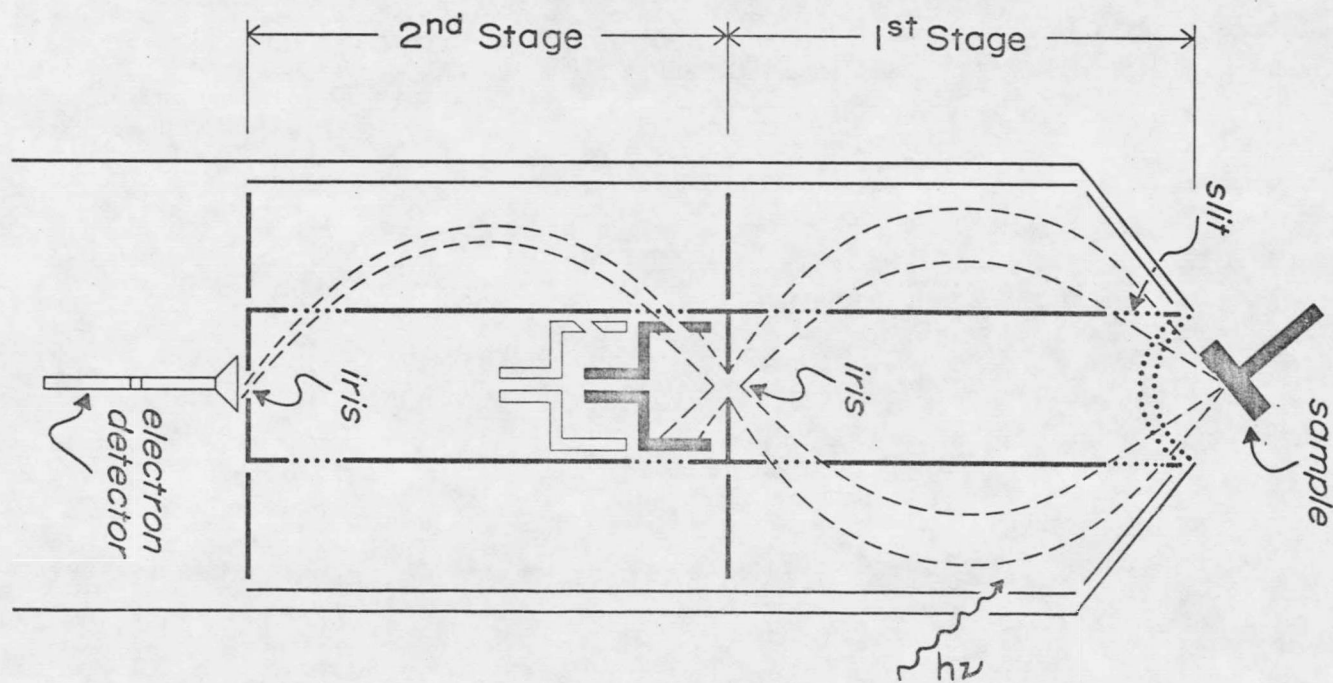


FIG. 16. Angle-resolving CMA.

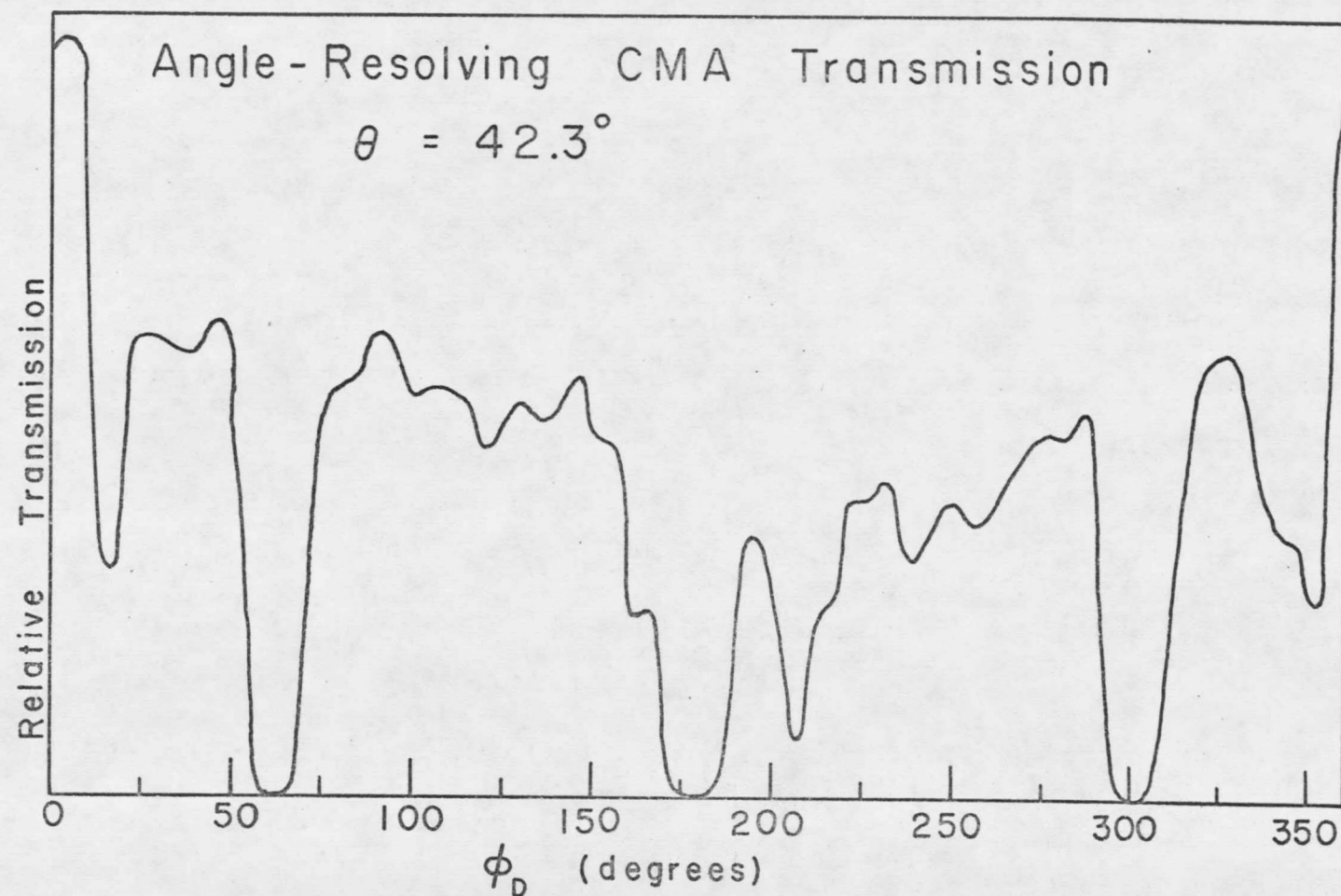


FIG. 17. Transmission of angle-resolving CMA.

the electron path within the CMA. The regions of zero transmission at 60° , 180° and 300° are due to support structures of the analyzer.

The orientation of the optical polarization could be changed in situ from s-polarization to partial p-polarization. The two positions are illustrated in Fig. 18. In s-polarization the light was incident normally to the surface, so that the electric vector $\vec{E}$ necessarily lay in the surface. With the sample manipulator rotated by 90° about the CMA axis, "p"-polarization was achieved. Actually pure p-polarization was not possible; only a component of $\vec{E}$ was perpendicular to the surface in what is being called "p"-polarization. What is called "p"-polarization is actually mixed s and p-polarization. On the other hand the s-polarization was pure s-polarization. The angle between $\vec{E}$ and the surface normal in "p"-polarization was 47.7° , while the angle between the incident light and the surface normal was 61.5° . For the case of $\text{SnO}_2(001)$, "p"-polarization allowed for a component of $\vec{E}$ to lie along the $\vec{c}$ axis of the crystal.

C. The Three Modes of Photoemission

In the one electron approximation, ignoring inelastic scattering, the photoemission experiment is governed primarily by the equation

$$h\nu = E_f - E_i, \quad (18)$$

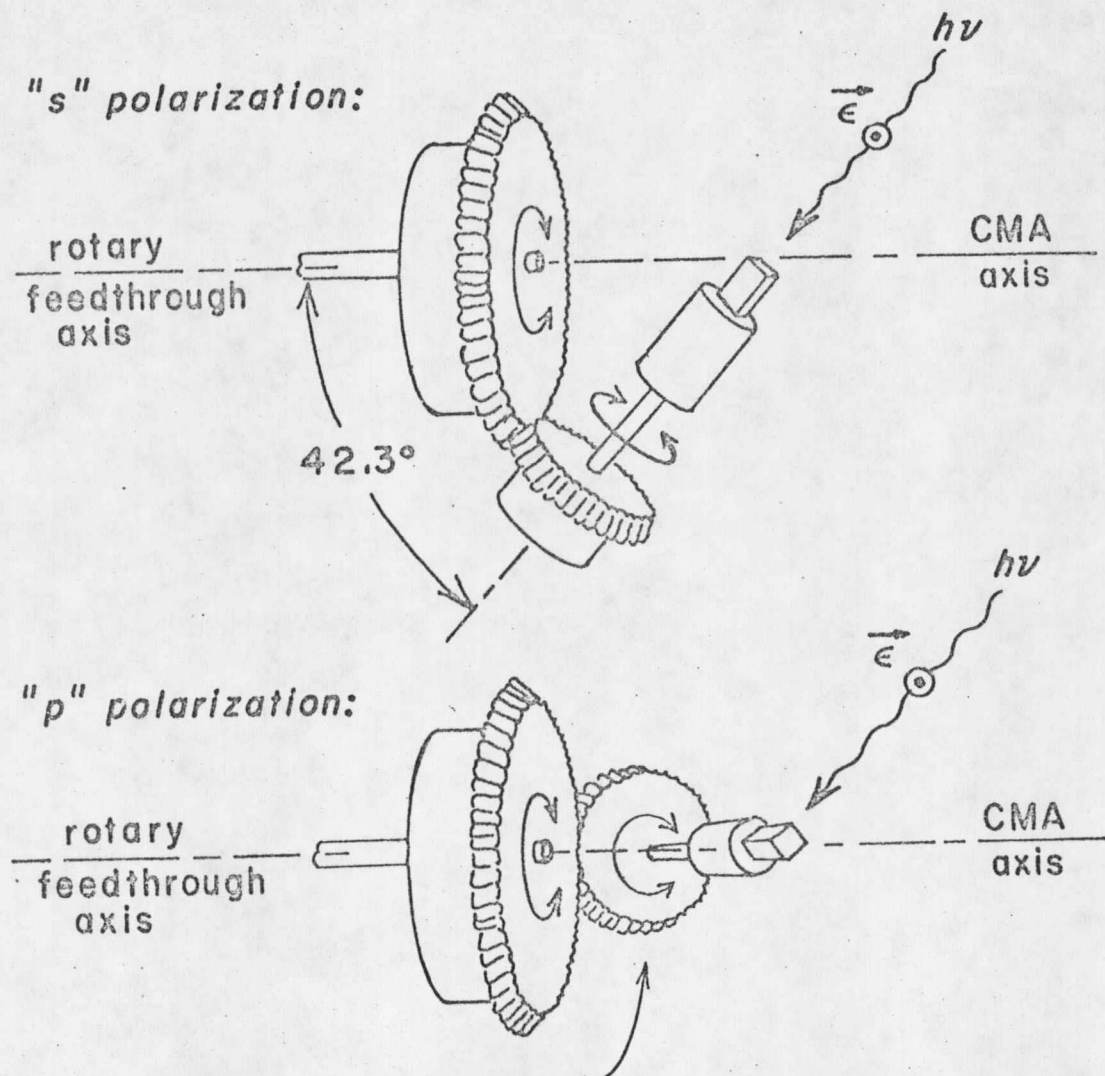


FIG. 18. Relative sample to light orientations for s and "p"-polarizations.

where $h\nu$ is the photon energy and E_i and E_f are the energies of the initial and final states, respectively. It is, of course, merely a statement of conservation of energy.

Ignoring emission and polarization angles as parameters for the moment, the electron emission intensity can only be considered as a function of two of the three quantities $h\nu$, E_i and E_f . Equation (18) does not allow them to all be independent. If we chose $h\nu$ and E_f as independent, then the emission intensity would be $N = N(h\nu, E_f)$. This is the equation of a surface, not unlike a topographical map, with horizontal distance replaced with the energies $h\nu$ and E_f , and the altitude replaced by the emission intensity, N .

Just as some physical structures such as ridges and peaks are better observed from different viewing angles, some structures in $N(h\nu, E_f)$ may be better observed looking along a line parallel to the $h\nu$ axis ($E_f = \text{constant}$), E_f axis ($h\nu = \text{constant}$), or some other angle, e.g., $h\nu - E_f = \text{constant}$. This is precisely what the three modes of photoemission allow one to do.

To illustrate the three modes, the photoabsorption process for a hypothetical substance is shown in Fig. 19. The shaded regions indicate the densities of states with the heavy shading indicating the normally filled valence bands and the light shading the normally empty conduction bands. The valence band maximum is chosen as the

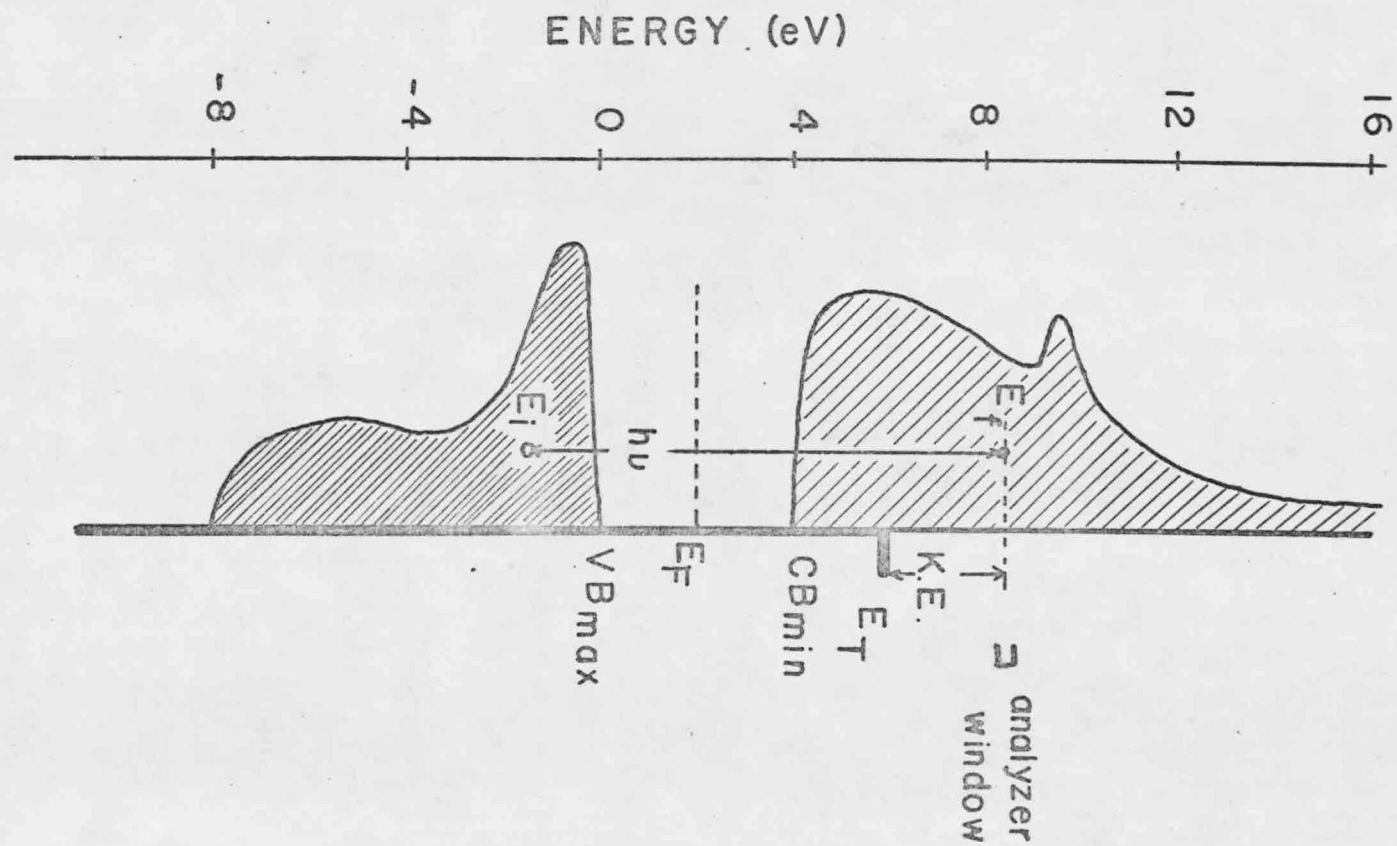


FIG. 19. DOS and energy levels for hypothetical sample.

energy zero. At $T = 0^\circ\text{K}$ all states below the Fermi energy E_F are filled and all above empty. E_T is the threshold for emission so that if $E_F > E_T$, the electron is energetically allowed to escape into the vacuum. Depending on impurities and other imperfections, E_F can fall anywhere within the band gap for insulators and semiconductors. For metals the valence band maximum, E_F and conduction band minimum (CBM) are all energetically degenerate, and E_T is then called the work function.

In the EDC (energy distribution curve), $h\nu$ is held fixed while the analyzer window is scanned through the pertinent range of kinetic energy. This is the classical mode of photoemission used exclusively with line source lamps and still the primary mode used even with synchrotron radiation. Since $h\nu$ is a constant, as the kinetic energy (hence E_f) is scanned, E_i is necessarily also scanned.

Both the constant initial state energy spectrum (CIS) and constant final state energy spectrum (CFS) involve scanning the photon energy. These two modes have been made possible with the availability of synchrotron radiation with its smooth continuum.

The simpler mode involving the scanning of $h\nu$ is the CFS. Here the analyzer window is held fixed while $h\nu$, and consequently E_i , is scanned. The resulting curve shows how initial states of various energies couple to final states of one particular energy.

The third mode is the CIS. It should be pointed out that no direct control can be exercised over E_i . $h\nu$ and E_f can be directly controlled, and E_i can then be determined from energy conservation. For the CIS, $h\nu$ and E_f are simultaneously scanned at the same rate so that $h\nu - E_f = -E_i$ will be a constant. A CIS then shows how states of one initial energy couple to the various final states.

Using the DOS of Fig. 18 an EDC, CFS and CIS are calculated and shown in Fig. 20. Matrix element effects, $\vec{k}$ conservation scattering are ignored, so the curves are mere joint densities of states. Some inelastically scattered electrons are always present in real solids, so the real EDC would extend to zero kinetic energy. Note that in the EDC also, the structure at ~ 3.5 eV is due to CBDOS while the structure at ~ 8 eV is due to VBDOS. On the other hand the CIS replicates only the CBDOS, while the CFS replicates the VBDOS (only backwards).

In principle, at least, all the available photoemission information could be extracted from a sufficiently dense set of EDC's, CFS's or CIS's, that is, the emission surface $N(E_f, h\nu)$ could be constructed. Advantages of one mode over another depend on the type of feature which one is attempting to illustrate plus which portion of the light spectrum is involved. These points will be discussed more fully in the chapter concerning the tin oxide data.

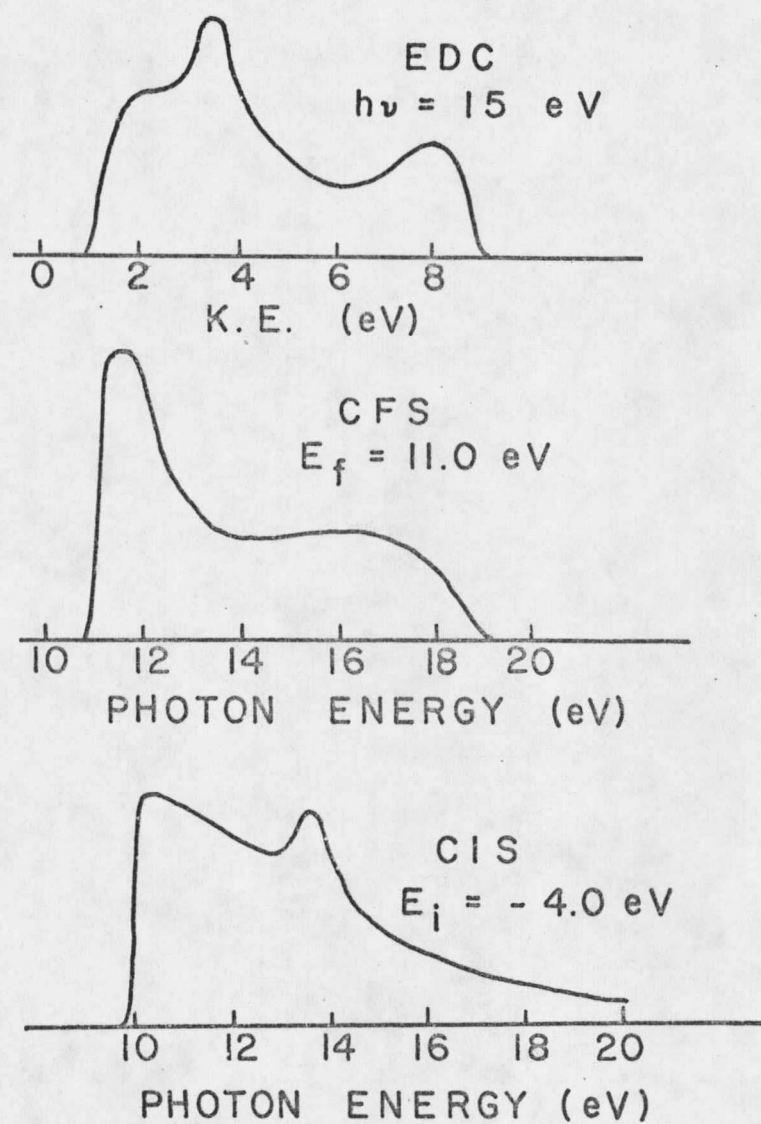


FIG. 20. Idealized UPS spectra from hypothetical sample.

D. Sample Preparation

1. Mounting and Cleaning. The antimony doped ($N_d = 10^{15} - 10^{16} \text{ cm}^{-3}$) stannic oxide single crystal was obtained in uncut form, an irregular piece with linear dimensions on the order of 0.5 cm. It was clear, with a glassy appearance, and included a single twin (011) plane. The crystal was first oriented using the Laue pattern from a back reflection x-ray camera. An (001) face which avoided the twin plane was then cut with a diamond saw and polished with successive alundum grits down to 0.05 micron. The polished crystal was then etched in H_3PO_4 and several times in NaOH following the recipe given by Fonstad.⁸ Further x-ray photographs indicated the polished and etched face to be within 2° of an (001) face. A (100) face was then cut to facilitate mounting in the crystal holder.

To prepare a clean surface in situ the crystal was sputtered with Argon ions from an ion gun and annealed. Depending on the condition of the surface prior to cleaning, sputtering times varied from a few minutes (10-15) to two to three hours. Various ion beam voltages (500 to 2000 volts) were used with no apparent resulting differences. Ion current densities were on the order of one microamp/cm².

After cleaning, the sample was annealed to remove the damage at the surface resulting from the sputtering. Various annealing temperatures from 550° to 835° C were used, with no observable difference in the results. Some of the higher temperature anneals did result in higher background pressures during annealing, and this occasionally caused contamination to again reappear on the surface. The cleaning procedure was then restarted. Normally, however, such contamination was not observed below 800° C. Annealing times on the order of 20 minutes proved to be ample.

The sample holder is shown in Fig. 21. The two cylindrical ceramic pieces served as a mount for a tungsten heater. Five mil tungsten wire was wrapped in the spiral grooves of the inner ceramic piece, while the outer piece prevented shorting or entanglement of the heater wire with other parts of the vacuum system, and also reduced heat losses due to radiation. With this crystal holder temperatures up to 835°C were obtained at the chromel-alumel thermocouple mounted just behind the crystal. The spring stainless tab provided a secure mount, while not producing undue stress on the crystal.

Fig. 22 shows EDC's for a dirty, clean but un-annealed, and clean and annealed sample. The overall UPS features inherent in tin oxide were observed prior to annealing. But as the figure shows, the VB primary emission was stronger after annealing.

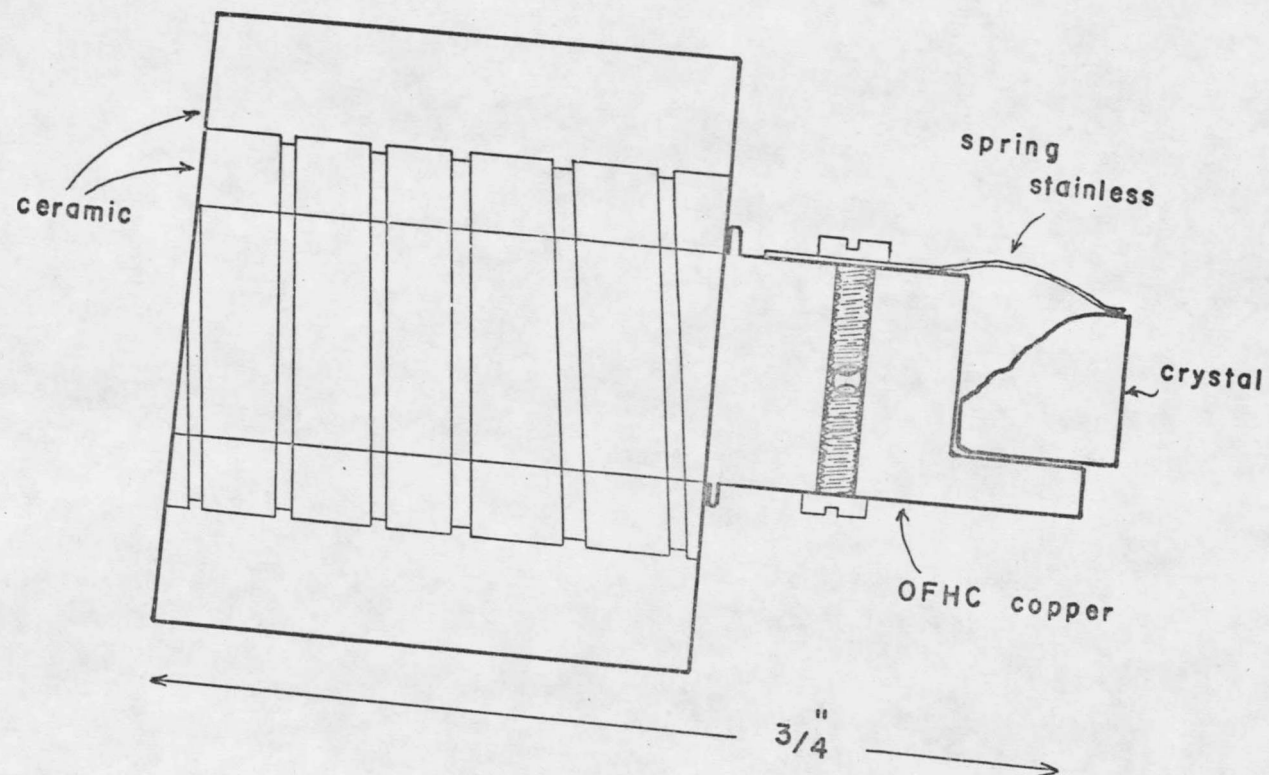


FIG. 21. Crystal holder.

