

Optical Density of States Ultraviolet Photoelectric Spectroscopy^{*1}

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The use of ultraviolet photoemission to determine the density of valence and conduction states is reviewed. Two approaches are recognized. In one, the photoemission as well as other studies are used to locate experimentally a limited number of features of the band structure. Once these are fixed, band structure calculations could be carried out throughout the zone and checked against other features of the photoemission data. If the agreement is sufficiently good, the density of states is then calculated from the band structure. The second method depends only on experimental data. Using this approach, features of the density of states are determined directly by the photoemission experiment without recourse to band calculations. In cases where bands are wide and \mathbf{k} clearly provides an empirically important optical selection rule, this is possible only for portions of the bands which are relatively flat. Successful determinations of this type are cited for PbTe, and GaAs. In metals with narrow d bands such as Cu, it has been found empirically that one may explain fairly well the experimental energy distribution curves in terms of transitions between a density of initial and final states (the optical density of states, ODS) requiring only conservation of energy.

The ODS determined by such ultraviolet photoemission studies have more strong detailed structure than the density of states determined by any other experimental method. Studies on a large number of materials indicate that the position in energy of this structure correlates rather well with the position in energy of structure in the calculated density of states. It is suggested, following the very recent theoretical work of Doniach, that \mathbf{k} conservation becomes less important (and nondirect transitions more important) as the mass of the hole becomes larger. This is due to the change in \mathbf{k} of electrons in states near the Fermi level as they attempt to screen the hole left in the optical excitation process. These electrons take up the excess momentum. One would expect the \mathbf{k} conservation selection rule to play an increasingly important role as the mass of the hole decreases. This is in agreement with experiment.

Key words: Copper; copper nickel alloys; density of states; GaAs; Ge; nondirect transitions; optical density of states; PbTe; ultraviolet photoemission.

1. Introduction

Photoemission can give a great deal of detailed information about the optically excited electronic spectra of solids. Adequate interpretation of photoemission data can produce detailed information on the electronic structure and, assuming that Koopmans' theorem [1] holds, on the ground state density of states.

The utility of photoemission lies in two factors: (1) The ability to determine the distribution in energy of

electrons excited by monochromatic light, and (2) the ability to study