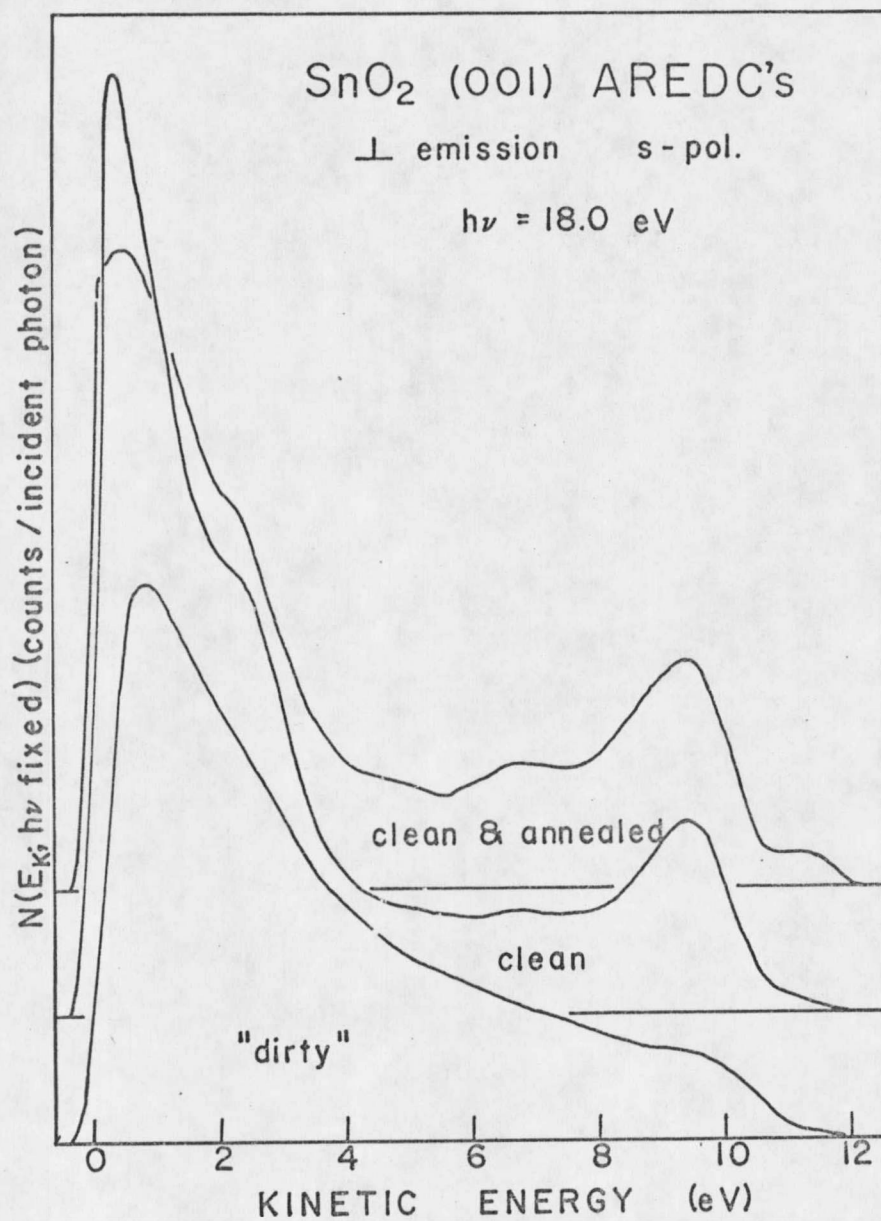


FIG. 22. AREDC's depicting sample preparation.

A more discriminating test for a well prepared crystalline face is to examine the emission anisotropy, which is demonstrated in Fig. 23. The ϕ -pattern shown was obtained by monitoring the emission intensity at a particular polar angle, 20° , as the crystal was rotated. Though the anisotropy was present prior to annealing, the increased sharpness and magnitude of the anisotropic feature indicated a well-ordered crystal.

2. Auger Analysis. Cleanliness of the crystal surface was monitored by Auger analysis. Auger analysis has become a useful technique in the study of surfaces,⁴⁵ and only a brief tutorial will be presented here.

The surface to be analyzed is bombarded with 2 - keV electrons. The electrons then leaving the surface are subsequently energy analyzed. However, most of these secondary electrons are of relatively low energy and provide only a broad structureless sloping background. Riding atop this background, however, are small ($\sim 10\%$ of background) relatively sharp structures due to the radiationless Auger decay of the atomic core holes. The Auger line structures are easily separated from the background by measuring the derivative of the kinetic energy spectrum.

The Auger process for atomic core levels is shown in Fig. 24. The deeper core (E_3) hole is created by a primary electron. An

SnO_2 (001) ϕ -patterns

$h\nu = 28.0 \text{ eV}$ $E_i = -13.2 \text{ eV}$

$\theta = 20^\circ$

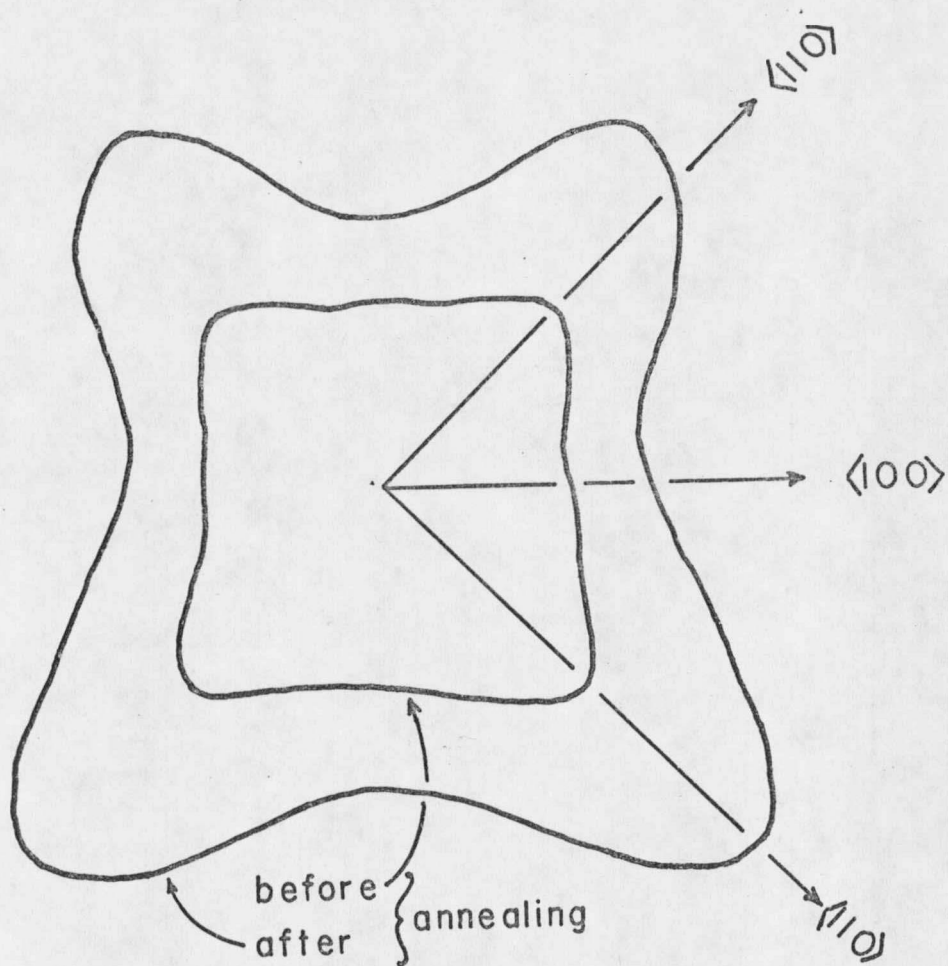
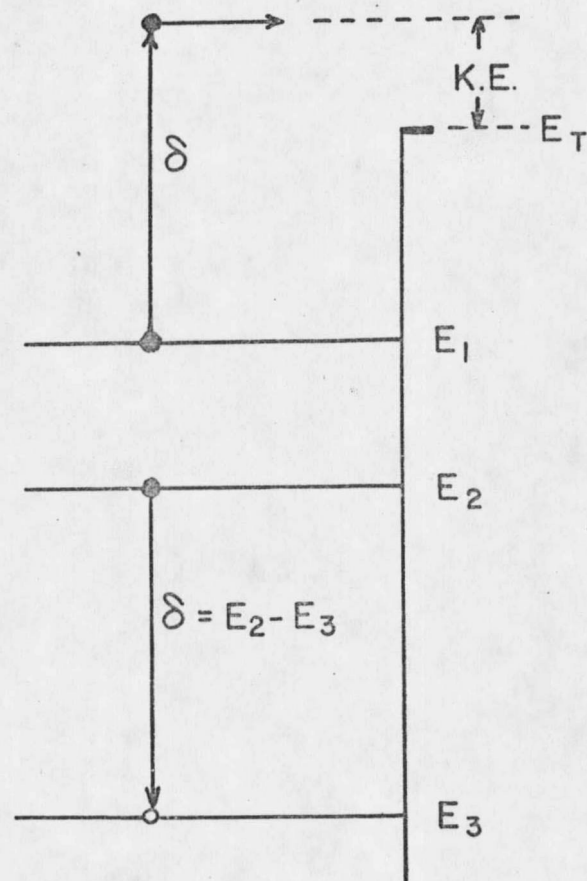


FIG. 23. ϕ -patterns before and after annealing of crystal.



Auger Process

FIG. 24. Atomic Auger process.

electron in a higher lying core level (E_2) then "drops" to fill the original core hole. The energy δ , instead of perhaps escaping the crystal as a photon, is transferred to another core electron (E_1), usually on the same atom. This electron then may have sufficient energy to escape the crystal. Note that the kinetic energy of the ejected electron is independent of the primary beam energy. The beam energy must just be sufficient to create the original core hole. Since core levels are only slightly affected by the chemical environment, and each element--excluding hydrogen and helium--has its own array of core levels, the Auger spectrum of an atomic species serves as its fingerprint. Moreover, since the inelastic scattering length for electrons of 50 - 1000 eV kinetic energy is $\approx 20 \text{ \AA}$, the sharp Auger lines in the spectrum result from electrons emitted by atoms in the uppermost surface layer.

Auger analysis is most often, as in this study, used as a qualitative tool--to find out what is on the surface. Fig. 25 shows the Auger spectra for the tin oxide crystal prior to and after ion bombardment. Phase sensitive detection methods were employed to obtain the derivative spectrum $dN(E)/dE$. Prior to cleaning carbon was the most common contaminant, probably resulting from the hydrocarbon solvent residues used to degrease the sample before placing it in the vacuum system. However, as the "clean" spectrum indicates,

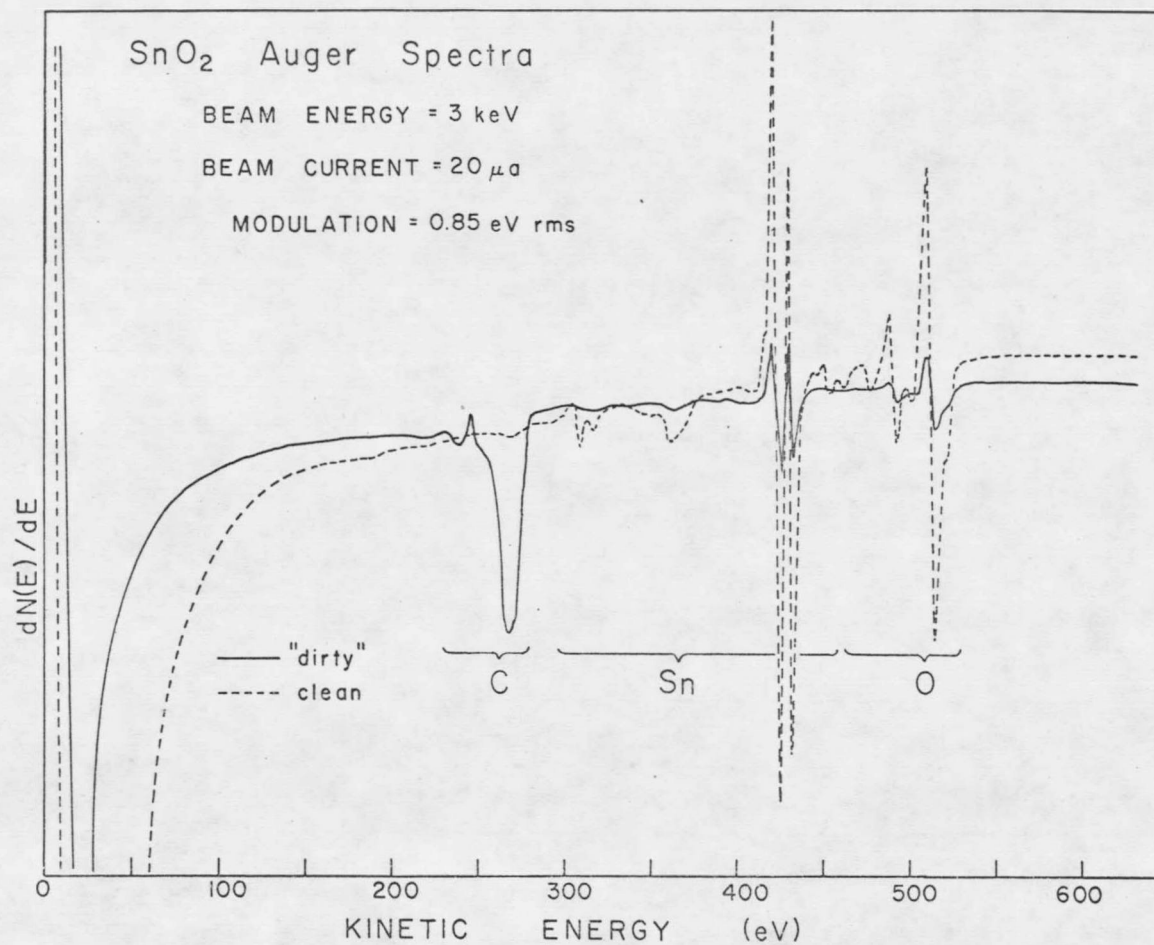


FIG. 25. Characteristic Auger spectra from SnO₂.

this carbon was essentially removed by the argon bombardment. This fact is further confirmed by the corresponding increase in the strength of the tin and oxygen lines in the spectrum.

Though amounts of most elements down to 0.1 atomic percent at the surface are generably detectable, Auger analysis must be considered semi-quantitative. An Auger signal due to element A may be proportional to the amount of atom A present at the surface, but many factors make it difficult to determine the absolute concentration to better than 20%. Cross-sections for ionization of cores, the probability of subsequent Auger decay and the probability of escape without inelastic scattering all contribute their uncertainties. For example, the cross-section for the ionization of the 2s core in metallic tin will be slightly different in tin and tin oxide, and the inelastic scattering lengths will also be different in the two cases. Thus while the absence of impurity atoms is determined rather straightforwardly, the quantitative data needed to determine a significant tin/oxygen ratio was not available.

V. EXPERIMENTAL RESULTS AND DISCUSSION

A. Angle-Integrated Study

1. Valence Band Emission. An overview of tin oxide's electronic structure is obtained with the CMA angle-integrated photoemission data. For this case the sample normal was antiparallel to the incident light, with the angle-resolving apparatus retracted. Since the unmodified CMA only collects a cone of electrons ($42.3^\circ \pm 6^\circ$ half angle) for energy analysis, this mode is referred to as CMA angle-integrated.

A representative set of CMA angle-integrated EDC's on sputtered and annealed tin oxide are shown in Fig. 26-29. The curves are plotted as a function of initial energy, E_i , to emphasize the structures due to valence band densities of states (VB DOS). Such structures are essentially constant in E_i . Structures moving uniformly to the left as $h\nu$ increases are straightforwardly interpreted as due to conduction band densities of states (CB DOS).

The observed emission for energies near the VBM was fairly weak. Therefore the VBM was not chosen as the reference energy, although it is conventional to do so. Instead the threshold energy, E_T , which corresponds to zero kinetic energy, was chosen as the energy zero. On this scale, then, $E_{VB} = -7.0 \pm 0.5$ eV, and final energy, E_f , is equivalent to the kinetic energy, E_K . To determine

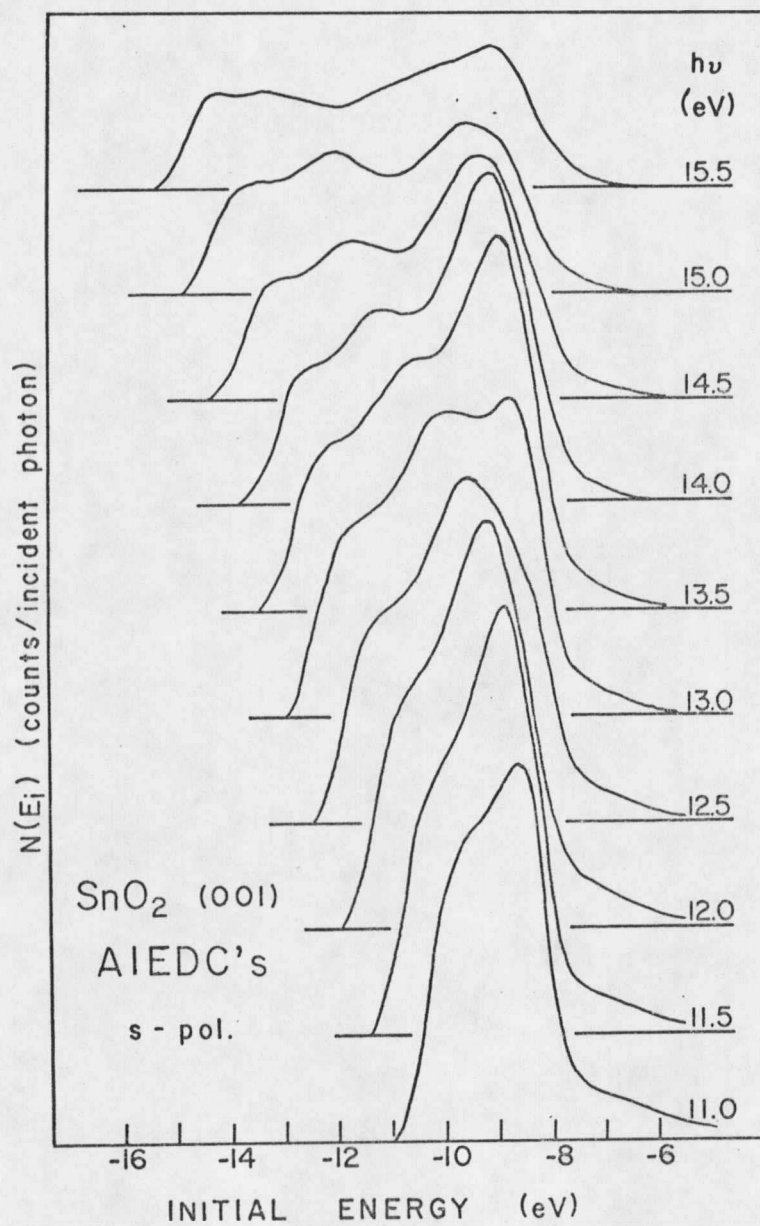


FIG. 26. AIEDC's for $h\nu = 11.0$ to 15.5 eV.

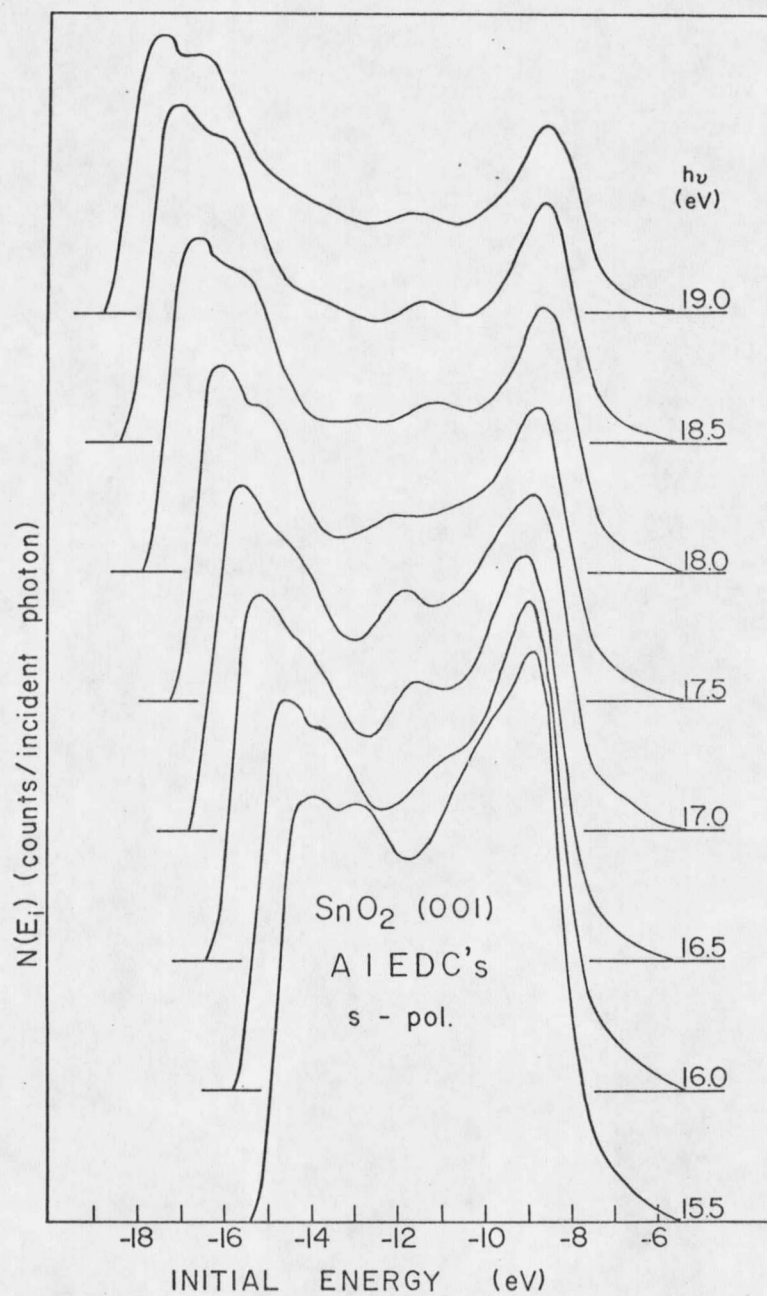


FIG. 27. AIEDC's for $h\nu = 15.5$ to 19.0 eV.

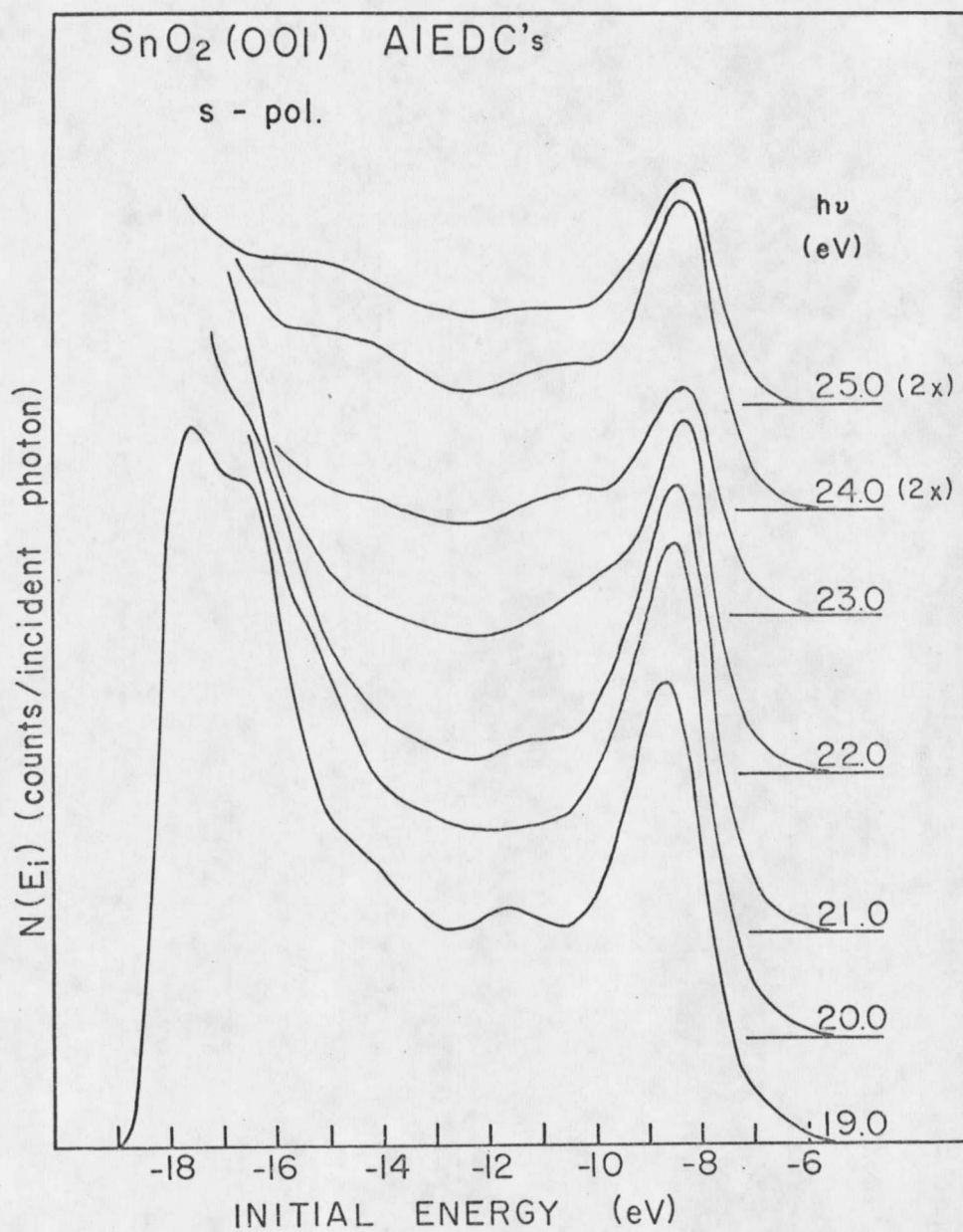


FIG. 28. AIEDC's for $h\nu = 19.0$ to 25.0 eV.

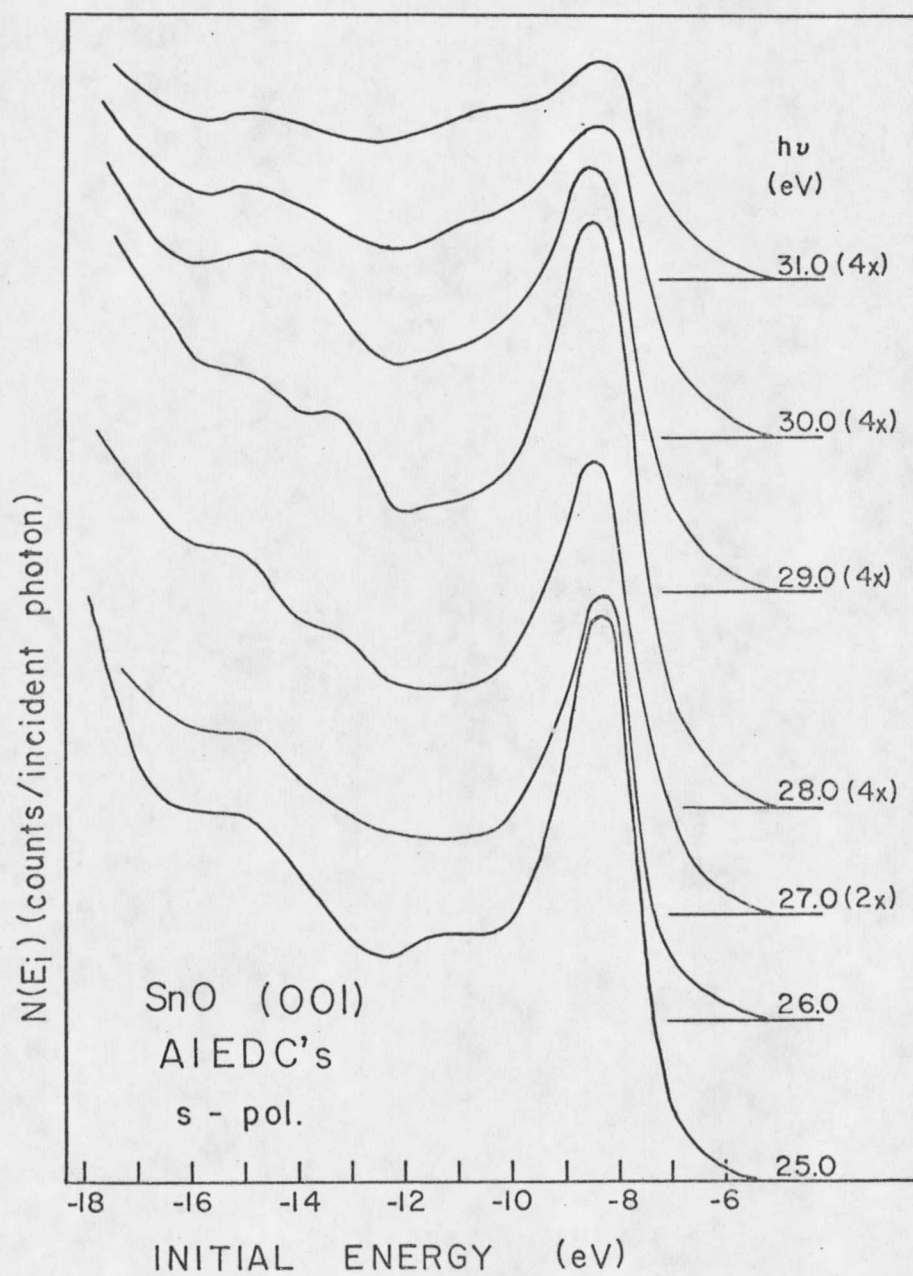


FIG. 29. AIEDC's for $h\nu = 25.0$ to 31.0 eV.

E_f for any point on one of the EDC's of Figs. 26-29, one merely adds the corresponding $h\nu$ and E_i .

At the lower photon energies, the VB emission is strongly modulated by the CBDOS. At higher photon energies, however, CBDOS effects becomes less prominent, and the structures due to the VB's become well defined. From these higher photon energy EDC's, it is possible to determine a total valence band width of about nine eV.

The prominent feature in the VB's is the large peak appearing at E_i between -9 and -8 eV. Its strength and relatively constant initial energy together with the major results of the band calculations^{19,20} suggest that it is probably due to the oxygen 2p derived bands. The remainder of the VB's show weaker emission in these angle-integrated data and cannot be so easily interpreted.

Since the CBDOS effects are considered less important at higher photon energies, the primary VB emission is expected to replicate the VBDOS at these larger $h\nu$'s. Using the band calculations, an estimated VBDOS have been obtained for tin oxide and are compared to the AIEDC taken at $h\nu = 35$ eV in Fig. 30. The shaded portion of the EDC indicates the emission due to inelastically scattered (secondary) electrons. With a bandgap of 3.6 eV and $E_{VB} = -7.0$ eV, none of the emission above $E_i = -10.6$ eV is considered as due to inelastically scattered electrons. The VBDOS estimates were obtained by dividing the published bands into .2 eV increments and

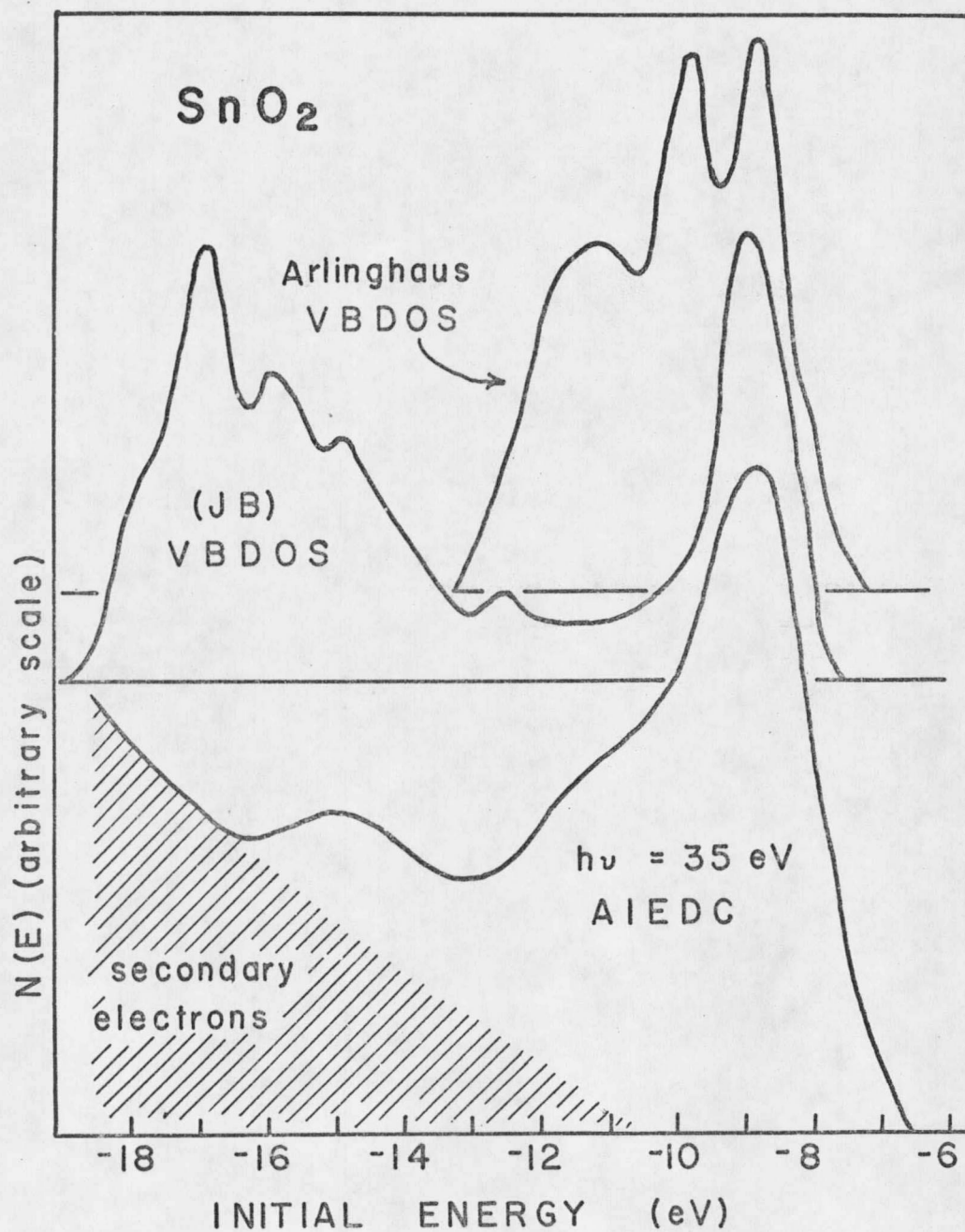


FIG. 30. Comparison of calculated VBDOS to experiment.

measuring the total length of all the bands that lay within each division. These VBDOS's were then smoothed assuming 0.5 eV resolution.

At first glance the agreement with the experiment is marginal at best. The observed VB width was about 9 eV, while the calculated widths are 5.4 and 11 eV. Each calculation does predict a large DOS at VBM, which corresponds to the -9 eV peak present in the data.

Actually, the agreement between the VBDOS estimate from Arlinghaus's calculation and the data is much better than Fig. 30 would seem to imply. Recall that tin derived 4d bands were also calculated in his APW calculation, but Arlinghaus chose not to publish the details of these 4d bands. The VBDOS estimate derived from the AP calculation therefore only contains the VBDOS due to the oxygen 2p bands. If the observed structure in the EDC below about -13 eV were indeed due to tin 4d bands, agreement would be quite good. Allowing the upper two peaks of Arlinghaus's VBDOS to coalesce into one broader peak results in good agreement for the upper five eV of the VB's. Again, this would not be a drastic step, since the energies in the APW calculation of Arlinghaus were only determined at a few specific symmetry points. The subsequent bands were estimated using compatibility relations and other symmetry considerations.

Conduction band (CB) features are found in the angle-integrated data. Emission features due to CBs manifest themselves in EDCs in two ways; first in the primary emission, where the CBs modulate the VB emission, and then in the secondary emission, where the CBs are filled with inelastically scattered electrons. Both of these effects are observed in the EDCs, but since the EDCs of Fig. 26-29 are plotted with respect to E_i , the final state features, CBDOS, are not evident by simple inspection. Instead of replotting the EDCs as a function of E_f , CISs have been chosen to illustrate the CBDOS. By virtue of the fact that E_i is a constant in a CIS, the final state features are directly manifested, as was mentioned previously.

A set of CMA angle-integrated CISs are shown in Fig. 31, plotted as a function of photon energy. The final state features observed at $E_f = 2.5$ and 4.5 eV are indicated by the heavy dots on each spectrum. These features are attributed to large densities of states in the CBs. A strong coupling of the initial states for E_i between -8.5 and -9.75 eV to the 4.5 eV final states is observed, which is a manifestation of the oxygen 2p bands coupling to the CBs. This latter coupling can be found in the EDCs for $h\nu \sim 14$ eV, while coupling to the $E_f = 2.5$ eV CB state is difficult to observe because of its proximity to the vacuum level. The spectra for $E_i < -10$ eV consist primarily of inelastically scattered primaries and consequently show little dependence on E_i . Also in evidence in these

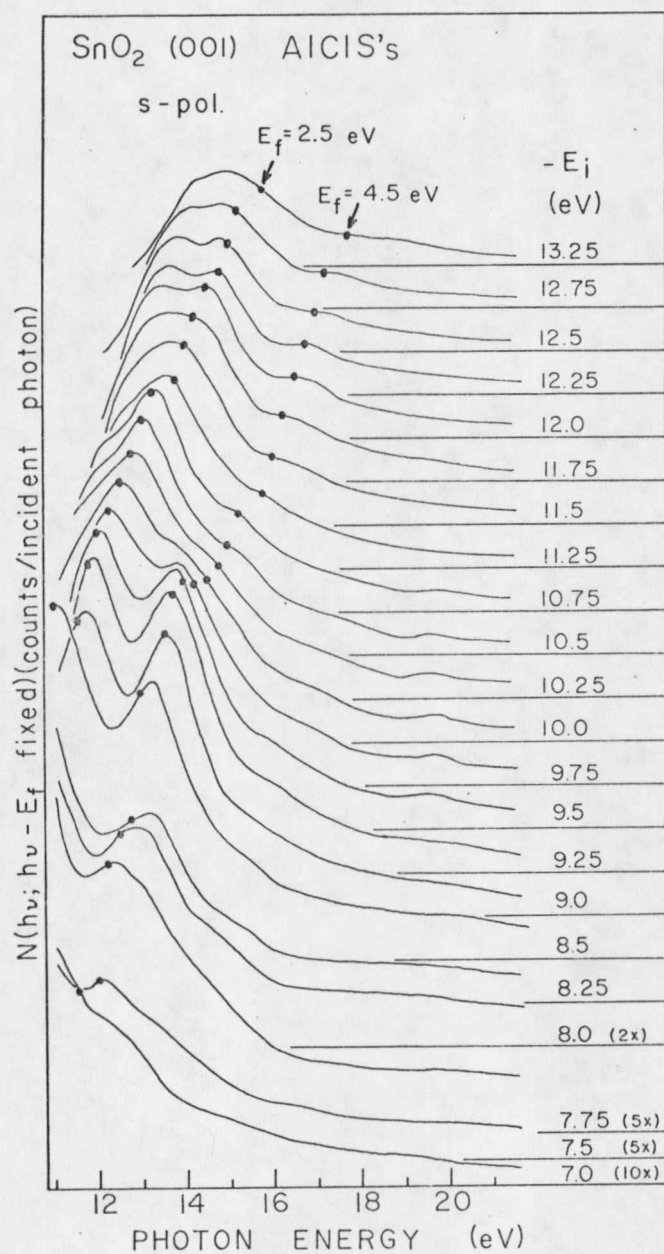


FIG. 31. AICIS's demonstrating CBDOS.

spectra is a feature at $h\nu \approx 19.7$ eV for E_i between -9.5 and -10.75 eV. Since this feature is not persistent for either a particular E_i or E_f , it is not interpretable by inspection. Its nearly constant $h\nu$ value suggests two possibilities: (1) hole decay for photoabsorption into states below the vacuum level or (2) a strong joint density of states due to parallel bands. The latter explanation is suggested, since no direct emission is observed for states lying near 19.7 eV below the CBM.

2. Primary Core Emission. Angle-integrated data taken at higher photon energies also revealed the presence of a core level centered at approximately $E_i = -30$ eV. This core state can be readily identified in the AIEDC's of Fig. 32. As in the VB emission, core emission is also strongly modulated by the CBDOS for $E_f \lesssim 5$ eV. The higher energy EDC's, however, conclusively demonstrate the primary core emission.

The atomic origin of this core emission is not obvious. Either the tin 4d or oxygen 2s states could conceivably be involved. According to the calculations of Jacquemin²⁶ and Arlinghaus¹⁹ (see Fig. 6), the oxygen 2s would seem to be a better choice because of its energy position. Moreover there is evidence that the tin 4d levels are contributing to the lower VB's (see angle-resolved data). They would thus not be so apt to also contribute to this core level.

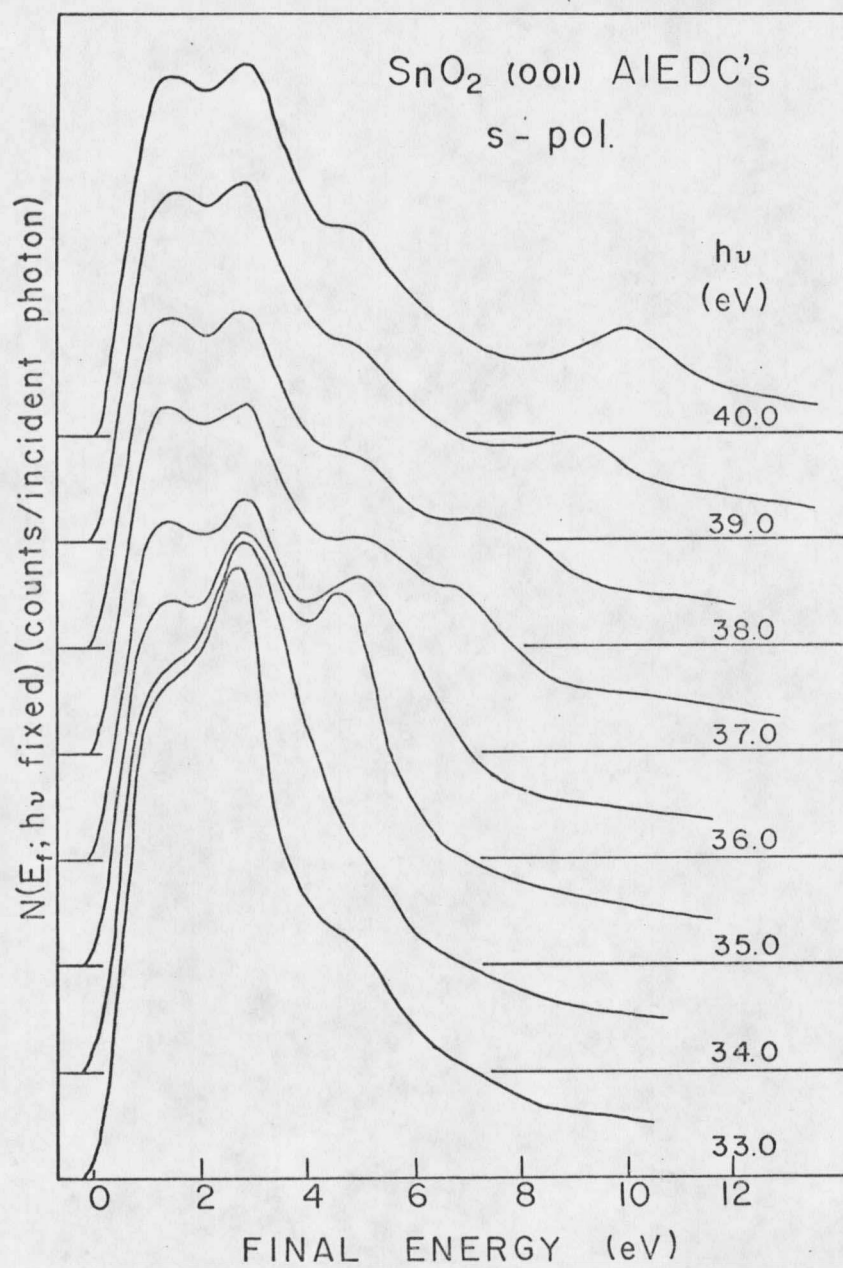


FIG. 32. AIEDC's showing SnO_2 core.

On the other hand photoemission from s cores in other materials has normally been so weak as to be essentially unobservable.⁴⁶ This core was strong enough to lead one to believe that it probably wasn't due to the oxygen 2s core. The exciton splitting (to be discussed next) also supports the tin 4d interpretation for the core level. Further discussion of this problem of the origin of the core emission will be left until later. At this time another feature due to the core, but not depending on its atomic origin, will be discussed.

3. Core Excitons. The emission due to the core was also studied utilizing the CFS. As mentioned before, this method serves to negate the modulation effects on the emission due to the CBDOS features. A few such AICFS's are shown in Fig. 33. The spectra are plotted as a function of photon energy, so as the final energy is increased from curve to curve, initial state features move to higher photon energies. As in the AIEDC's of Fig. 32 the primary core emission is broad, with no internal splitting resolved. Note, however, the relatively weak structures at constant photon energies of 25.9 and 26.9 eV. These "hv features" cannot be interpreted as due to mere VB or CB effects in a strictly interband transition picture. With $E_{VB} = -7.0$ eV and a band gap of 3.6 eV, the energies of these hv features correspond very closely to the core to CBM energy.

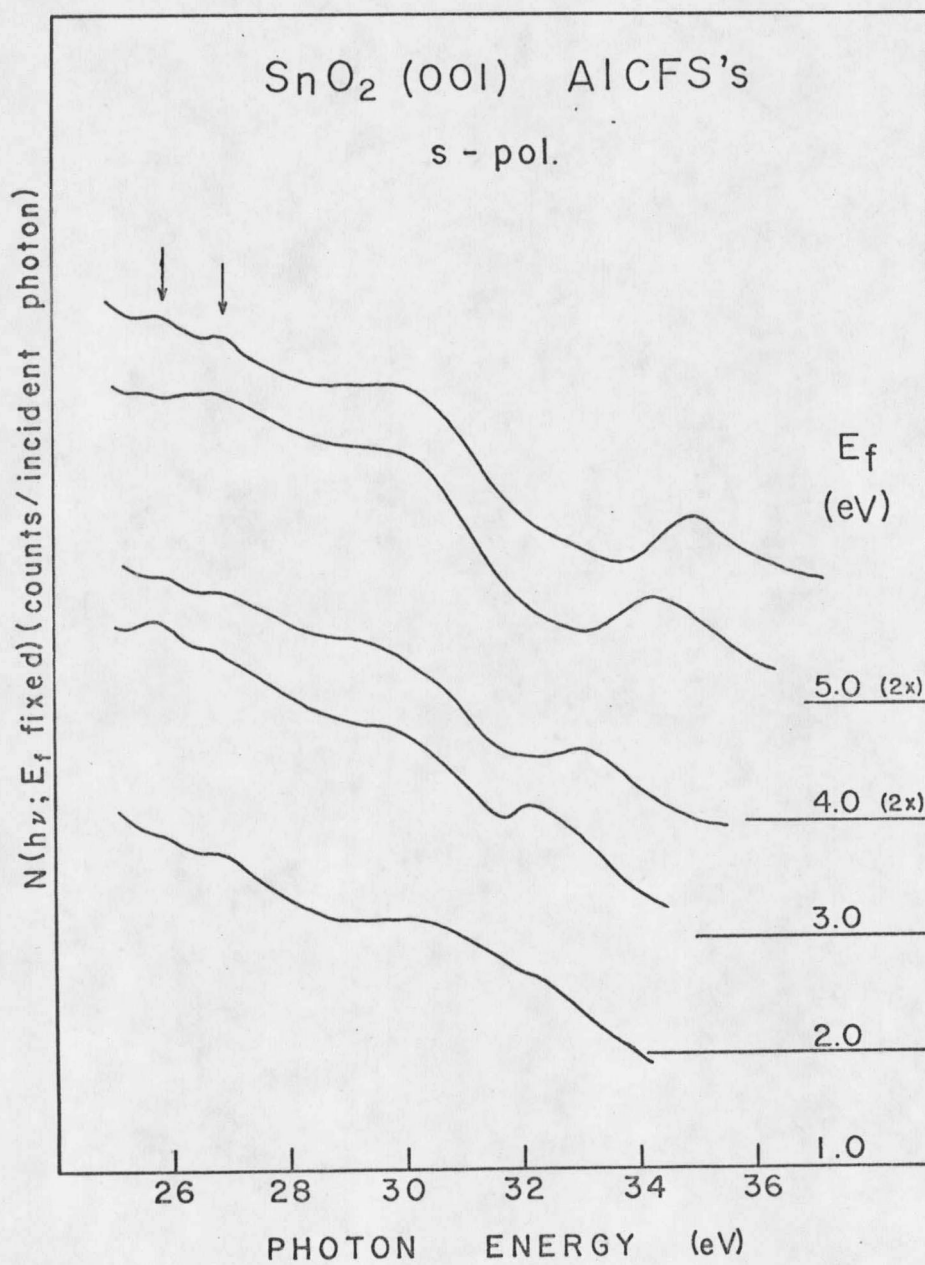


FIG. 33. AICFS's showing SnO_2 core.

More AICFS's up to $E_f = 16.0$ eV are shown in Fig. 34 for photon energies from 24 to 30 eV. Both $h\nu$ features persist, though feebly at times, up to $E = 13.0$ eV. These $h\nu$ features are interpreted as due to the Auger decay of core excitons.^{47,48} The radiationless Auger decay of the exciton is shown in Fig. 35. The process is similar to the Auger process described before, except that here the hole filling and ejected electrons originate from the valence bands instead of other core levels. Only VB electrons at the top of the VB's are shown as utilized in the decay process, while, in principle, the electrons could originate from anywhere in the VBs. The case shown results in the ejected electron having the maximum energy for the Auger transition. Another point should be mentioned. As the Auger process is typically represented by an energy level diagram, the electron which was originally part of the exciton would be stranded at an energy below CBM. Since this level only exists for the exciton, which is now gone, this is not allowed. Exactly what happens to this electron is not certain, but it is probable that it is transferred to the CBs. The binding energy of the exciton, δ , must then be accounted for. The simplest argument would indicate that this energy is merely subtracted from the ejected electron, thus lowering the Auger distribution by the amount δ , usually on the order of an eV or less.

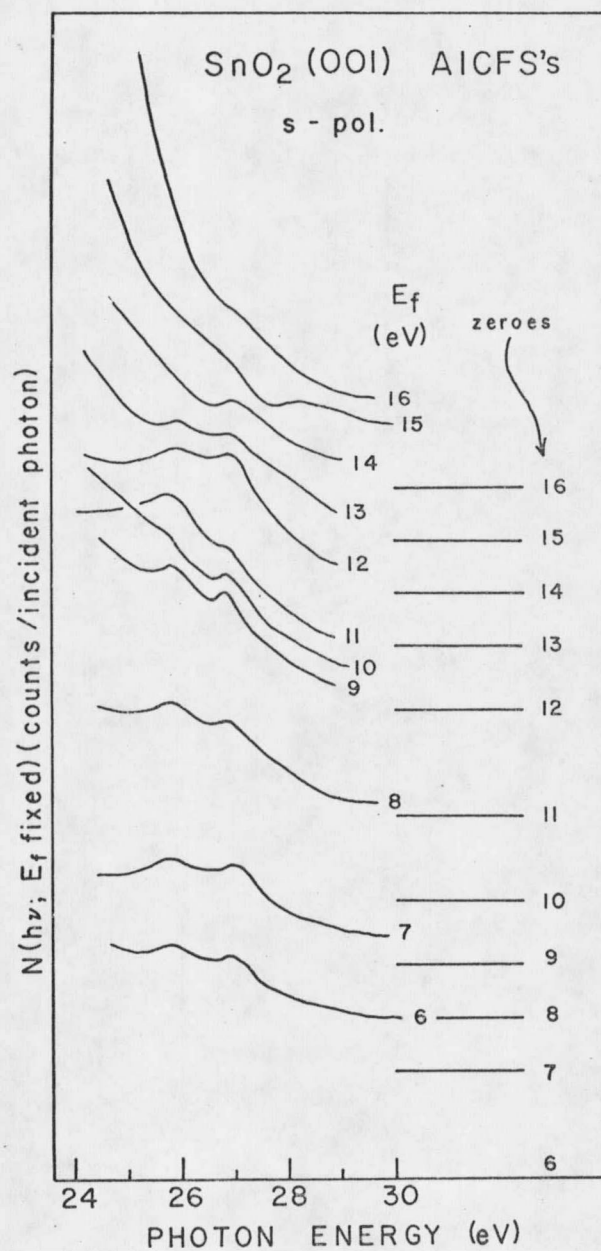


FIG. 34. AICFS's demonstrating exciton Auger decay.

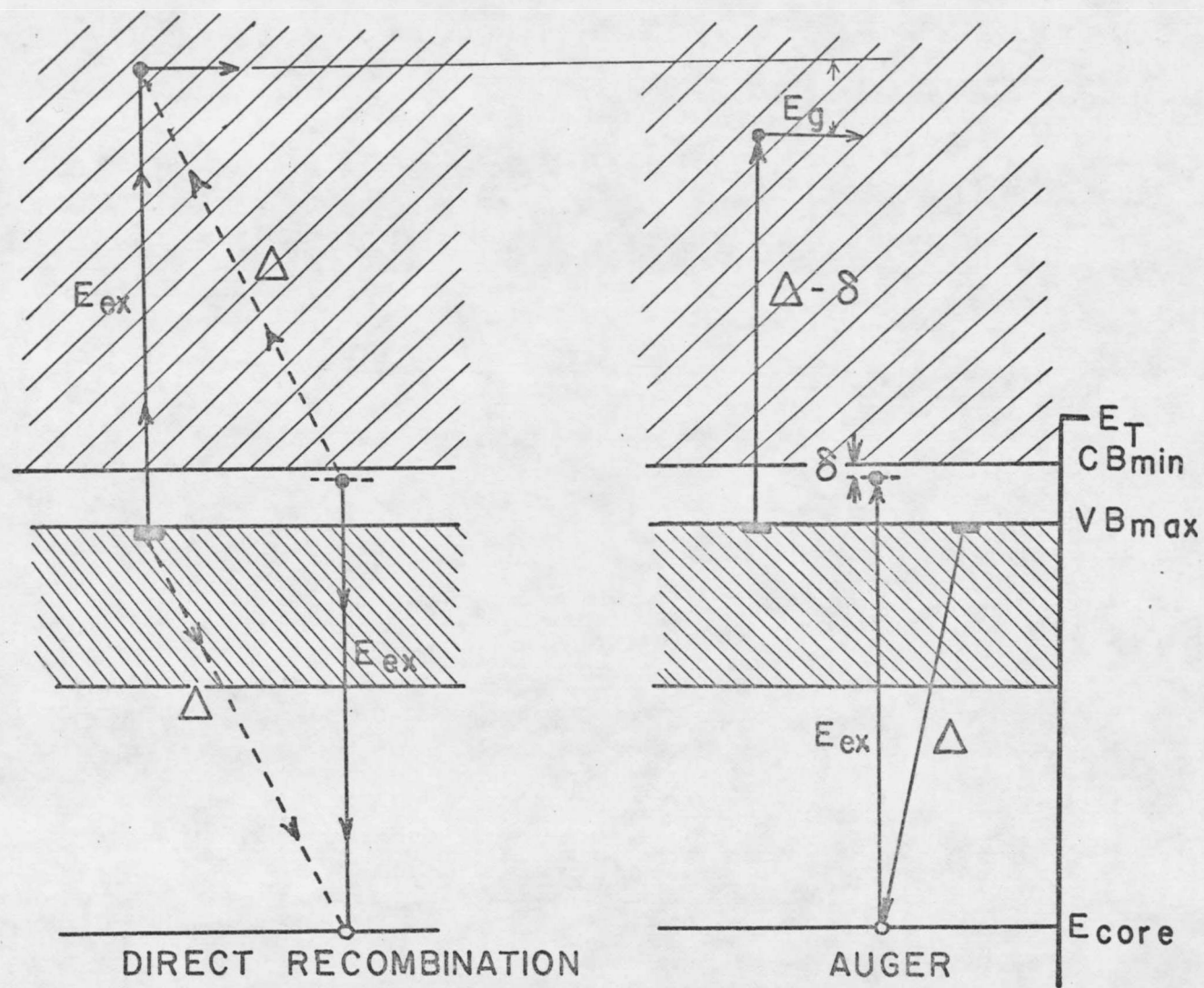


FIG. 35. Direct recombination and Auger decay modes of core exciton.

By ignoring matrix element effects, the distribution of the ejected Auger electrons should be given by the self-convolution of the VBDOS. The highest energy Auger electron would have energy $E_{\text{ex}} + E_{\text{VB}} - E_{\text{g}}$. For the case of tin oxide, then, the highest energy electron resulting from the Auger decay of the 25.9 eV exciton would be $E_{\text{f}} = 15.3$ eV. The 26.9 eV exciton would yield a similar distribution, shifted to higher energy by one eV.

Such a predicted Auger distribution for the 25.9 eV exciton was calculated using the experimental VBDOS of Fig. 30. The resulting curve is shown in Fig. 36. Note that although the earlier arguments indicated that the distribution would extend to 15.3 eV, the calculation shows that the enhanced emission due to the Auger decay of the 25.9 eV exciton should be very weak above 14 eV final energy. This is consistent with the data. The 25.9 eV enhancement is observed in the 13 eV CFS, but not in the 14 eV CFS, while the 26.9 eV enhancement was still observed in the 14 eV CFS, and not for the 15 eV CFS. This agreement is considered ample justification for the excitonic interpretation.

The exciton can also decay via the direct recombination (DR)^{47,48} process diagrammed in Fig. 35. The figure shows two indistinguishable DR processes indicated by the solid and dashed arrows, respectively. Whether the exciton "collapses on itself" transferring the energy to a VB electron, or a VB electron fills the core hole transferring

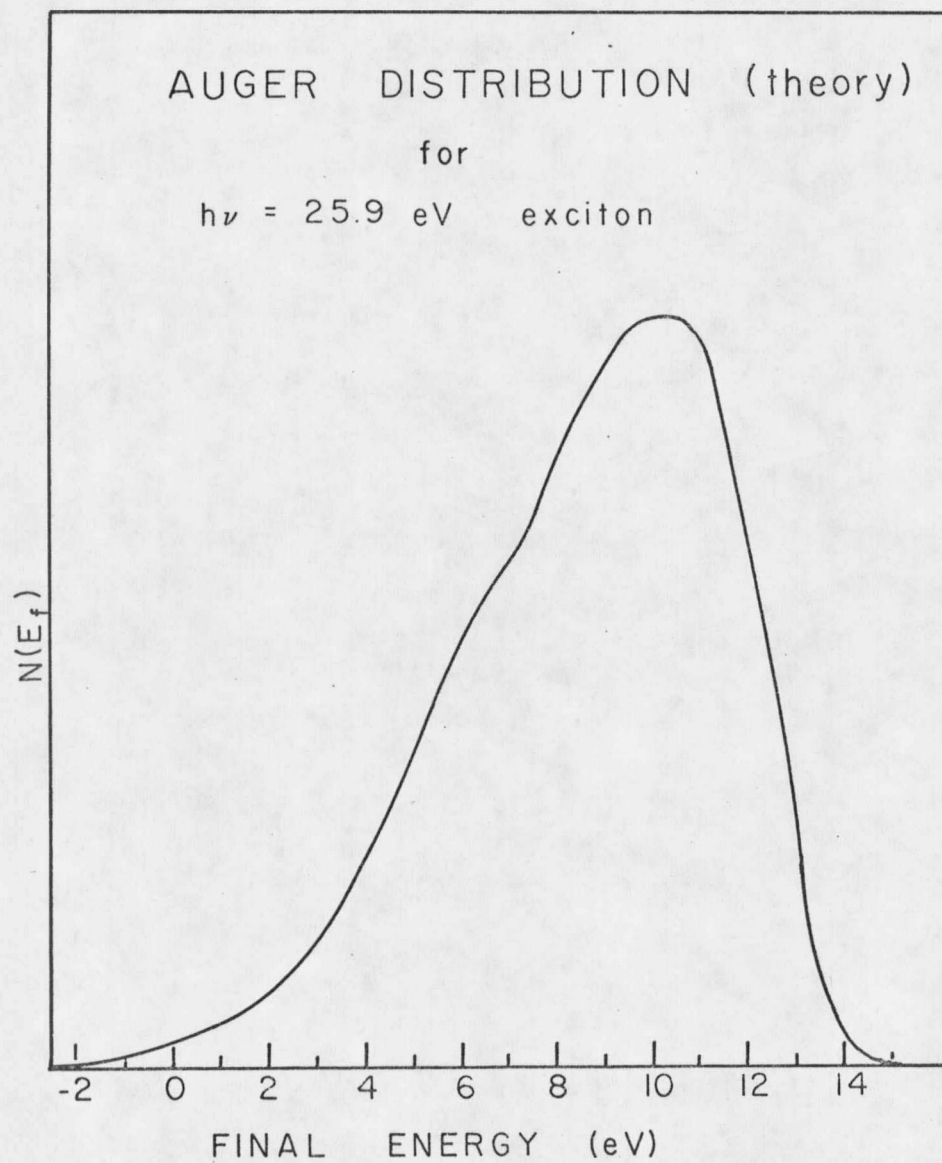


FIG. 36. Predicted Auger distribution using experimental VBDOS.

the energy difference to the electron which was part of the exciton, the resultant excited electron has the same energy. The maximum energy of a DR electron is $E_{\text{ex}} - E_{\text{VB}}$, just the same as the maximum energy for the primary emission from the VBs for this photon energy, but E_g higher than the maximum energy for the Auger decay of a similar exciton. Only one VB electron is involved in the DR process as opposed to two for the Auger process. Consequently a simple model ignoring matrix element effects predicts that the DR enhancement should replicate the VBDOS. So at the exciton energies one would expect slightly more apparent VB primaries than just to either side of those energies. Moreover, the extra DR emission would be expected to be proportional to the VBDOS corresponding to each respective initial energy.

To check for the existence of this DR process, CIS spectra were taken for initial energies near the top of the VBs. In this manner gross VBDOS features were eliminated, and the kinetic energies involved were too high for any of the enhanced emission to be due to Auger electrons. Selected VBCISs are shown in Fig. 37. For $E_i \gtrsim -7.25$ eV, the $h\nu$ features appear again in the spectra. The existence of these DR enhancements is considered further evidence for the excitonic interpretation to these features.⁴⁶

There is, however, another complication. The CISs for $E_i = -8.0$ to -11.0 eV do not show any enhancement at the exciton

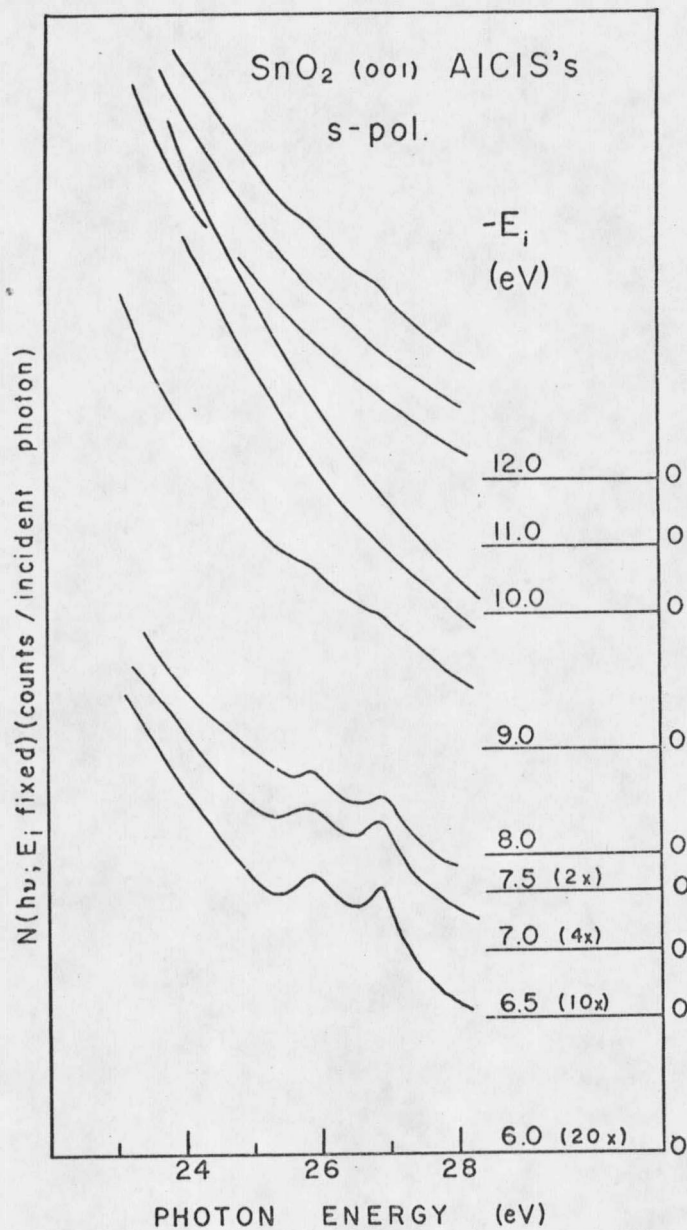


FIG. 37. AICIS's demonstrating DR enhancement.

energies. The simple model put forth predicted enhancement throughout the VB primaries. Moreover, the DR enhancement is strongest for initial energies slightly above what has been called VBM. These occupied states above VBM are interpreted as defect derived (next section) and not indicative of bulk, stoichiometric tin oxide. It is proposed that the excitons decay by DR preferentially at these defect sites, transferring the exciton energy to electrons in the associated defect state. This is not mere conjecture. Such processes are also believed to occur in alkali halide crystals, where the defects in those cases are F-centers.⁴⁹ The oxygen vacancies in tin oxide are more numerous at the surface, so that electrons resulting from the DR process at these sites would have a higher probability of escape and ultimate detection. The DR process involving the bulk VBs could be ignorably weaker in this case.

The exciton features just discussed are good examples of the utility of the CIS and CFS modes of photoemission. Even though the exciton enhancements were very weak, they were directly observable in the CIS's and CFS's because of their photon energy dependence. EDC's at 26.5, 26.9 and 27.2 eV are shown in Fig. 38. The curves are not appreciably different. The VB primary attenuation due to inelastic scattering easily overshadows any additional enhancement due to the exciton decay in the 26.9 eV EDC. True, the enhanced emission is there, but it could only be deciphered by taking very

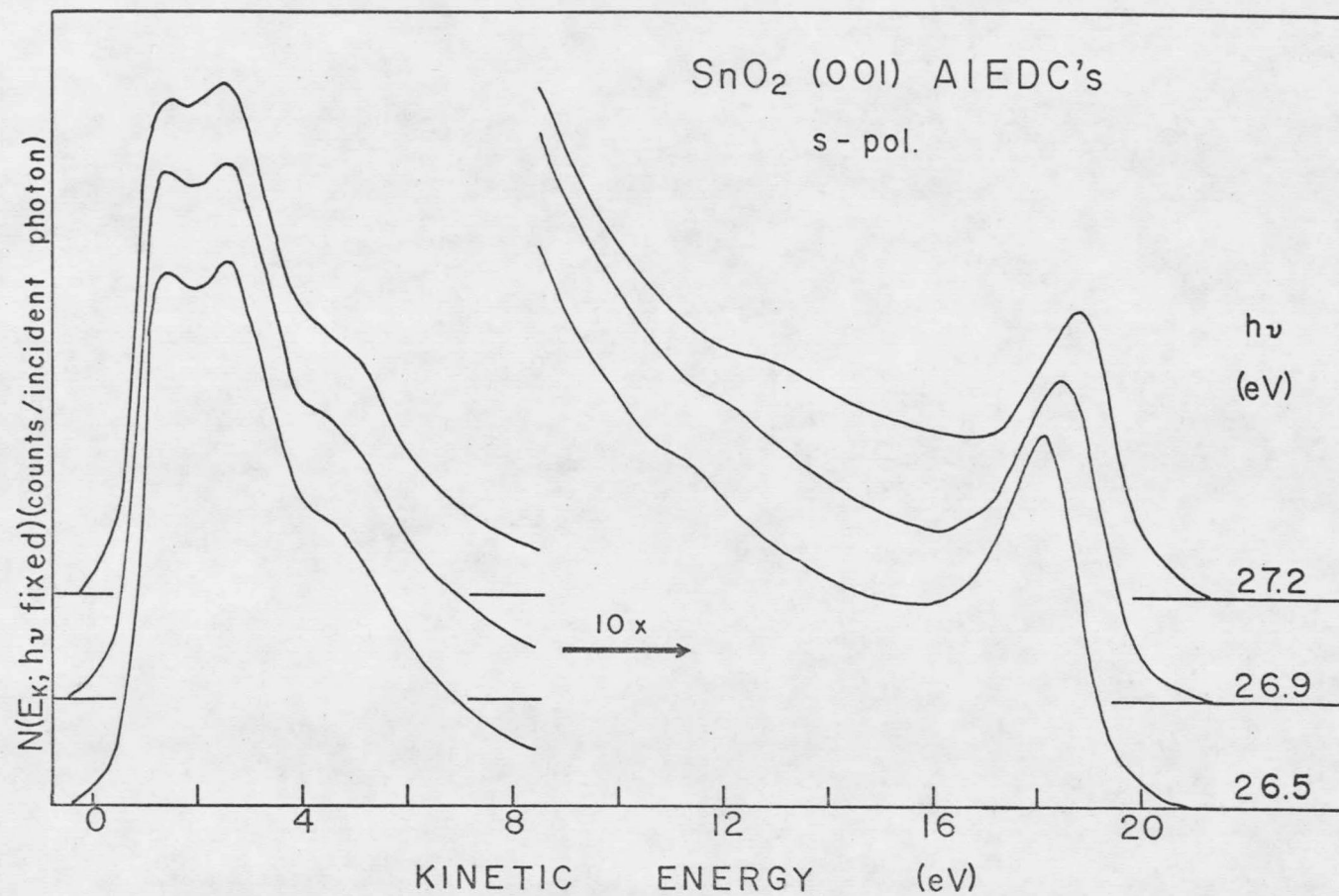


FIG. 38. AIEDC's at photon energies near and at exciton energy.

accurate difference curves - an arduous task, which one would not consider unless he had previous knowledge of the existence of the exciton enhancement.

4. Discussion of the Atomic Origin of the Core. It was mentioned earlier that the exciton data tended to support the tin 4d interpretation for the core level observed at $E_i \sim 30$ eV as opposed to an oxygen 2s interpretation. The splitting of the two excitons is ~ 1.0 eV. Within the instrumental resolution, this matches the spin-orbit splitting of the tin 4d core in metallic tin.

Fig. 39 shows several EDCs taken on vapor deposited films of tin. The energy of these core levels is 23.9 and 24.9 eV, respectively, below the Fermi energy, E_F . This agrees with the x-ray data, tabulated by Bearden and Burr, which indicates the onset of tin 4d to E_F transitions to be 23.9 ± 0.3 eV.⁵⁰

If the observed core were indeed due to atomic like tin 4d levels, it would seem that primary emission from the core should be resolved as it is for the metallic case. To check if poor instrumental resolution was possible the cause of the lack of resolution of the core spin-orbit splitting, a thin film ($\sim 50 \text{ \AA}$) of metallic tin was evaporated over the tin oxide crystal. CFS's taken on this sample are shown in Fig. 40. Both the cores are in evidence, with the oxidized cores still unresolved. Obviously poor instrumental

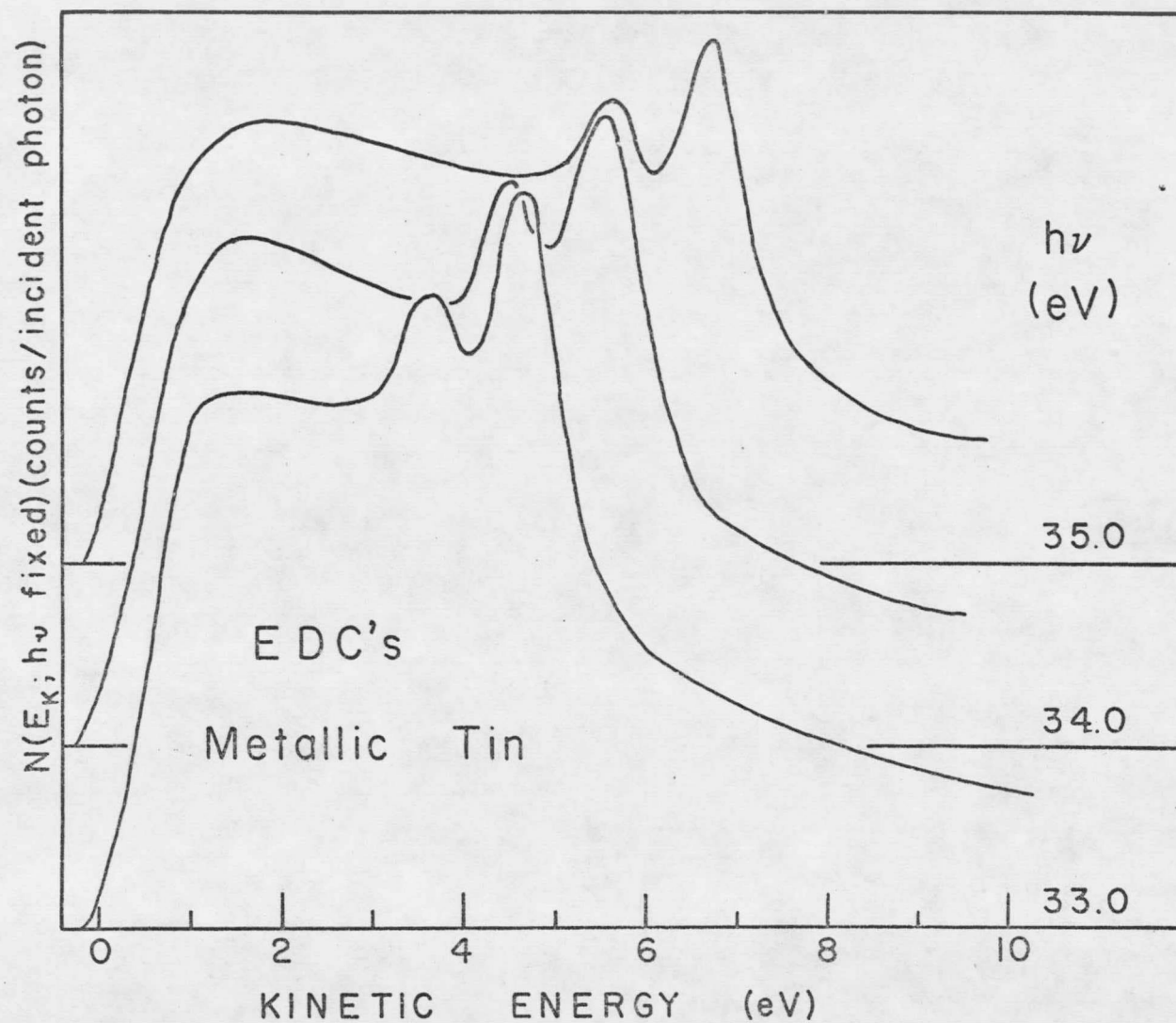


FIG. 39. EDC's of metallic tin showing 4d core emission.

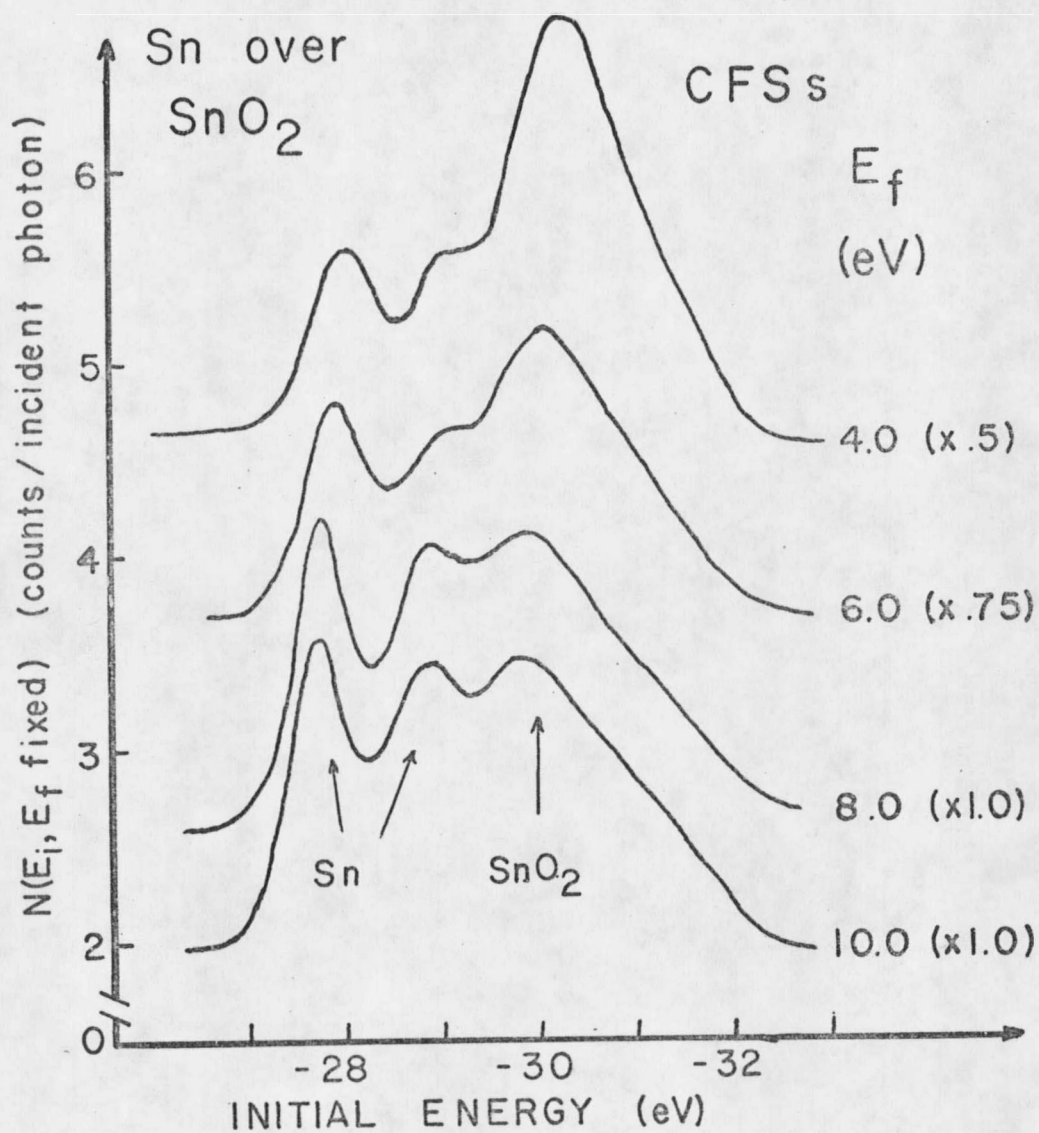


FIG. 40. AICFS's on SnO_2 with Sn overlayer.

resolution was not responsible for the broad unresolved core emission from tin oxide.

Lifetime broadening could easily account for the resolution differences in the two cases. The final state of the crystal when a core electron has been transferred to the CBs not only consists of the excited electron, but the core hole as well. If the lifetime of the core hole is short, its energy uncertainty will be correspondingly large. The excited electron must also have a similar spread in energy.

The lifetime of the hole is dependent on valence electron density - the more valence electrons, the greater the probability of hole decay, hence the shorter the lifetime. Metallic tin has four valence electrons per atom, while tin oxide has 12 valence electrons per SnO_2 . Taking into account the crystal structures, one finds valence electron densities of $.15 \text{ electron/\AA}^3$ in metallic tin and $.33 \text{ electron/\AA}^3$ in tin oxide.

Because of screening, the exciton is much longer lived than a normal core hole.⁴⁷ Consequently the observed exciton enhancement width is more a function of instrumental resolution than lifetime broadening. This would account for the presence of the resolved exciton enhancements and the absence of resolved primary emission splitting.

By assuming a gaussian distribution for each core level and the normal 3:2 statistical ratio for the $j = 5/2$ and $j = 3/2$ 4d levels, curves were calculated to fit the data of Fig. 40. The best fit occurred for the oxide cores shifted to 2.1 ± 0.2 eV below their metallic counterparts. This corresponds to initial energies of -29.8 and -30.8 ± 0.2 eV for the $j = 5/2$ and $j = 3/2$ states, respectively. The binding energy for each exciton (assuming $E_g = 3.6$ eV) is then 0.5 ± 0.2 eV, well within the normal range of exciton binding energies.

B. Angle-Resolved Data

1. General Angle-resolved Techniques. Polarization dependent angle-resolved ultraviolet photoemission spectroscopy (PARUPS) data can be collected in a number of ways. For a given polarization orientation, emission can be gathered as a function of $h\nu$, E_f , θ or ϕ , where θ and ϕ are the emission angles relative to the crystal as defined previously. With θ and ϕ fixed, EDC's CIS's and CFS's may be taken as in angle-integrated data. On the other hand, $h\nu$, E_f and θ can be held constant while ϕ is varied. This was normally done by rotating the sample and is called a sample ϕ -pattern. Unfortunately, due to the idiosyncrasies of the angle-resolving system, it was not possible to hold ϕ constant and continuously vary θ . (See Appendix B).

Different techniques were used depending on the portion of the emission hemisphere and photon energy range that were involved. For instance, at normal emission, $\theta = 0$, EDC's, CIS's and CFS's were taken as in the angle-integrated case. In surveying the data sample ϕ -patterns were taken for various polar angles for photon energies and final energies that corresponded to important features, e.g., large CBDOS, VBDOS and core levels. In searching for critical points in the BZ, the CFS was employed extensively. Since in a CFS, E_f is constant, then for a given θ and ϕ , $\bar{k}_{\parallel}$ is also constant. In the direct transition model, this $\bar{k}_{\parallel}$ also corresponds to the $\bar{k}_{\parallel}$ for the initial and final states involved in the transition. A judicious choice of θ , ϕ and E_f allowed the observation of transitions originating along lines of high symmetry in the BZ. For the (001) face of SnO_2 the $k_{\parallel} = \text{constant}$ lines surveyed were λ , V and W .

For $\theta \neq 0$, $\bar{k}_{\parallel}$ is not a constant for EDC's and CIS's, since E_f changes in each of these. However EDC's were still used frequently for $h\nu \gtrsim 25$ eV.

2. Normal Emission. The simplest emission angle to study with angle-resolved UPS is normal emission, $\theta = 0$. For this case $\bar{k}_{\parallel} = 0$, so for SnO_2 (001) only transitions occurring along the λ line of the Brillouin Zone are involved, assuming direct transitions.

A set of normal emission, s-polarization EDC's is shown in Figs. 41-43. The overall features of the data are very similar to the angle integrated data considered before. The strongest VB emission still occurs for $E_i \sim -9$ eV, and the CBDOS features are also similar. The deeper VB emission, however, is much weaker in the current data, although the total VB width is still recognizable.

The most prominent difference between this normal emission data and the angle-integrated data is the initial state structure just above VBM, extending to about $E_i = -6.0$ eV, 1.0 eV above the VB edge. This "foot" is not interpreted as due to the intrinsic VBs of tin oxide, but rather is attributed to extrinsic effects derived from oxygen deficiencies. Discussion of this point represents a significant digression.

3. Extrinsic Emission. A number of combined factors provide the rationale for excluding the weak emission above $E_i = -7.0$ eV as being due to the bulk VBs. The first of these is its weakness, combined with the fact that it is at the top of the VBs. As a general rule, semiconductors and insulators have large DOS at VBM. This is derived from the fact that semiconductors and insulators have filled bands and empty bands only. There are no partially filled bands as in metals. Moreover the maximum of any band must be flat, $\vec{\nabla}_{\vec{k}}(E) = 0$. This normally results in a high DOS at VBM.

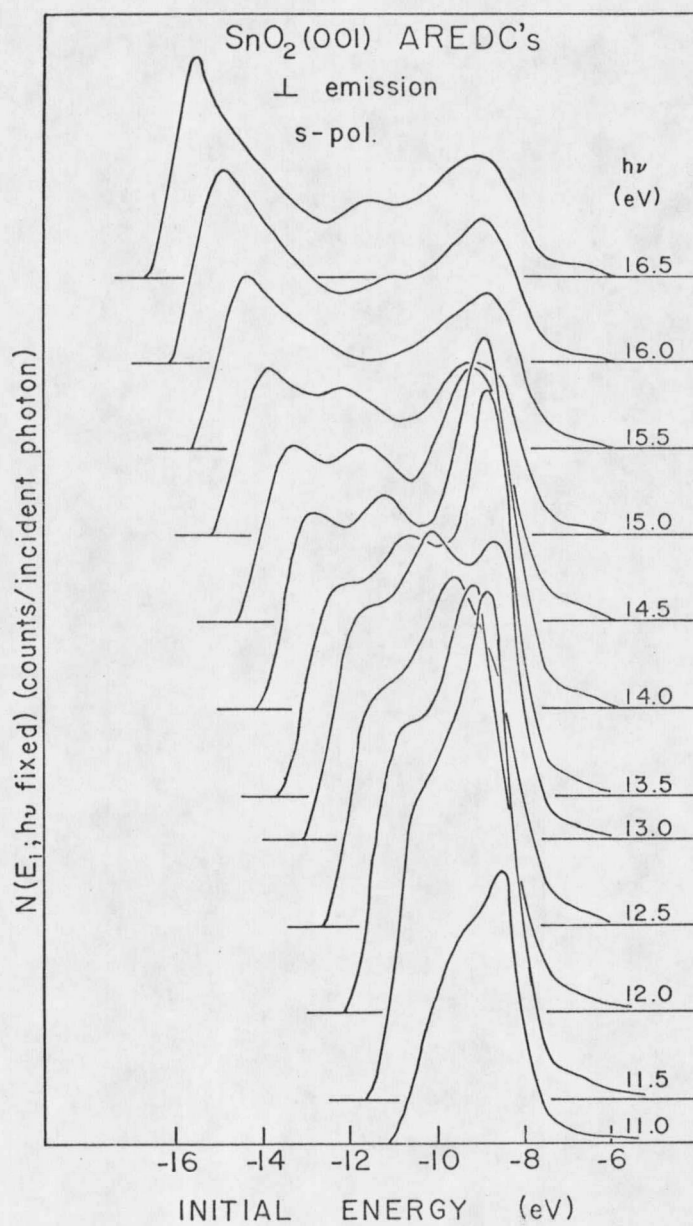


FIG. 41. Normal emission AREDC's for $h\nu = 11.0$ to 16.5 eV.

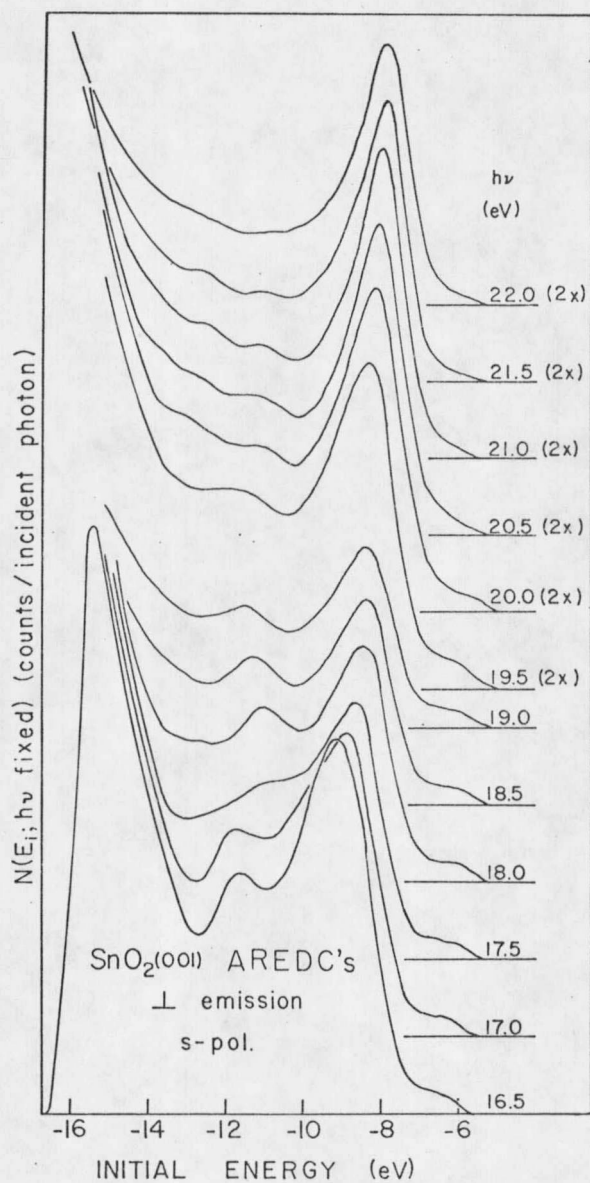


FIG. 42. Normal emission AREDC's for $h\nu = 16.5$ to 22.0 eV.

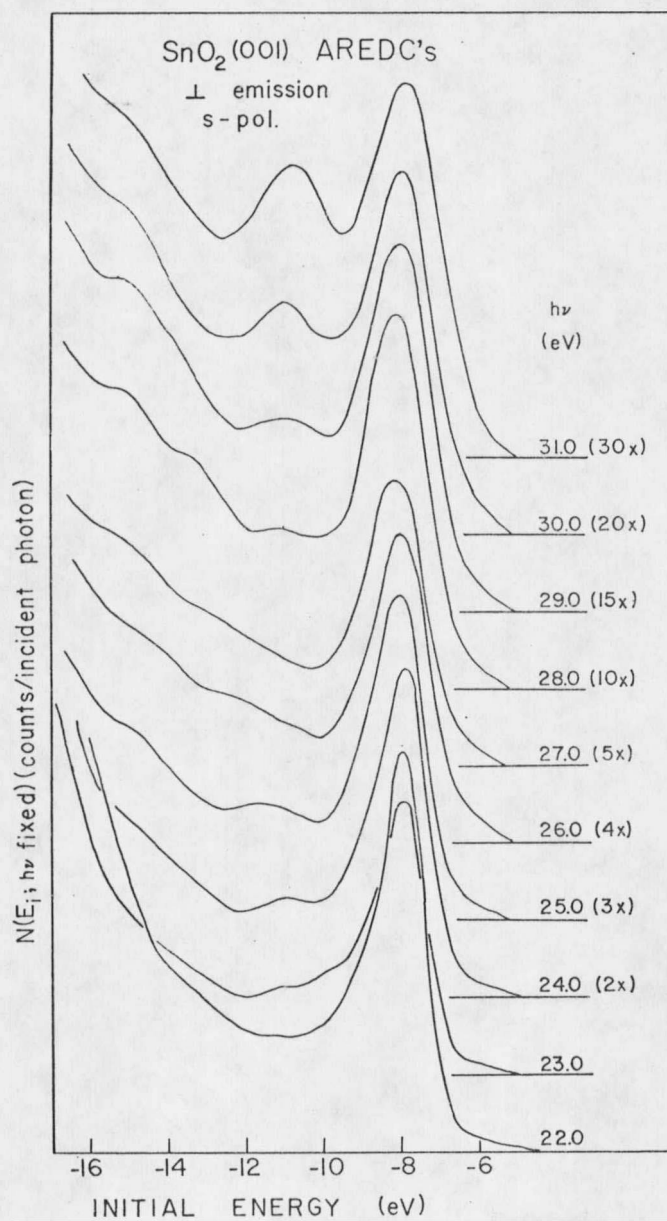


FIG. 43. Normal emission AREDC's for $h\nu = 22.0$ to 31.0 eV.

Also frequently two or more bands are degenerate at VBM, further increasing the VBDOS at VBM. A high DOS at VBM was predicted by the band calculations of both JB²⁰ and Arlinghaus¹⁹. (Recall Fig. 30.) This foot, on the other hand, occurs essentially only at normal emission (within 20° of $\theta = 0$), so throughout the emission hemisphere, even at its strongest, the foot contributes only about 1/1000th of the total primary emission. Fig. 44 shows EDCs taken for a variety of polar angles. Spectra taken at other photon energies, azimuthal angles and other polarization conditions demonstrated a similar behavior. That is, the emission from states for $E_i \gtrsim -7.0$ eV was mostly confined to within 20° of normal emission.

Probably the strongest argument against the foot as emission from stoichiometric bulk VBs lies in the location of the Fermi level. Tin oxide is strongly n-type, which should result in a Fermi level very near the CBM. If one considers the foot to be due to intrinsic VB emission, then VBM would be at -6.0 eV. Then the 3.6 eV band gap and measured Fermi level of $E_F = -3.8$ eV would place the Fermi level only 0.4 eV above midgap. The location of the Fermi level was determined by evaporating a tin film onto the crystal. The highest kinetic energy photoelectrons from this film corresponded to emission from the Fermi level. This determination is illustrated in Fig. 45.

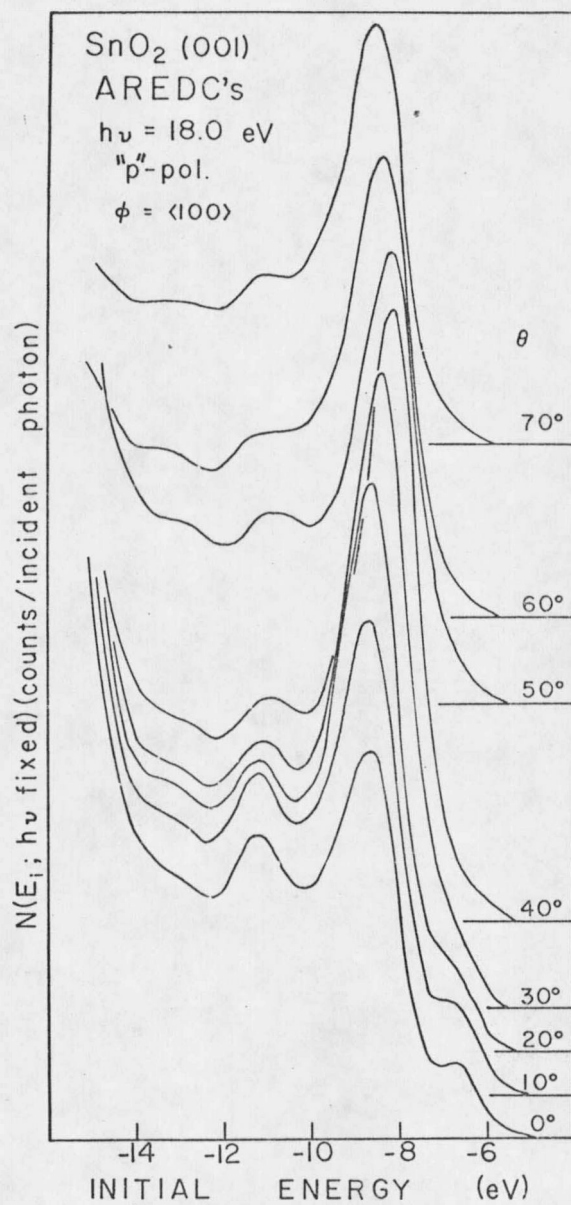


FIG. 44. AREDC's taken at $h\nu = 18.0 \text{ eV}$, $\phi = \langle 100 \rangle$.

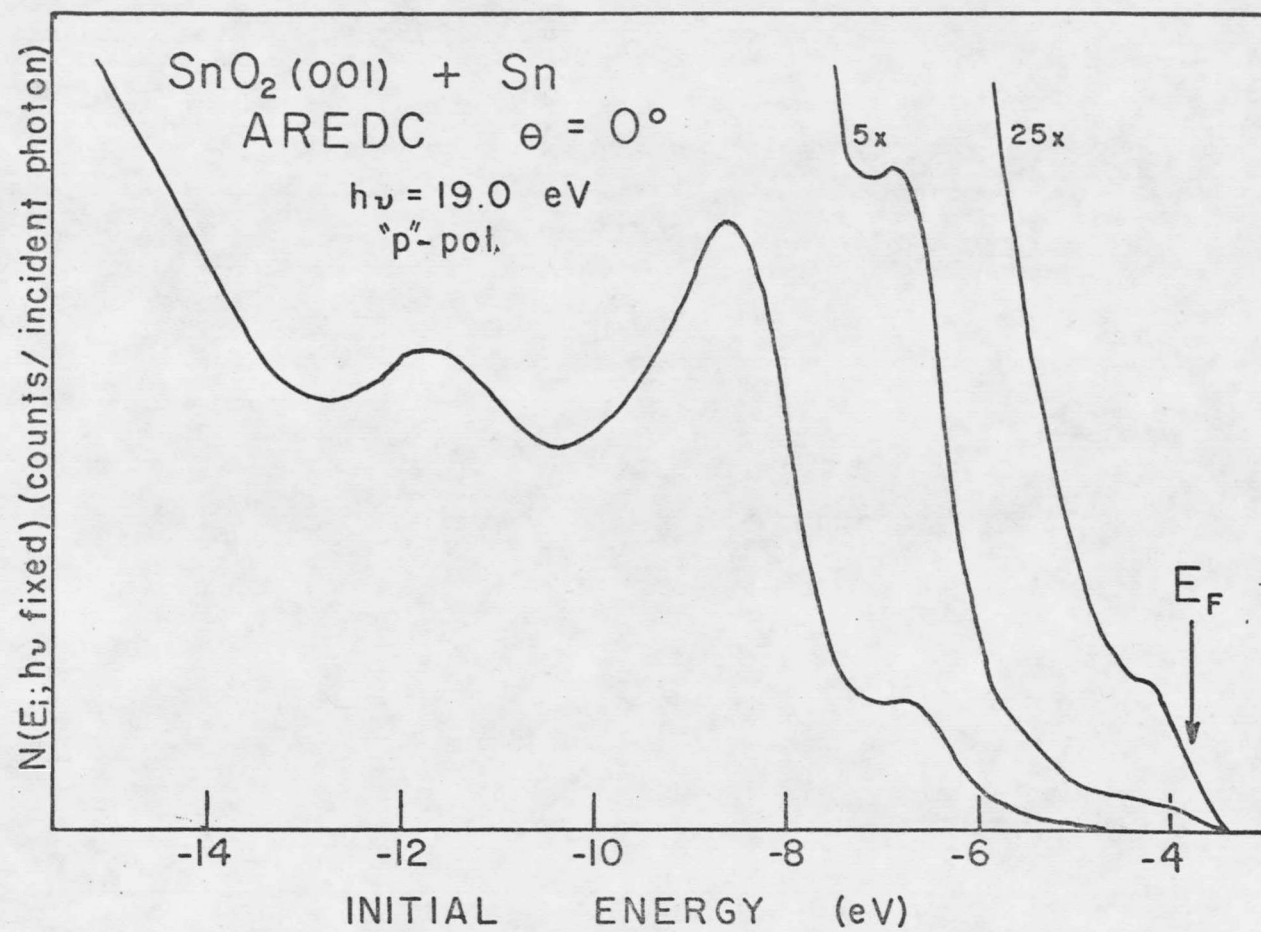


FIG. 45. EDC of SnO₂ with Sn overlayer showing emission at E_F .

One may perform a simple model calculation for the Fermi level to see if the latter value is reasonable. Assuming parabolic bands with equal effective masses, E_F can be calculated as a function of donor concentration N_d .⁵¹ The results of such a calculation for a semiconductor with $E_g = 3.6$ eV are shown in Fig. 46. The donors levels were chosen to be degenerate with CBM. For E_F to be only .4 eV above midgap would require a donor concentration of about 1 cm^{-3} . The actual donor concentration was estimated from the literature to be about $10^{15} - 10^{16} \text{ cm}^{-3}$.⁸ For this donor concentration level, E_F would lie approximately 3.2 eV above VBM, i.e., 1.4 eV above midgap. This agrees with an assignment of ~ -7 eV instead of ~ -6 eV for the VBM.

The defect interpretation is also consistent with the angle-integrated data taken on the core exciton. Recall that the DR enhancement was observed only in the foot and not for emission for $E_i \sim -7$ eV. Apker and Taft⁴⁹ first observed a similar phenomenon in the yield of alkali halide crystals. They interpreted that DR exciton decay occurred preferentially at F-centers, transferring the energy to electrons trapped in the anion vacancies. The effect may be the same in the case of SnO_2 , except that oxygen vacancies instead of halogen vacancies provide the electron traps.

Assuming the emission for $E_i \sim -7.0$ eV was not due to bulk, stoichiometric SnO_2 , the question arises: what is the origin of

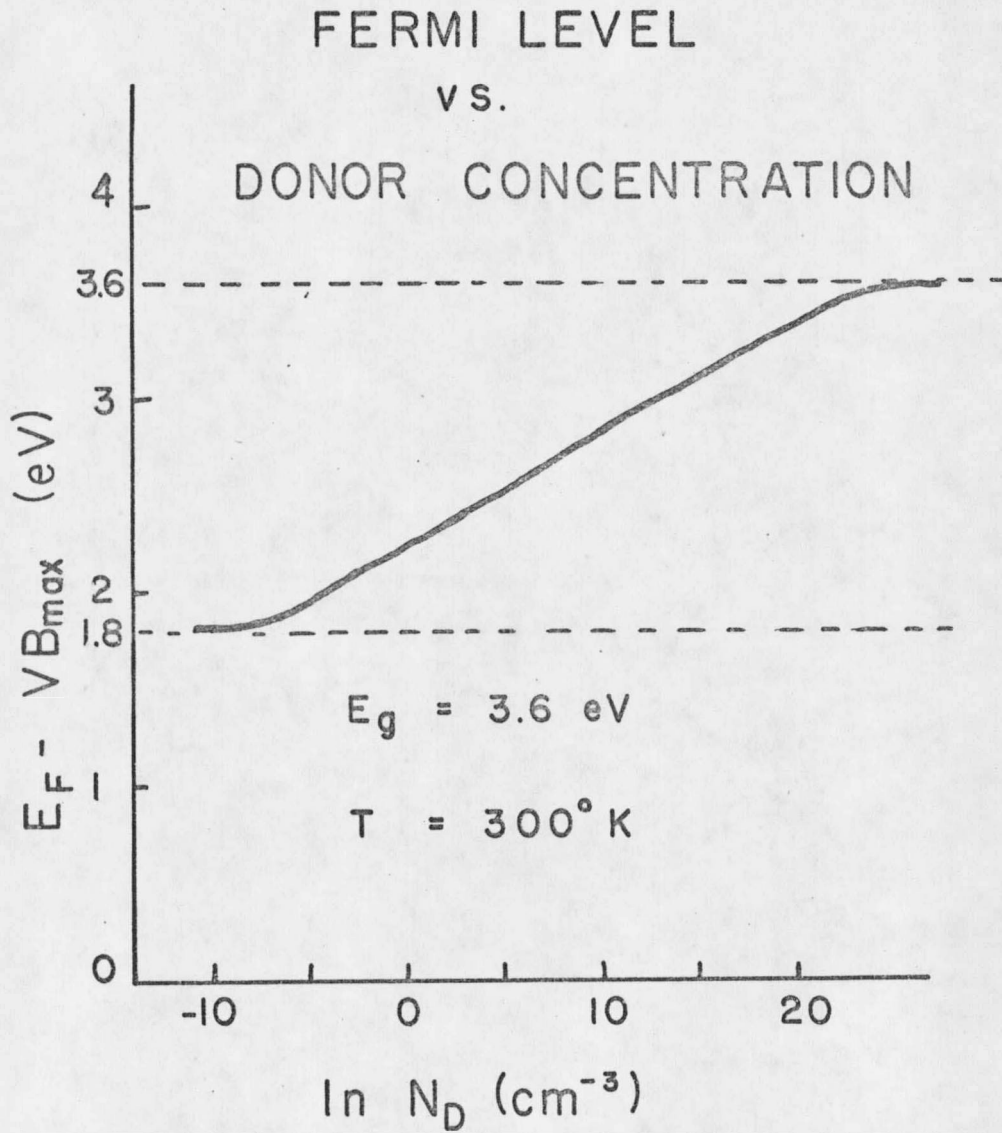


FIG. 46. Graph of E_F as a function of donor concentration.

this emission? There appear to be three possibilities: (1) surface states, (2) surface or near surface imperfections derived from sample preparation, and (3) inherent bulk imperfection throughout the crystal.

A surface state is a result of the termination of an otherwise infinite crystal. It can be explained in some cases by reconstruction of the surface, that is, by changing of bond angles from normal bulk values, or it can be changed by mere interruption of the periodic potential, without the shifting of atoms. In any case, these surface states, when they exist, have normally been found to result in very sharp UPS structures and to be very sensitive to surface contamination.^{6,7,52} This, of course, does not say that relatively broad structures that are relatively insensitive to surface contamination cannot result from the termination of an otherwise perfect crystal; it merely says that experimentally, these have been the accepted criteria for a surface state.

The relatively broad foot in tin oxide was found to be relatively insensitive to surface contamination. CO, H₂ and O₂ exposures up to 10⁶ L (L=10⁻⁶ torr-seconds) only affected the foot proportionately to the balance of the VB emission. Both the large O₂ and CO exposures resulted in carbon residing on the surface, as determined by Auger analysis, but the foot persisted. Tin metal was also

evaporated onto the surface, but even with enough metal so that photoemission at the Fermi level was detectable, the foot was still present (see Fig. 46). Within the normal criteria, mentioned above, the foot emission in tin oxide is not interpreted as resulting from a surface state.

Aside from the antimony doping ($N_d \sim 10^{15} - 10^{16} \text{ cm}^{-3}$), total bulk impurities, most of which was silicon, was less than 10 ppm as determined by spectrochemical analysis.⁸ Though the foot emission was weak ($\sim 1/1000$ th the bulk emission), it was still at least 2 orders of magnitude larger than should be expected from any impurities, even the most abundant antimony. A more plausible explanation may lie in non-stoichiometry.

Conductivity and optical experiments have indicated that the dominant native defect in tin oxide is oxygen vacancies.^{9,10,15,16,17} Moreover, heating of the crystal in vacuum increases the concentration of these oxygen vacancies. So the annealing process may indeed have increased the number of oxygen vacancies.

Could these vacancies be abundant enough to result in the observed foot emission? To be observed at about $1/1000$ th the bulk VB emission would require concentrations on the order of $10^{19} - 10^{20} \text{ cm}^{-3}$. With this concentration the model calculation would put E_F at about 3.4 eV above VBM, which would not be totally inconsistent with the measured value of 3.2 eV. On the other hand

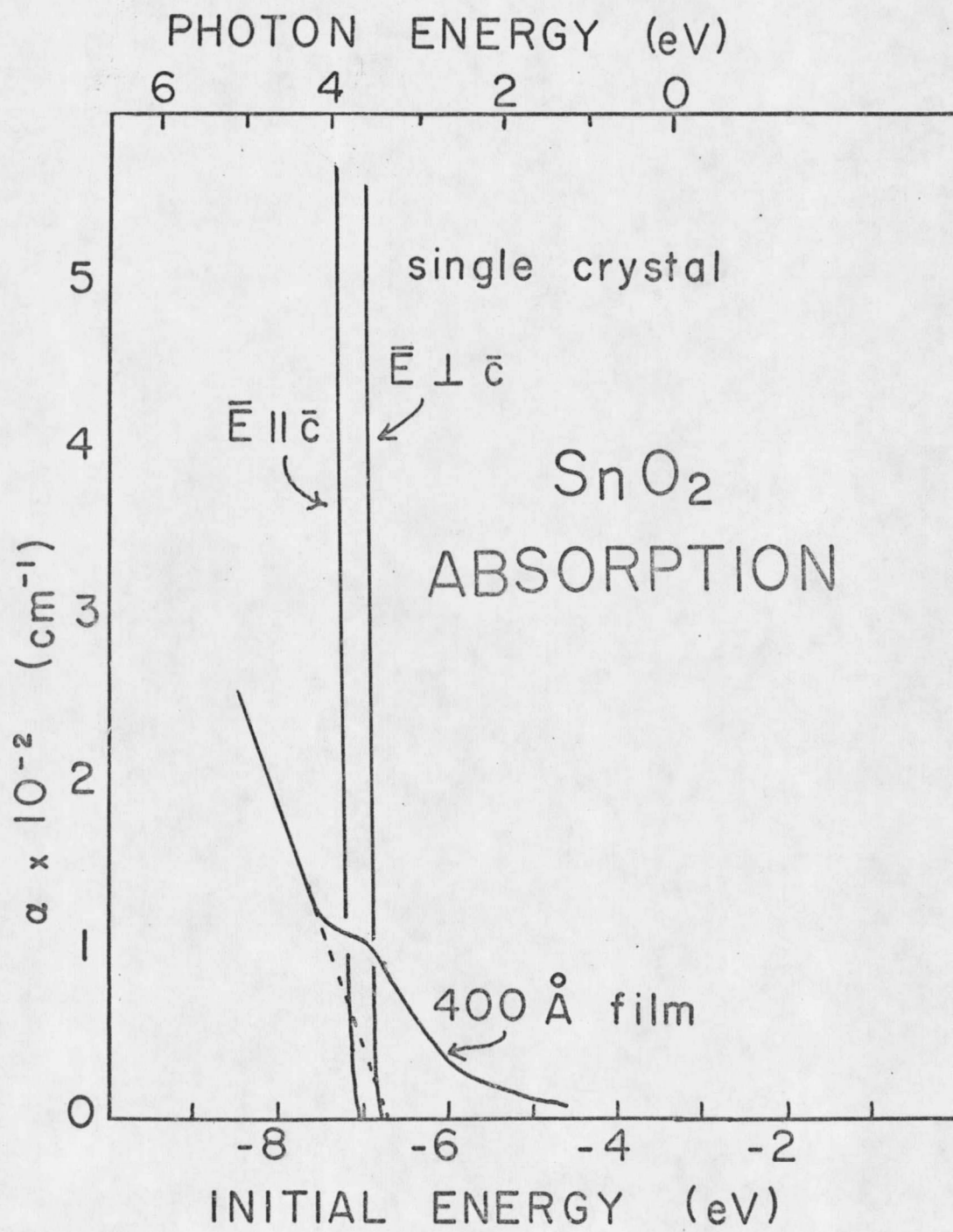
concentrations on this order should result in a substantial absorption edge at about $h\nu = 2.6$ eV, but measurements on tin oxide single crystals show no such absorption edge.^{12,13,14}

However, suppose that the oxygen vacancy concentration was much higher at the surface than within the bulk of the crystal. The absorption measurements on relatively thick (~ 100 micron) samples would not be expected to be very sensitive to the small amount of absorption due to oxygen vacancies occurring within $100 \text{ \AA}$ or less of the surface. In fact, it is reasonable that the oxygen vacancy concentration would be much higher at the surface.

Consider the following Gedanken Experiment on a hypothetical oxide crystal. Suppose first that no oxygen is lost from the crystal during heating, even in high vacuum. Then when the crystal is heated, individual oxygen atoms will diffuse through the crystal, as will the native vacancies. Some oxygens will reach the surface, but will be merely turned back. The density of oxygen atoms and oxygen vacancies will not change but will remain essentially uniform throughout the crystal. Now consider the same crystal, but allow some oxygens to escape through the surface upon heating (as is the case in tin oxide). The density of vacancies should not now be expected to be uniform. Note that an oxygen atom can only escape the crystal in one jump if it is within the first few monolayers at the surface; one $5000 \text{ \AA}$ deep would have a vanishingly low probability

of escaping through the surface in only one jump. There would be a concentration gradient of vacancies from the surface to the bulk of the crystal, with the high vacancy concentration naturally at the surface. When the crystal cools, this gradient will be frozen into the crystal, resulting in an inordinately high concentration of oxygen vacancies near the surface.

Measurements on very thin films of 400 Å of tin evaporated in an oxygen atmosphere and subsequently annealed in oxygen at a pressure of 10^{-4} torr do show absorption at about $h\nu = 2.6$ eV. Fig. 47 shows data from the thin film work of Spence¹⁸ and the single crystal work of Summit, Marley and Borelli (SMB).¹² The lower initial energy scale is used so comparison with EDCs is more readily accomplished. For the SMB data, the band gap was found to be direct ($E_g = 3.6$ eV); no absorption due to indirect transitions was observed. Spence interpreted the foot in his data as due to defects or excitons. It is the defect interpretation that is suggested here. An oxidized film would not be expected to be as stoichiometric as a single crystal. Moreover, the oxygen vacancy defects, being more numerous near the surface, would tend to stand out in the film. The thinnest crystal used by SMB was still over 10^3 times, or 70 microns, thicker than the 400 Å film of Spence. That the remainder of the absorption in the thin film case results from SnO_2 is

FIG. 47. SnO_2 absorption data.

supported by the fact that the extrapolated absorption edge (dashed line in Fig. 47) agrees well with the single crystal data.

The absorption due to oxygen vacancies near the surface is not observed in absorption data on single crystals, but it is interesting that it has in the current UPS measurements. The reason is primarily one of escape depth. Typical inelastic scattering lengths are on the order of 5-50 Å. Consequently, even though much of the light may reach a depth of a micron or more, an insignificant fraction of the hot electrons originating at these depths will ever escape the crystal unscattered. Essentially all the photoemitted electrons then can be considered as having originated very near the surface - where the oxygen vacancies are more abundant.

This interpretation is further supported by the EDCs of Fig. 48. Shown are a p-polarization normal emission EDC of this work and an EDC of oxidized tin from the work of Powell and Spicer (PS).³⁰ The two curves are plotted with a common Fermi energy ($E_F = -3.8$ eV). The Fermi energy for the PS oxidized film would be expected to lie higher relative to the SnO_2 VBs, because it would have even a higher concentration of oxygen vacancies, and thus donors. In fact, the SnO_2 structures in the two curves would indeed line up better if the PS curve were shifted about .2 eV to the right. Perhaps more importantly, however, one should note that the foot emission is proportionately much stronger in the oxidized films. This is the

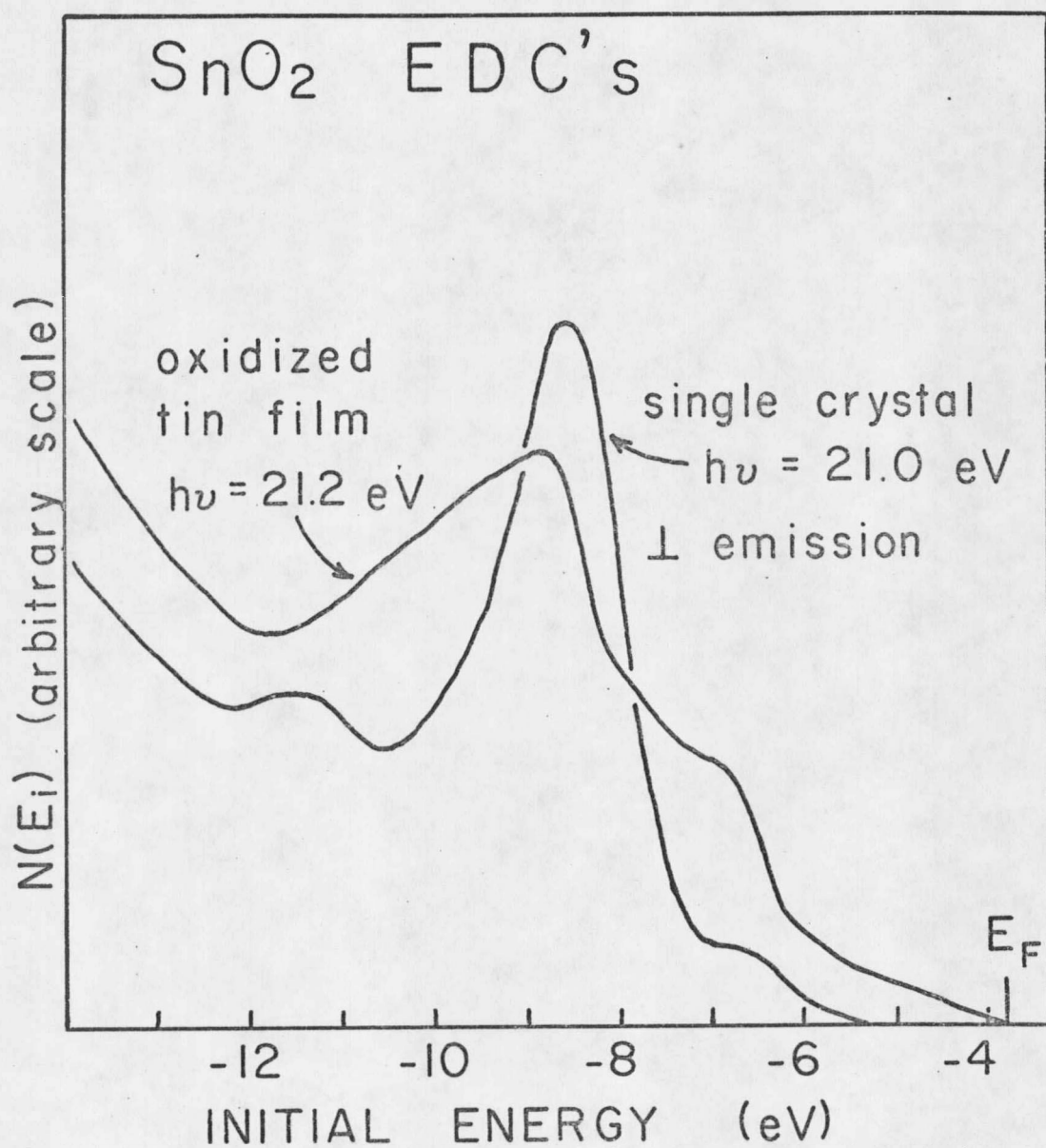


FIG. 48. Comparison of single crystal and oxidized film EDC's.

case even though the single crystal curve is for normal emission, where the foot is most evident, while the PS curve is necessarily angle-integrated. Even though PS observed the two tin oxide peaks growing together with increased oxygen exposure, it should not be interpreted that the tin was becoming more completely oxidized. It would be more correct to say that just more of the tin was being oxidized to form SnO_2 , but this SnO_2 had a large proportion of oxygen vacancies - even larger than in the single crystal SnO_2 .

Oxidation of vapor deposited tin films was studied in the current investigation. Attempts to oxidize a thin film of tin at room temperature by introducing O_2 into the chamber ($P \sim 10^{-5}$ torr) were unsuccessful. Relative success was achieved, however, by evaporating the tin very slowly ($\sim 1 \text{ \AA}/\text{sec}$) in an atmosphere of oxygen ($P \sim 10^{-5}$ torr). The results of this procedure are demonstrated in Fig. 49. Shown are three EDCs: (A) is for a metallic tin film, (B) is from a partially oxidized film prepared by the above procedure, and (C) is reproduced from the work of PS. Curves A and B are normalized to one another, but could not be normalized to the curve of PS. The differences in A and B indicate the effect of the oxidation during evaporation. Comparing curve B to the curve of PS, one notes the similarities. The "foot" at 3 eV below E_F is large relative to the peak 5 eV below E_F , in contrast to the single crystal data (Fig. 48). The two structures at 5 and 6.5 eV below E_F in curve

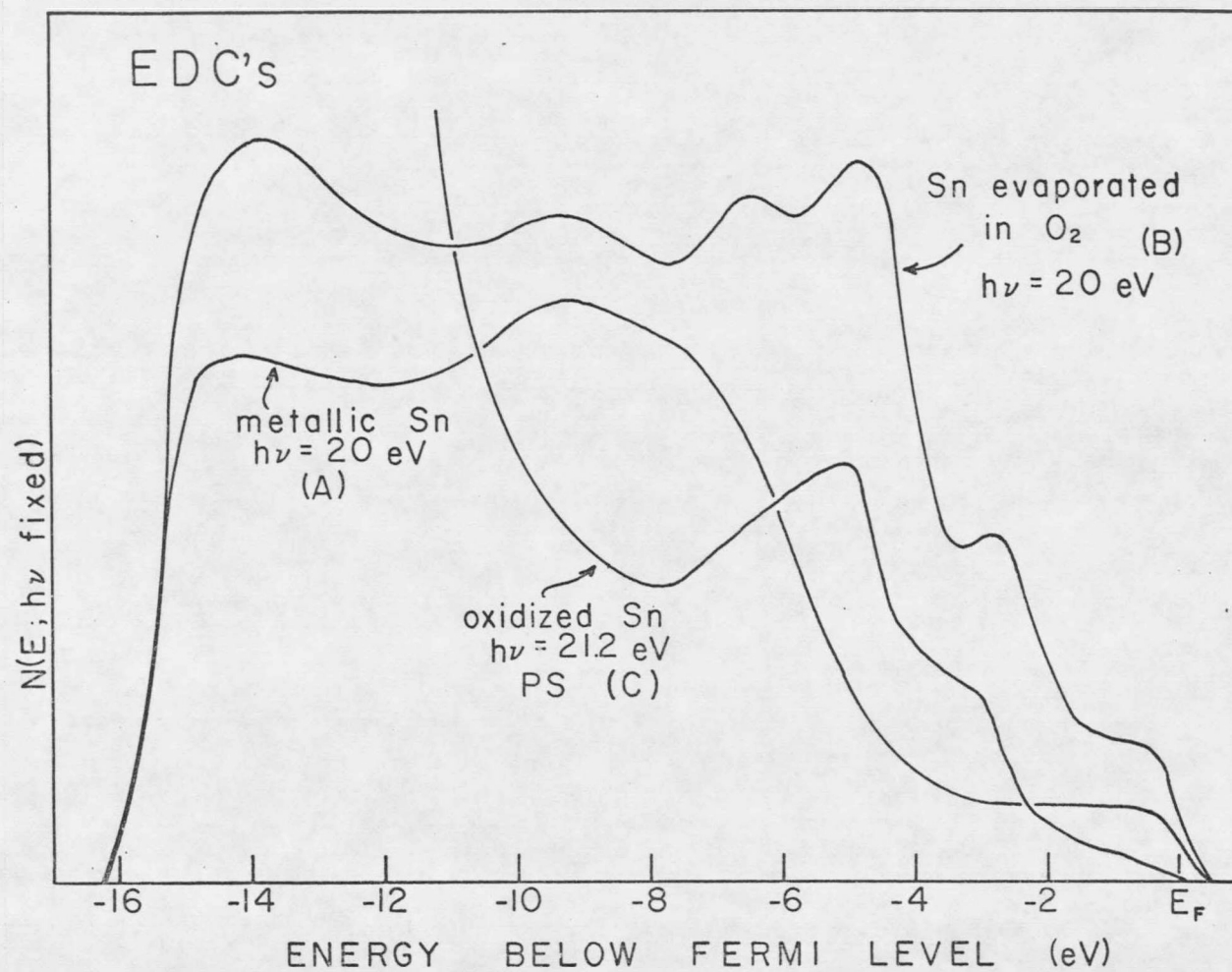


FIG. 49. Comparison of metallic tin and oxidized tin EDC's.

B are not resolved in the EDC of PS, but the total widths compare well. Though the emission at E_F is much stronger in curve B than in the PS curve, it is felt that these spectra are more similar to one another than to either curve A (metallic tin) or the single crystal tin oxide data.

Higher energy EDCs containing core emission for the tin film evaporated in the presence of O_2 are shown in Fig. 50. The core emission in the spectra is essentially that observed for vapor deposited films of metallic tin (Fig. 39). The former show only the tin 4d cores and no additional core structure reminiscent of the single crystal data. Furthermore, the CB features observed just above the vacuum level in the single crystal data are not found in the oxidized samples. This is considered as further evidence that the oxidized tin films (both of this work and of PS) were not representative of bulk stoichiometric SnO_2 .

In an attempt to fill a substantial proportion of the oxygen vacancies, the tin oxide crystal was heated in oxygen pressures up to 10^{-4} torr to temperatures from a few hundred to $835^\circ C$. However, the foot persisted. Apparently the relatively low pressure used in the current work was insufficient to result in a net transfer of oxygen to the crystal. Other workers have used temperatures up to $1350^\circ C$ and oxygen pressures on the order of one atmosphere to decrease the oxygen vacancy concentration.¹⁶ One has even reported

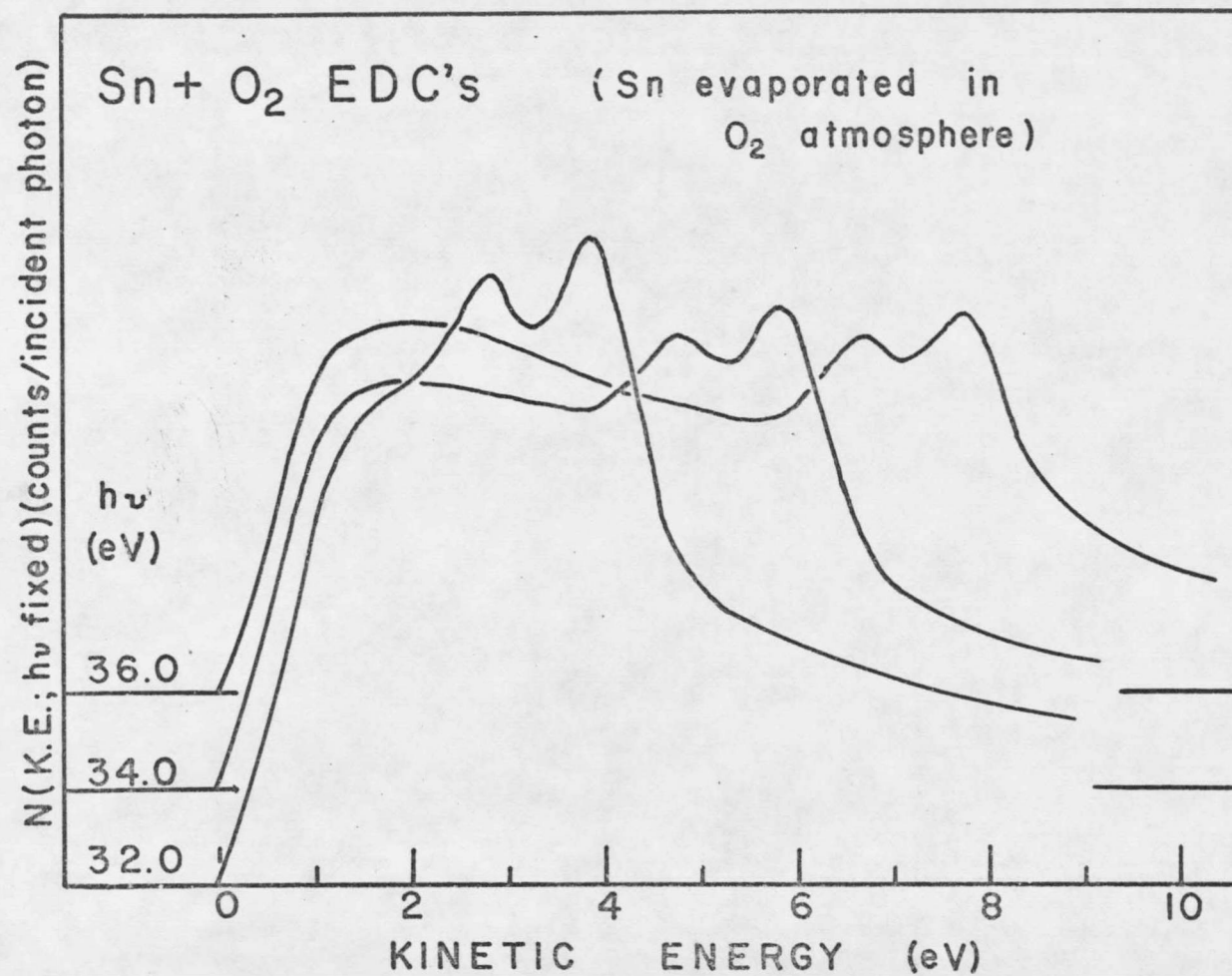


FIG. 50. EDC's showing tin 4d core in oxidized tin film.

an apparent loss of oxygen from tin oxide crystals even at room temperature.¹⁷

On balance, it does appear as though oxygen vacancies do provide the best interpretation for the emission from states above $E_i = -7.0$ eV. In light of tin oxide's well-documented n-type conductivity, interpretation of the foot emission as intrinsic is inconsistent with the observed location of the Fermi level. Furthermore, comparison of the absorption data of Spence and SMB indicates a surface origin to the structure. Along with the well-documented oxygen losses at elevated temperatures, these observations strongly suggest that the high concentration of oxygen vacancies at the surface are responsible for the foot emission.

Why this emission occurred primarily for normal emission is not understood. However, it should not be surprising that the emission due to oxygen vacancy states should have some angular dependence. The vacancies would not be expected to lie in any periodic fashion, so $\vec{k}$ would not be a good quantum number for electrons involved in these defect states. However, one can consider only the oxygen vacancy and its three nearest neighbor tin atoms as a sort of defect molecule. Though distributed somewhat randomly throughout the crystal, each of these "molecules" would have the same basic orientation. Fig. 51 shows this hypothetical molecule. The three tin atoms as well as the oxygen vacancy lie in the same

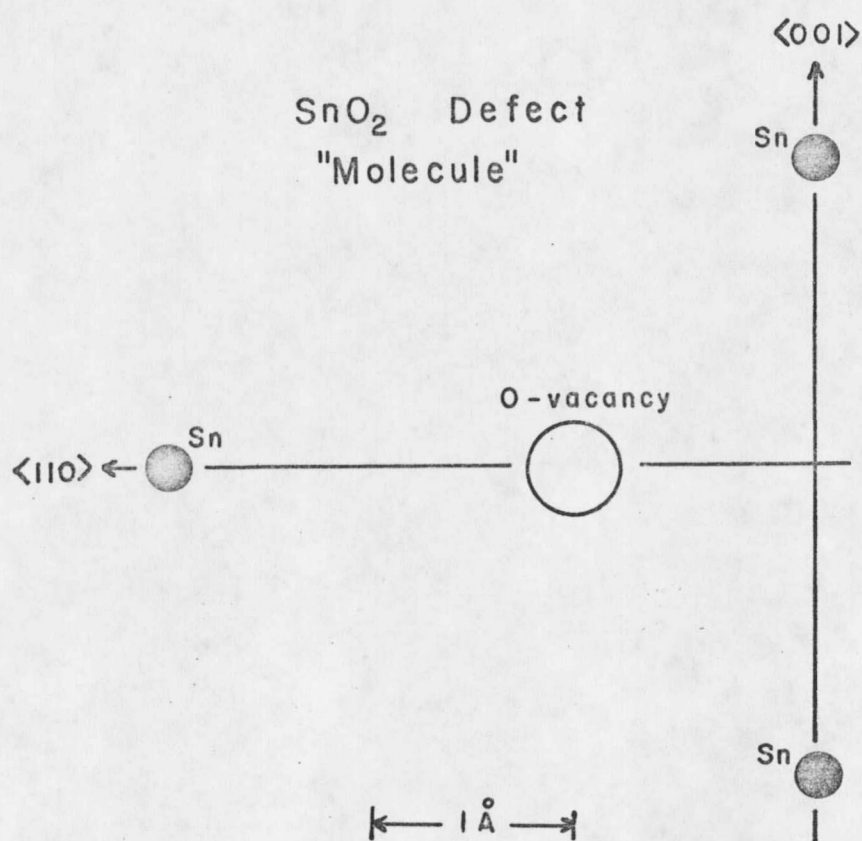


FIG. 51. Oxygen vacancy defect "molecule".

(110) plane which is perpendicular to the surface plane. Other similar defects in the crystal would be identical except for being rotated by $n \times 90^\circ$ about the c-axis, where n is an integer. The tin atoms are shown in their undisturbed positions, as they would be found in the perfect crystal. In a real defect these tin atoms would naturally move to new equilibrium positions. But whatever the new equilibrium positions may be, they would presumably be the same for each oxygen vacancy. This would result in a non-periodic array of similar defect "molecules," each of which is in one of only four possible orientations. Photoemission from this array should not be isotropic, but anisotropic.

4. "P"-polarization Data. A set of normal emission "p"-polarization EDCs is shown in Fig. 52, 53 and 54. The spectra's strong oxygen 2p emission and coupling to the CBs are similar to the s-polarization spectra. Two differences should, however, be noted. First the foot emission is substantially stronger in these "p"-polarization spectra than it was in s-polarization. This could be an effect of the polarization, but could also be due to the fact that the incident light is more grazing in "p"-polarization. The latter interpretation is consistent with the surface derived interpretation for the foot emission, since more grazing light would result in the photoabsorption occurring nearer the surface. The

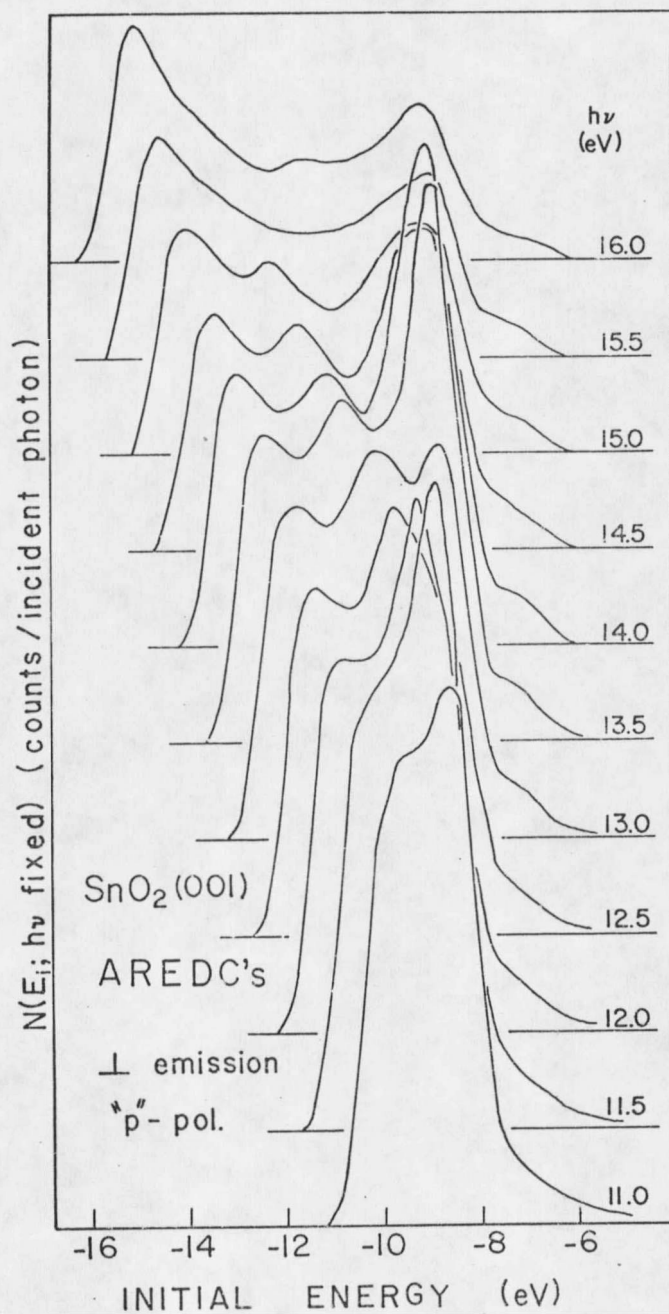


FIG. 52. "P"-polarization normal emission EDC's for $h\nu = 11.0$ to 16.0 eV.

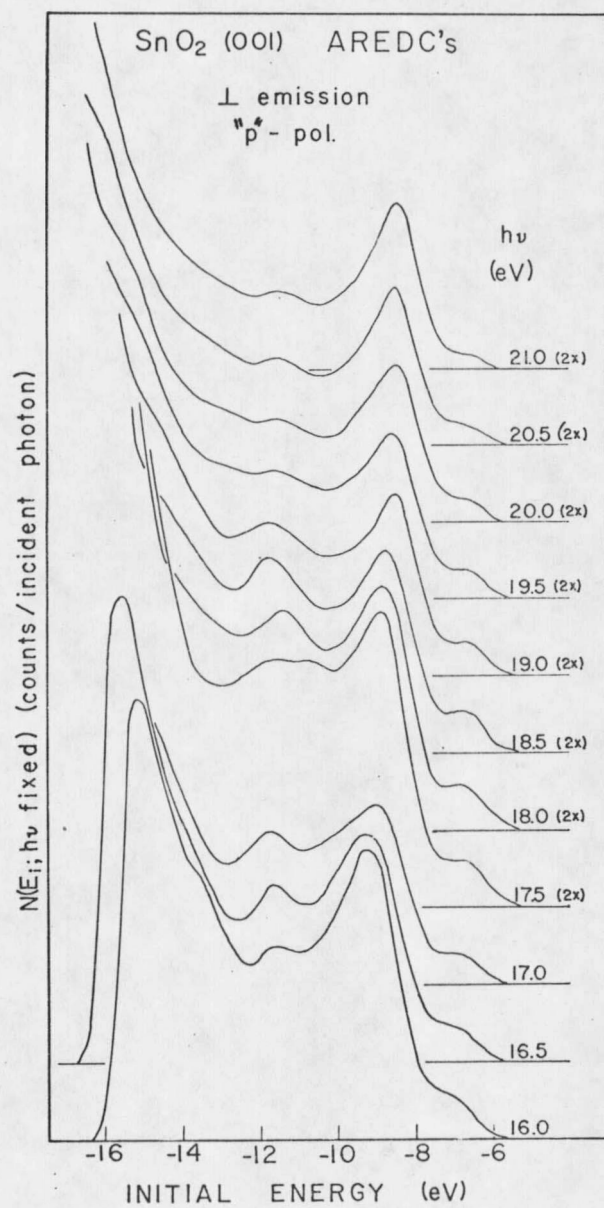


FIG. 53. "P"-polarization normal emission EDC's for
 $h\nu = 16.0$ to 21.0 eV.

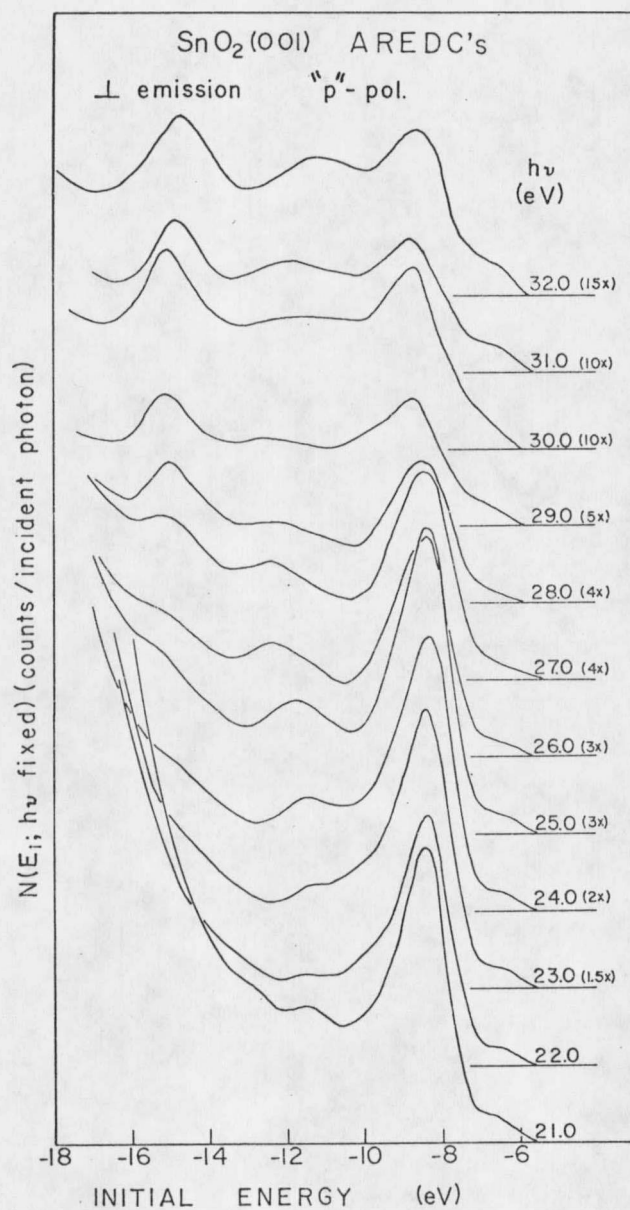


FIG. 54. "P"-polarization normal emission EDC's for
hν = 21.0 to 32.0 eV.

second difference between the "p"-polarization and s-polarization EDCs begins to appear at $h\nu \sim 27$ eV. An initial state feature at $E_i = -14.8$ eV begins to show at this point and continues through $h\nu = 35$ eV. Its strength is comparable to the omnipresent VB peak at $E_i \sim -9$ eV in this range.

To investigate this feature more closely other "p"-polarization data was also taken at non-zero polar angles. Fig. 55 shows a set of "p"-polarization EDCs for which $\phi = \langle 100 \rangle$, while θ was changed from curve to curve. The spectra are plotted as a function of initial energy and have been normalized to the photon flux and the analyzer transmission. The $E_i = -14.8$ eV peak is seen to have its maximum amplitude at normal emission. However, the feature also was significant throughout the emission hemisphere, and demonstrated no azimuthal dependence off normal emission. Interpretation of this feature is left until later.

5. Non-normal Emission. A relatively simple method of surveying the emission properties at non-normal emission is to measure the azimuthal dependence when the sample is rotated about its normal. This is termed a sample ϕ -pattern. A polar angle, photon energy and final energy would be chosen, with the emission monitored as the crystal was rotated. Tin oxide does not have a 4-fold rotation about the c-axis as an operation in its point group. However as

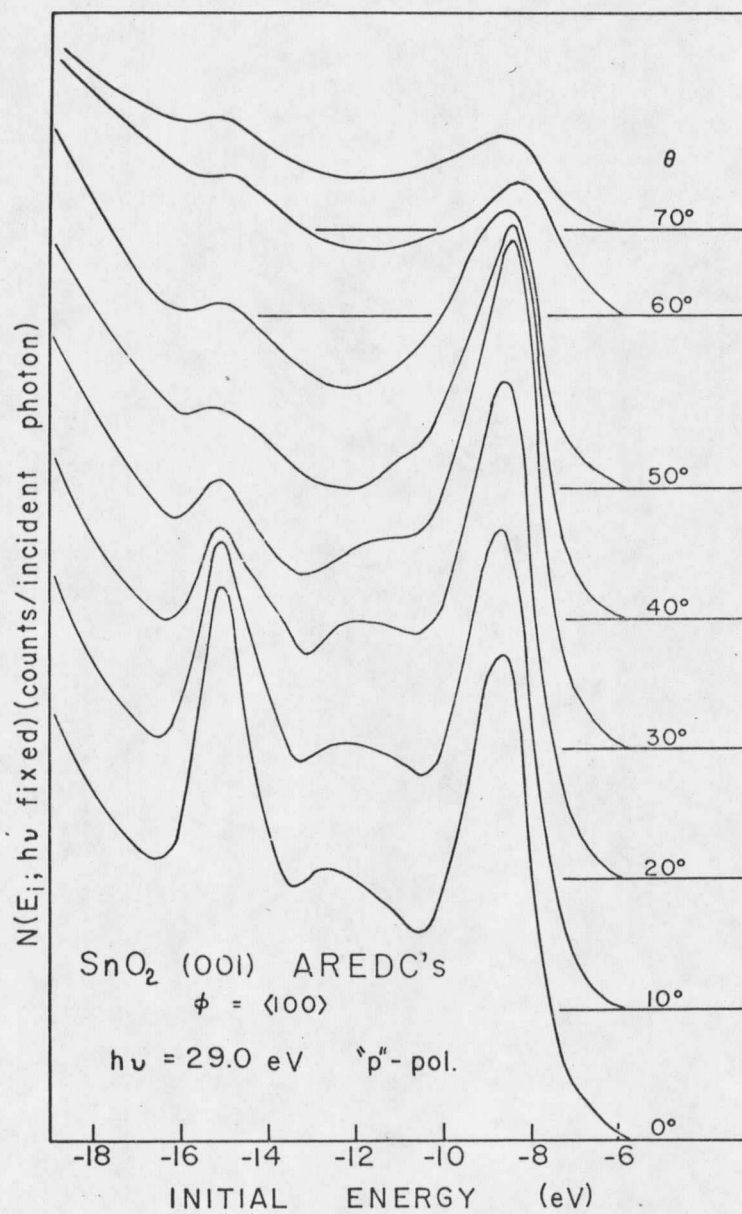


FIG. 55. $\hat{p}''$ -polarization EDC's for $h\nu = 29.0 \text{ eV}$, $\phi = \langle 100 \rangle$.

reference to Figs. 1 and 2 should indicate, 4-fold rotational symmetry in the emission should be expected. The surface in Fig. 2 is idealized. Actually the surface would contain numerous steps, so that an equal number of O-Sn-O "dumbbells" would be oriented each way on the surface layer.

On the clean annealed crystal, 4-fold symmetry was indeed observed. Fig. 56 shows two ϕ -patterns taken for $E_i = -8.0$ eV. This corresponds to the large oxygen p-like peak near VBM. Though for $h\nu = 20$ eV the maximum emission is along the $\langle 100 \rangle$ azimuth, at $h\nu = 25$ eV, the maximum has shifted to the $\langle 110 \rangle$ azimuth. Recall that the $\langle 110 \rangle$ direction is along the Sn-O bonds.

A general notion of how the maxima of ϕ -patterns shift as $h\nu$ is changed is illustrated in the ARCISS of Fig. 57. The initial energy is $E_i = -8.0$ eV for each curve, as in the previous ϕ -patterns. It can be seen directly that from $h\nu \approx 13$ eV to $h\nu \approx 16.5$ eV, very little ϕ -dependence is observed. Anisotropic ϕ -patterns should result for $h\nu$ between 17 and about 20 eV with the maximum in the $\langle 100 \rangle$ direction. For $h\nu \gtrsim 20.5$ eV, the ϕ -patterns for this initial energy and polar angle should change so that the maximum is in the $\langle 110 \rangle$ direction. This is, of course, consistent with the ϕ -patterns of Fig. 56.

The straightforward interpretation of the data in Figs. 56 and 57 is that the observed azimuthal dependence to the emission is a

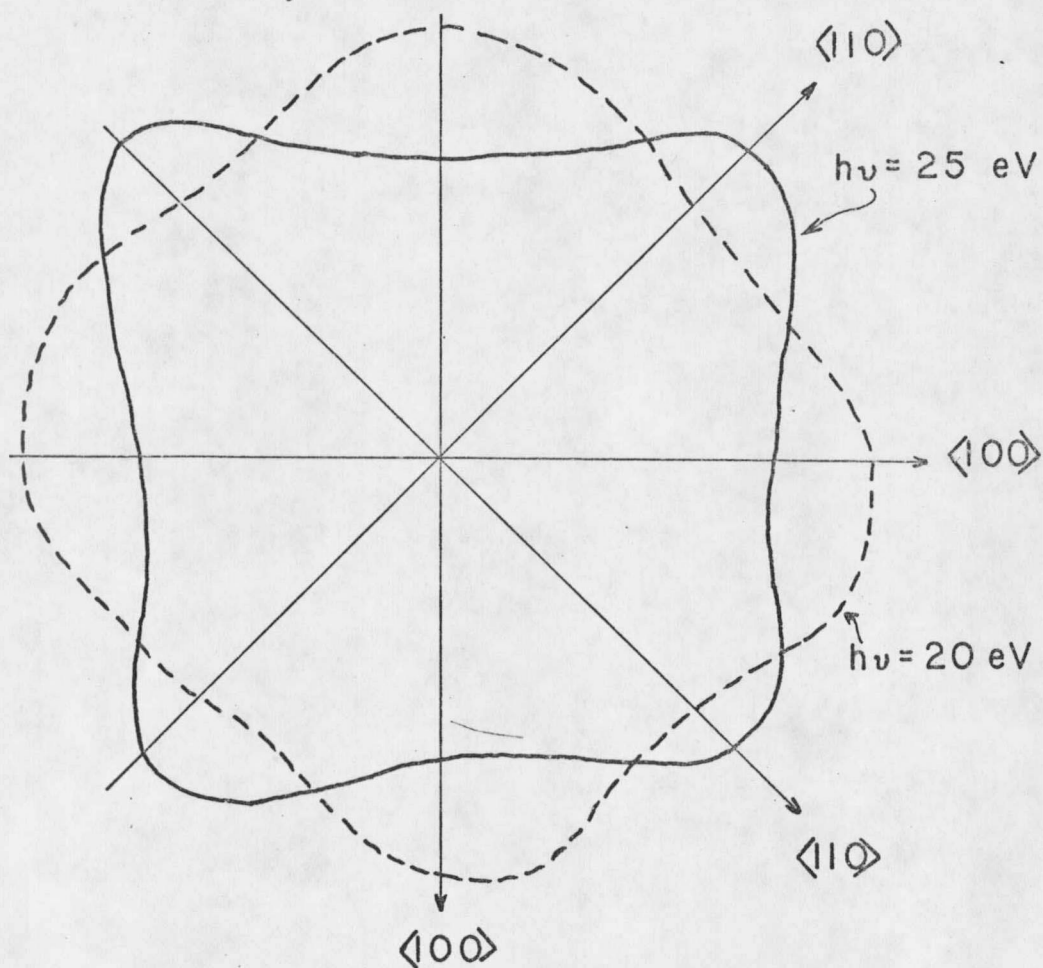
SnO_2 (001) ϕ -patterns

 $E_i = -8.0 \text{ eV}$

s-pol.

 $\theta = 45^\circ$

arbitrary scale


 FIG. 56. SnO_2 ϕ -patterns.

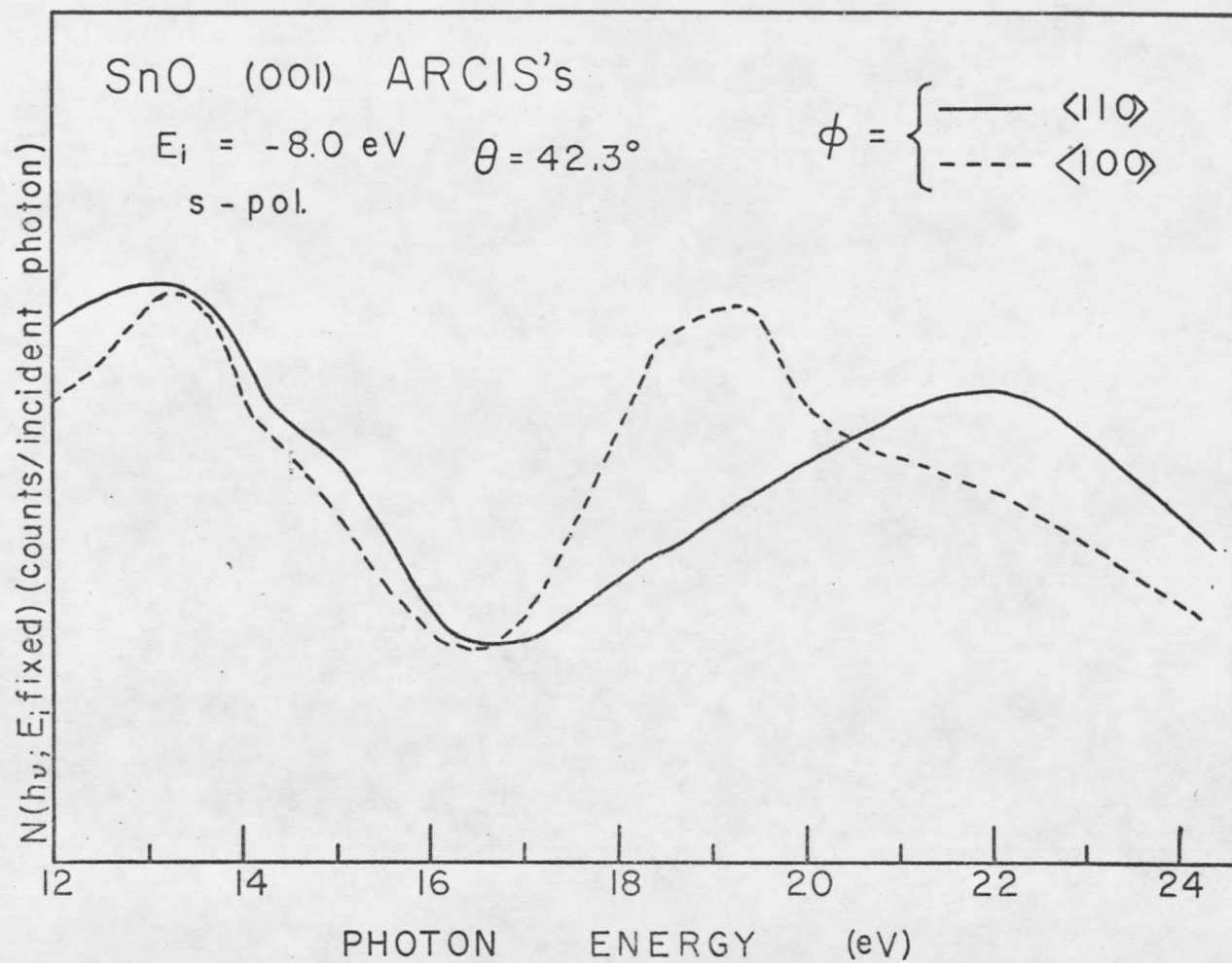


FIG. 57. ARCIS's for $E_i = -8.0 \text{ eV}$.

manifestation of both the selection rule on $\vec{k}$, $\vec{k}_i - \vec{k}_f = \vec{G}$, and matrix elements, $\langle f | x | i \rangle$. Both $\vec{k}$ conservation and the matrix element effects rely equally on the final and initial states of the electron. Though there is a tendency to assign initial or final state character to emission features, it is noted that both states must be considered. True, VBDOS effects are frequently large and tend to overshadow CBDOS effects, but both must be involved. Had the azimuthal maximum of the $E_i = -8$ eV emission remained in one direction for all photon energies, it might have been reasonable to disregard the final states. But since the maximum emission changed from the $\langle 100 \rangle$ to the $\langle 110 \rangle$ azimuth, the final states must not be ignored.

Similarly it would also be an oversimplification to assign the observed angular features strictly to the final states. The inelastically scattered electrons are known to fill the lower final states. The emission resulting from these high CBDOS was easily observed in both angle-resolved and angle-integrated spectra, but did not demonstrate any measureable azimuthal anisotropy. Moreover, an $E_i = 13.2$ structure was at a maximum in the $\langle 110 \rangle$ direction when coupling to final states at $E_f = 14.8$ eV. The oxygen 2p-like bands, however, showed their maximum emission in the $\langle 100 \rangle$ direction when coupling to the $E_f = 14.8$ eV final states.

For SnO_2 , then, it seems that the angular anisotropies should be assigned to the optical transition, that is, the total matrix

element, including $\vec{k}$ conservation. Both initial and final state symmetries are important in determining the emission angle of the photoelectron.

Two factors should be mentioned which both contributed to the relative weakness of the ϕ -patterns taken on SnO_2 . One reason for the relative lack of angular anisotropies lies in the complex crystal structure and the resulting large number of valence bands. For instance, GaAs, which has demonstrated strong angular anisotropies, has only four valence bands over a total VB width of about 12.5 eV.^{3,7} Tin oxide, however, has twelve valence bands distributed over only about nine eV. So the average density of valence bands, in bands/eV, is about four times greater for SnO_2 than for GaAs. To resolve features of the data in tin oxide as well as features in GaAs would then require four times the experimental resolution, on the average.

Also contributing to the weakness of most ϕ -patterns was the relatively large background of inelastically scattered electrons. This point is illustrated in Fig. 58. The AREDCs show the strong anisotropic feature at $E_i = -13.2$ eV riding atop the background. The structure is dramatic when shown in this manner. ϕ -patterns taken on this feature are shown in the inset. The dashed curve was constructed from the AREDCs by subtracting the constant background. By comparison, the solid ϕ -pattern, which includes the

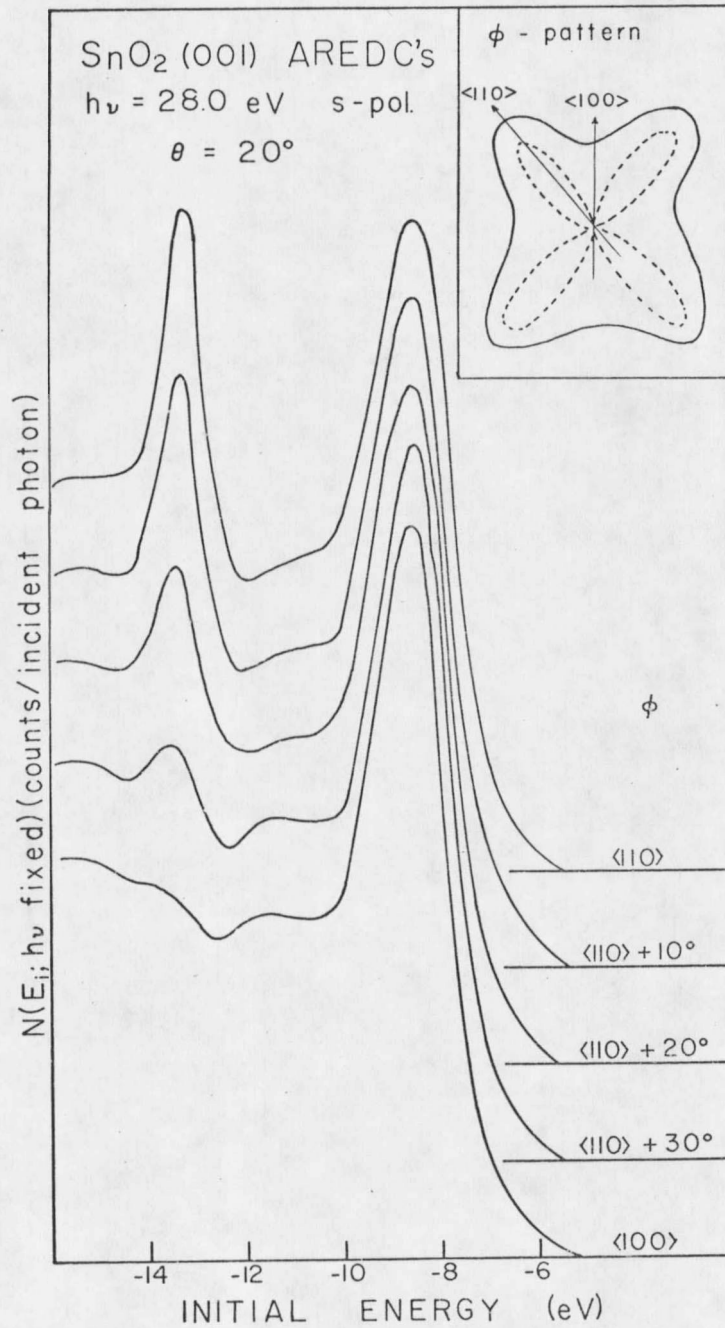


FIG. 58. S-polarization AREDC's for $h\nu = 28.0$ eV, $\theta = 20^\circ$.

background, is relatively bland. As such it does not adequately demonstrate the anisotropic nature of the structure.

The polar dependence of the $E_i = -13.2$ eV peak is demonstrated in the AREDCs of Figs. 59 and 60. The spectra of Fig. 59 are for ϕ in the $\langle 100 \rangle$ direction, while those of Fig. 60 are for ϕ in the $\langle 110 \rangle$ direction. The spectra have been normalized to the analyzer transmission. The -13.2 eV feature appears only in the $\langle 110 \rangle$ azimuth for $\theta = 20^\circ$, 30° and 34° .

There is another feature of Figs. 59 and 60 which is of interest. In both the $\langle 100 \rangle$ and $\langle 110 \rangle$ azimuths, emission from the oxygen 2p derived peak at $E_i = -8$ to -9 eV is more pronounced for $\theta = 30^\circ$ to 50° than for near normal emission ($\theta = 0^\circ$). This was the general observation for other photon energies above ~ 20 eV. Most likely this can be correlated to the bond angles in tin oxide. The polar angle between the $\bar{c}$ axis and the Sn-O bond is 38.5° , and lies in the $\langle 110 \rangle$ azimuth. This would lend support to the covalent model for tin oxide. A purely ionic tin oxide crystal would have spherical charge distributions on the oxygen atoms (and tin atoms), while the covalent model demands that the charge distributions be distorted along the bonds.

The feature at $E_i = -13.2$ eV just discussed was not originally observed with a ϕ -pattern or AREDCs, but with the ARCFs technique. A set of ARCFs was taken for which $|k_{\parallel}| = .94 \text{ \AA}^{-1}$, and ϕ was along

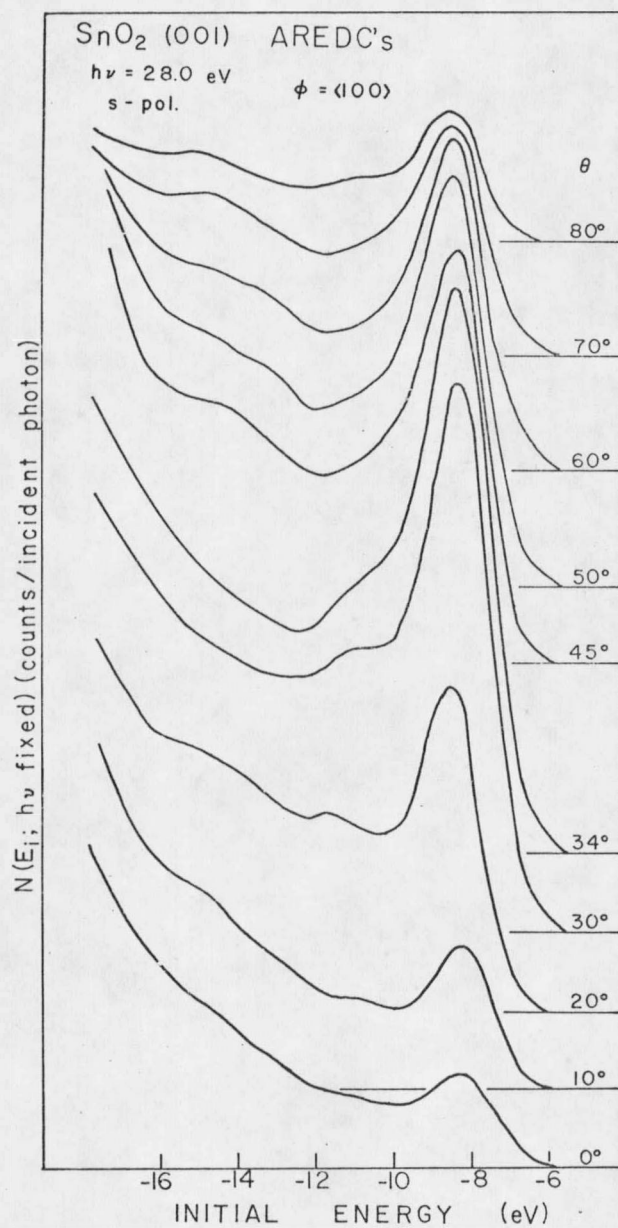


FIG. 59. S-polarization AREDC's for $h\nu = 28.0$ eV, $\phi = \langle 100 \rangle$.

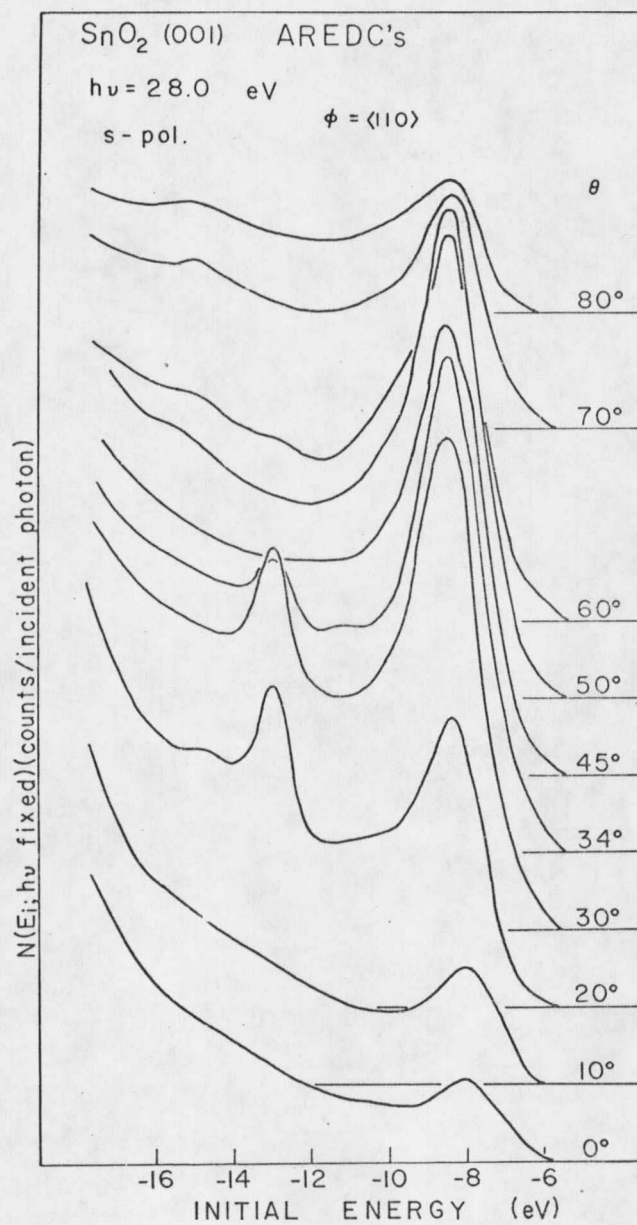


FIG. 60. S-polarization AREDC's for $h\nu = 28.0$ eV, $\phi = \langle 110 \rangle$.

the $\langle 110 \rangle$ direction. This corresponds to observing transition along the V symmetry line in the Brillouin Zone. These normalized data are shown in Fig. 61. The spectra are plotted as a function of initial energy. For $E_f \gtrsim 10$ eV, a peak begins to become apparent for $E_i = -13.2$ eV, which was absent in other CFS spectra taken along W and λ . To compare with the AREDCs on this feature, one notes that for $|k_{\parallel}| = .94 \text{ \AA}^{-1}$ and $h\nu = 28$ eV, the corresponding polar angle is 28.5° . This is consistent with the AREDCs of Fig. 60 in which the magnitude of the $E_i = -13.2$ eV peak is at a maximum in the $\theta = 20^\circ$ to 30° range. It is then justifiable to interpret this peak as due to a large joint density of states along the V symmetry line in the BZ.

Two other factors make this feature particularly interesting. First it was the strongest angular anisotropy found in the data. Second it was not found to couple strongly to any CBs for which $E_f \lesssim 10$ eV. This second factor in itself is not any particular anomaly. However another feature also in the lower part of the VBs demonstrated a similar behavior in "p"-polarization, which was described in Section 3. Interpretation of these two features will be discussed in the following section.

6. Lower Valence Bands Interpretation. The PARUPS data for valence band emission shows two strong features near the bottom of

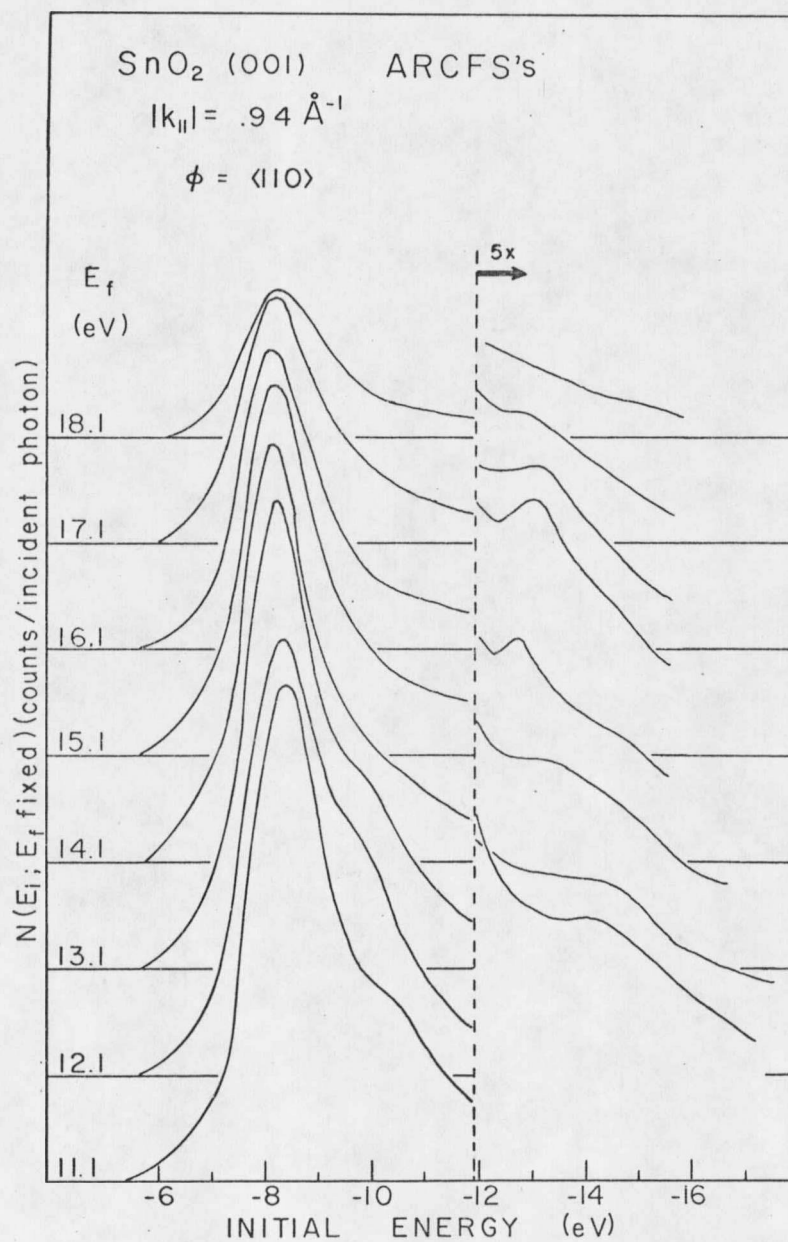


FIG. 61. S-polarization ARCFS's for $|k_{\parallel}| = .94 \text{ \AA}^{-1}$.

the bands, in the E_i range of -13 to -15 eV which show strong directional properties. In summary, one is observed to be emitted from the VBs at $E_i = -14.8$ eV in the normal direction with cylindrical symmetry, but only for "p"-polarization. The other is emitted from the VBs with $E_i = -13.2$ eV into only non-normal directions for only s-polarization. The dominant emission of this latter feature is observed in the $\langle 110 \rangle$ azimuth at polar angles between 20° and 35° . Both of these states are emitted only into the higher lying CBs for $E_f \gtrsim 10$ eV. As a result of the similarities in the initial and final energy characteristics the states are considered to be derived from similar atomic symmetries. These observations for the bottom of the VBs are qualitatively different than the observations for the oxygen 2p derived states at the top of the VBs which show weak polarization and direction dependences, and which couple strongly to the CBs below $E_f \approx 10$ eV. As a result of these marked differences the conclusion is made that the bottom VBs are not p-like. It is instead suggested that they have d-like character. This interpretation compares well with the APW calculation of Arlinghaus¹⁹; see Fig. 6. Although Arlinghaus did not publish the explicit bands, he did note that d-bands were predicted to lie from ~ 7 to ~ 12 eV below VBM, which is consistent with our observation.

Since only the lowest CBs have been calculated^{19,20} and are primarily 5s and 5p atomic-like tin states, some higher lying CBs could

easily be tin 4f derived. This is appealing, since d→f transitions are known to be strong, much stronger than d→p, which are also allowed. Moreover, p→f transitions are dipole forbidden, so the oxygen 2p derived bands would not be expected to couple well to the higher lying f-like CBs. Of course at these energies there are also numerous oxygen derived CBs available, so that emission from the oxygen 2p bands would not be expected to "turn off" as the 4d-bands "turn on."

A problem arises if the tin 4-d states are associated with the lower VB features. That problem is in the interpretation of the observed core level. The thrust of the previous discussion was to favor a tin 4d interpretation for the core level. The ionic modeled band calculations do not predict tin 4d states both in the valence bands and 15 eV lower in a core level as well.

Suppose a covalent model is applied to SnO_2 instead. Could this allow tin 4d character in both the lower VBs and the core? In analogy with TiO_2 as discussed earlier, let us assume that covalent bonding in SnO_2 is derived from the d^2sp^3 and sp^2 hybrid orbitals centered on the tin and oxygen atoms, respectively. To a first approximation, the energy of the hybrid orbital is just the weighted average of the component orbitals. The d^2sp^3 hybrid along z-axis is

$$\psi_z = \sqrt{1/6} s + \sqrt{1/2} p_z + \sqrt{1/3} d_{z^2}. \quad (19)$$

For the case of tin oxide, the energy of this orbital would then be

$$E_{\psi_z} = (1/6)E_{5s} + (1/2)E_{5p} + (1/3)E_{4d}. \quad (20)$$

Using the atomic energy levels of Herman and Skillman,³⁶ one gets

$$E_{\psi_z} = (1/6)(-5.9) + (1/2)(-12.5) + (1/3)(-35.1) = -18.9 \text{ eV} \quad (21)$$

where the energies are measured relative to the ionization limit.

Note that the hybrid energy of -18.9 eV is 16.2 eV higher than the 4d energy of -35.1 eV.

Since only two d orbitals are utilized in the hybrids, the other three could remain essentially undisturbed. This would yield both 4d-like VBs and 4d-like cores separated by ~16 eV. Fig. 62 shows the five d-orbitals. The dark spheres represent oxygen atoms octahedrally coordinated about the tin. The shaded orbitals represent the d_{z^2} and the $d_{x^2-y^2}$ orbitals. These two have their maxima in the directions of the oxygen atoms. Consequently they are most likely the orbitals used to help form covalent bonds with the oxygens. The other three orbitals have their maxima between oxygens and would not therefore be as apt to contribute to covalent bonds with the oxygens.

It is interesting to note that a reasonable model can be developed which allows both the ionic and covalent character. One can begin with the ionic character. After the four 5s and 5p

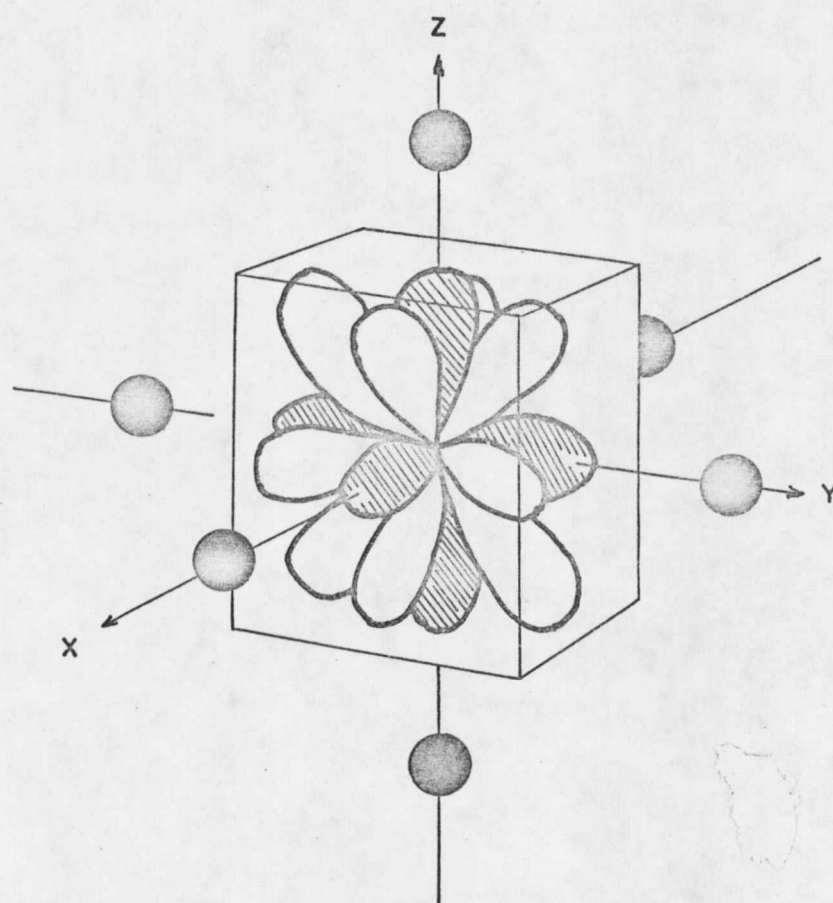


FIG. 62. Angular d-functions with octahedral coordination.

electron have been removed from the tin, the remaining tin electrons, particularly the 4d electrons, will be bound more strongly. In fact the fifth ionization potential of tin, 80.7 eV^{53} , is just the energy necessary to remove a 4d electron from the Sn^{4+} ion. On the other hand the energy necessary to remove a 4d electron from neutral atomic tin is calculated to be 35.1 eV^{36} . The loss of the screening effect of the outer 5s and 5p electrons has increased the binding energy of the tin 4d's by $80.7 - 35.1 = 45.6 \text{ eV}$. Now when the negative oxygen ions are brought in around the Sn^{4+} ion, the binding energy of all electrons on the tin ion will be reduced. The resulting upward shift in energy is calculated using the Madelung potentials of Van Gool and Piken⁵⁴ to be 42.8 eV . The 4d electrons on the tin then are at $45.6 - 42.8 = 2.8 \text{ eV}$ below their original atomic levels. Note that this shift compares well with the 2.1 eV shift relative to E_F observed in the metallic tin and tin oxide cores. (Fig. 40.)

The ionic modeled band calculations^{19,20} have presumably taken these effects into account. Yet apparently the bonding effects cause the 4d levels to be broadened and further raised in energy - particularly in the APW calculation. Perhaps, as in the suggested covalent model, one now allows only the d_{z^2} and $d_{x^2-y^2}$ orbitals to be involved in the bonding. Then only they would be broadened and raised in energy. The remaining 4d orbitals could then remain

relatively unbroadened and near their atomic levels. This type of argument had its beginnings in the ionic model, but still required the covalent character to allow the separation of the 4d states into the VBs and the core level.

The VBs have thus been interpreted in light of a model requiring covalent character. The oxygen 2p orbitals are involved in the sp^2 hybrids centered on the oxygens, while the tin 4d, 5s and 5p states combine for the d^2sp^3 hybrids. This covalent picture is of value for a number of reasons.

(1) Crystalline TiO_2 , which has essentially the same rutile structure as SnO_2 , has a greater electronegativity difference than does SnO_2 , but still is described in terms of the covalent picture.³⁵

(2) The covalent model allows the tin 4d states to be involved in both the VBs and the observed core level, while the ionic modeled band calculations do not.

(3) The angle-resolved UPS data indicate considerable non-sphericity in the charge distributions. A purely ionic model would require spherical charge distributions.

The foregoing preliminary interpretation is necessarily a first approximation to the actual electronic structure of SnO_2 . It must be remembered that the correctness of any model can only be measured by how well the model's predictions fit the observations. If subsequent experiments indicate that, say, the observed core is

indèed the oxygen 2s core, or that it is an artifact of the oxygen vacancies and not representative of stoichiometric tin oxide, then the more ionic model may prove to be the better alternative.

VI. SUMMARY

The first photoemission studies of stannic oxide, SnO_2 , have been completed. Both angle-resolved and angle-integrated data were taken on the (001) face of the single crystal which had been cleaned in situ by argon bombardment and subsequently annealed. With synchrotron radiation providing a photon energy range of 10 to 40 eV, the valence bands, lower conduction bands and a shallow core level were studied. Fig. 63 summarizes the experimental results.

The valence bands (VBs) were found to consist of two major portions, with the total width being about nine eV. Emission from the upper five eV of the VBs demonstrated only weak angular, photon energy and polarization dependences, and has been interpreted as being from oxygen 2p-like bands. On the other hand, the emission from the lower VBs showed two features which were strongly dependent on angle and polarization. Moreover these latter features were found to couple strongly only to conduction bands above about 10 eV final energy. Since the lower VBs demonstrated such different emission characteristics from the upper VBs, it was suggested that the lower VBs are derived from different atomic symmetries, in particular, tin 4d symmetry. The conduction bands above 10 eV to which these d-bands were found to couple were interpreted as tin 4f-like bands. These findings are consistent with the APW calculation of Arlinghaus.¹⁹

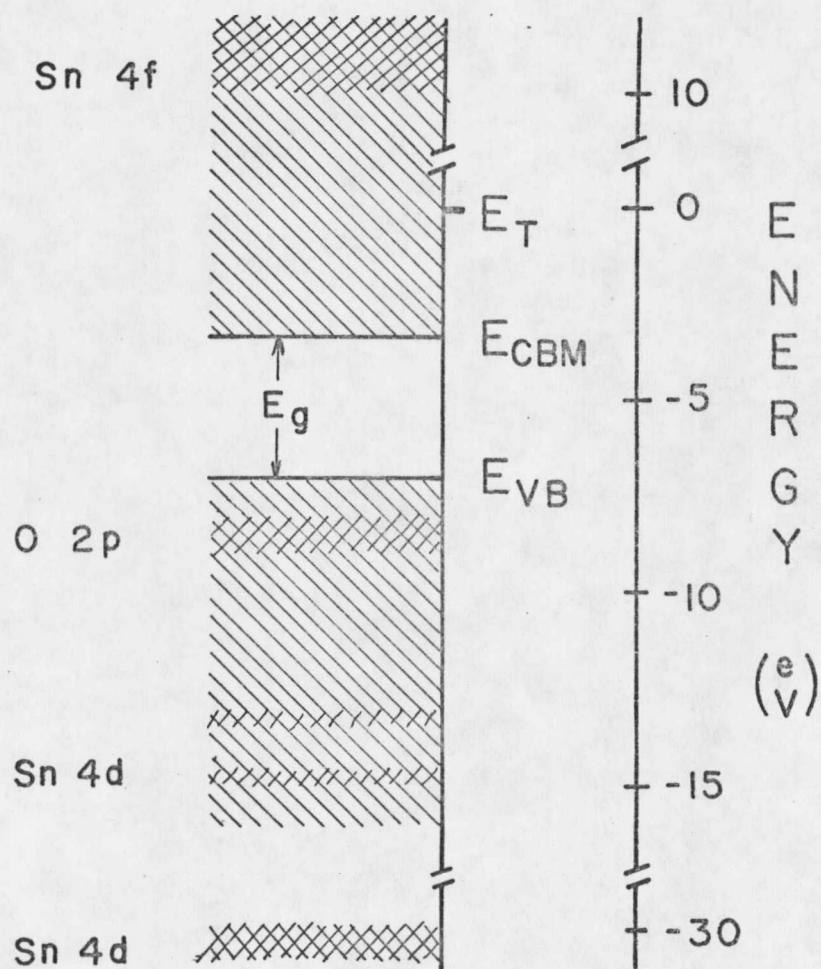


FIG. 63. Experimentally Determined Energy Level Diagram with Interpreted Atomic Origins.

A core level centered about 30 eV below the vacuum level and its associated excitons were also studied. The excitons were detected by measuring the emitted electrons resulting from the exciton decay. Both the Auger and direct recombination processes were identified as decay modes for the excitons.^{47,48} By comparing the core exciton splitting of 1.0 eV to the spin-orbit splitting of the tin 4d core in vapor deposited tin films, this core in tin oxide has also been interpreted as tin 4d derived. The available band calculations^{19,20} were based on an ionic model and did not predict tin 4d character in both the VBs and the core. A covalent bonding model utilizing hybrid orbitals was suggested which allows tin 4d character in both the lower VBs and the observed core.

A relatively weak initial state structure slightly above VBM was observed in normal emission which was not interpreted as due to bulk stoichiometric SnO_2 . The location of the Fermi level, the well-documented n-type conductivity of SnO_2 and the accepted value of 3.6 eV for the band gap combined to provide the strongest case against a bulk stoichiometric interpretation for this feature. Surface states and contaminants were discounted as possible sources of this feature. The best interpretation to this feature seems to lie in a high concentration of oxygen vacancies near the surface, primarily induced by annealing the crystal in vacuum.

Since this was the first study of its kind on a material with the complicated rutile structure, all interpretations are possibly subject to change with either subsequent experiments or calculations. In the experimental area a number of experiments could be beneficial. Other materials with similar gross properties could be studied. GeO_2 and PbO_2 would be good examples. Both crystallize in the rutile structure, and both germanium and lead are from the fourth column of the periodic table and have filled d levels - 3d and 5d, respectively.

Further UPS experiments on SnO_2 using photon energies up to 100 eV could also be performed. The photon energy dependence of the photoionization cross section of 4d electrons is well-documented⁴⁶ and could provide strong evidence for the existence, or non-existence, of 4d character in both the lower VBs and the core.

Either a (110) or (100) face of the SnO_2 crystal could also be studied. This would change the critical points in the BZ that would be available at certain $\vec{k}_{\parallel}$ values and would presumably result in different UPS spectra. The (110) face might be particularly interesting since the Sn-O bonds would either be parallel or perpendicular to the surface. This could easily demonstrate strong polarization and emission angle dependences.

As far as theoretical work is concerned, it would also be of interest to calculate the electron energy bands using a covalent

model instead of the ionic model. This would, of course, be a non-trivial matter because of the complexity of the rutile structure. However the results of such a calculation would allow a more critical evaluation of the data interpretations made thus far.

APPENDICES

APPENDIX A

Conservation of $\vec{k}_{\parallel}$

Consider the interface between a semi-infinite solid and the vacuum. With $z = 0$ as the surface, wave functions for an electron in the solid ($z < 0$) and in vacuum ($z > 0$) can be written down directly.

$$\Psi(\vec{r}) = \begin{cases} e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r}) & , z < 0 \\ A e^{i\vec{q} \cdot \vec{r}} & , z > 0 \end{cases} \quad (22)$$

In the solid the wavefunctions are the normal Bloch states, with $\vec{k}$ being the quantum number known as the crystal momentum. $u_{\vec{k}}(\vec{r})$ is a function which has the same periodicity as the lattice. For $z > 0$, A is a constant and $\vec{q}$ is the momentum of the electron, that is, $\hbar\vec{q} = m\vec{v}$.

Since $u_{\vec{k}}(\vec{r})$ is a periodic function, it can be expanded in a Fourier series, namely

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} U_{\vec{G}} e^{i\vec{G} \cdot \vec{r}}, \quad (23)$$

where the $\vec{G}$'s are reciprocal lattice vectors and the $U_{\vec{G}}$'s are expansion coefficients.

The two wavefunctions and their gradients must be matched at the boundary, $z = 0$. This yields

$$A \exp[i(q_x x + q_y y)] = \sum_{\vec{G}} U_{\vec{G}} \exp[i(k_x + G_x)x + i(k_y + G_y)y], \quad (24)$$

and

$$q_j A \exp[i(q_x x + q_y y)] = \sum_{\vec{G}} U_{\vec{G}} (k_j + G_j) \exp[i(k_x + G_x)x + i(k_y + G_y)y], \quad (25)$$

where j denotes x , y and z , successively. Substituting from the first equation into the second, and noting that all the $\exp[i(k_j + G_j)j]$ are linearly independent, one gets

$$k_j + G_j = q_j. \quad (26)$$

For $j = x$ or y , corresponding to the parallel components, the G_j are the normal finite reciprocal lattice vectors for the x and y directions, respectively. So it is said that $\vec{k}$ is conserved within a reciprocal lattice vector.

When $j = z$, however, the equation still holds, but the G_z are not the bulk G_z , since the period in the z -direction is now infinite. The translational symmetry has been broken by the surface. Consequently consecutive G_z are now infinitesimally separated. Thus a specific q_z can result from any k_z . The selection rule derived from matching the wavefunctions at the surface is then

$$\vec{k}_{\parallel} + \vec{G}_{\parallel} = \vec{q}_{\parallel}. \quad (27)$$

APPENDIX B

Derivation of Emission Angles as a Function of ϕ_D

For angle-resolved photoemission, with the rotation axis of the sample aligned with the light axis, the direction of the collected electrons with respect to the sample varies in a non-trivial fashion as the drum angle is changed. The perspective drawing of Fig. 64 shows the pertinent angles and lengths. Coordinate systems are assigned to the sample and the CMA - O' and O , respectively. As shown the O' system is derived from the O system by a rotation of 42.3° about the y axis plus a translation along the negative z axis. In this manner the z' axis passes through the point P_1 at the top of the CMA cone. The object is to derive the relationship between the angle of the drum, ϕ_D , and both θ' and ϕ' , the polar and azimuthal angles, respectively, as measured with respect to the crystal surface.

One can calculate the length of the chord L using the law of cosines; which yields

$$L^2 = 2R^2 (1 - \cos \phi_D), \quad (28)$$

but also

$$L^2 = 2r^2 (1 - \cos \theta'). \quad (29)$$

Moreover at $\phi_D = 180^\circ$, $L = 2R$ and $\theta' = 84.6^\circ$. This yields

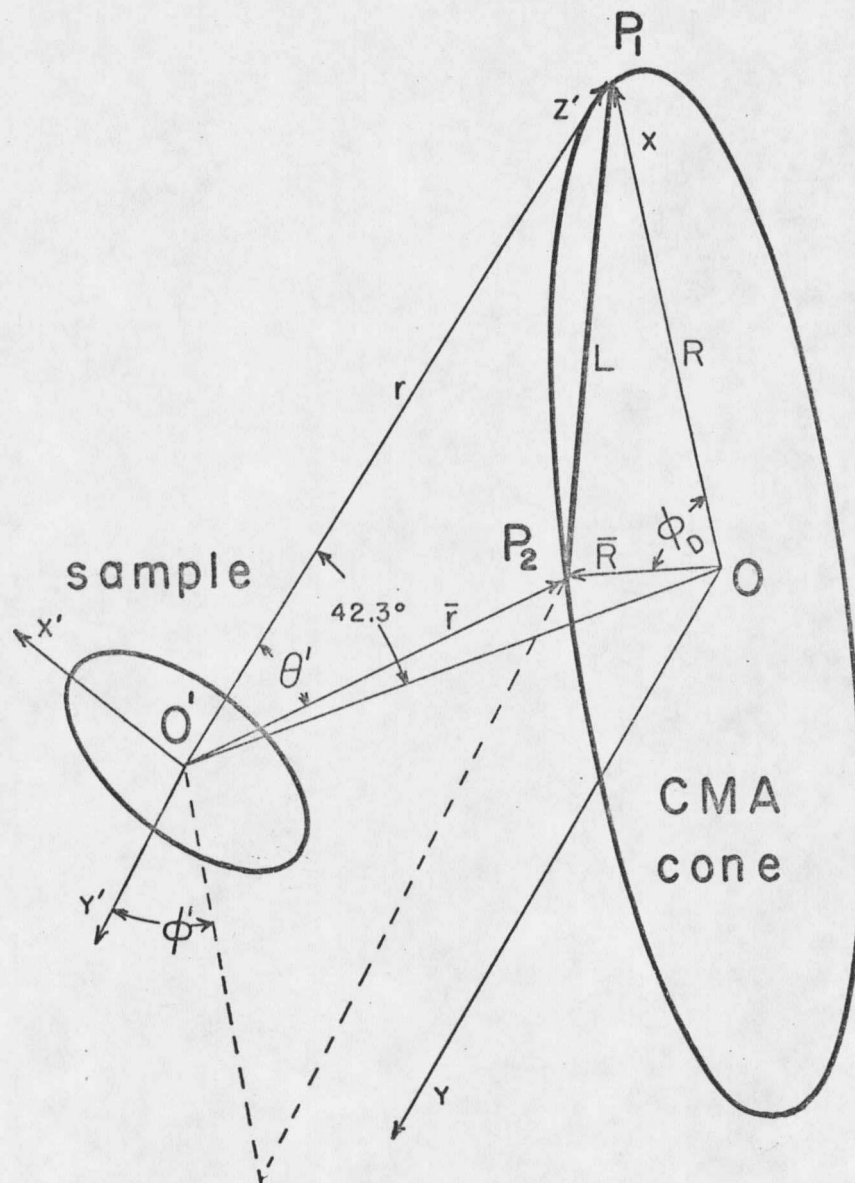


FIG. 64. Schematic depicting relationship between the drum angle and the emission angle.

$$r^2 = 2R^2/(1 - \cos 84.6^\circ). \quad (30)$$

Combining the three preceeding equations gives the required result:

$$\theta' = \text{Arccos} \left\{ 1 - \frac{(1 - \cos 84.6^\circ)(1 - \cos \phi_D)}{2} \right\} \quad (31)$$

To get an expression for ϕ' , we note that due to the transformation relating O and O' , the y components of $\vec{R}$ and $\vec{r}$ must be equal, that is,

$$R \sin \phi_D = r \sin \theta' \cos \phi'. \quad (32)$$

Then using equation (30), ϕ' is found as a function of ϕ_D and θ' :

$$\phi' = \text{Arccos} \left\{ \left[\frac{\sin \phi_D}{\sin \theta'} \right] \left[\frac{1 - \cos 84.6}{2} \right]^{\frac{1}{2}} \right\}. \quad (32)$$

The results are shown graphically in Fig. 65.

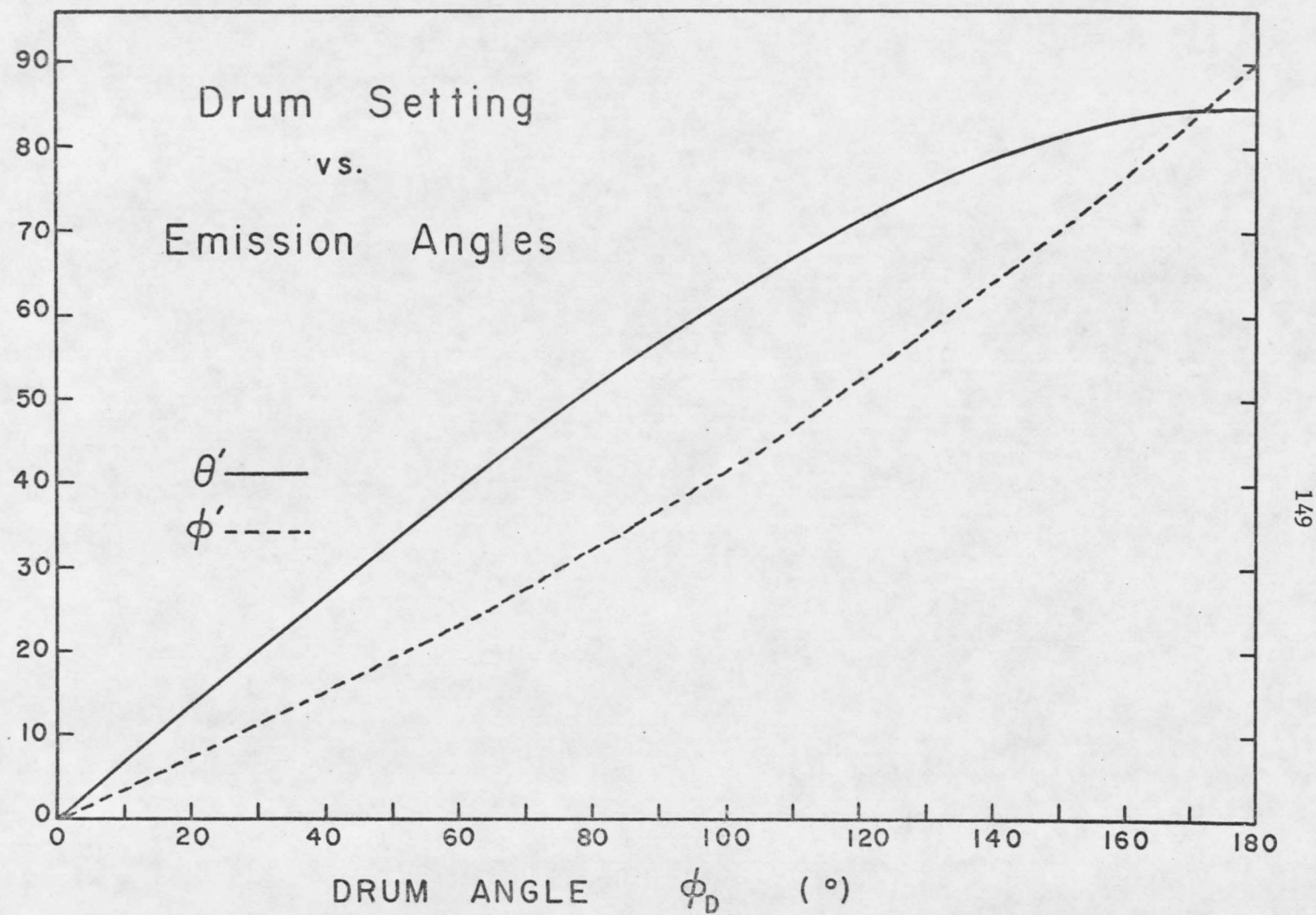


FIG. 65. Graph of drum angle versus emission angle.

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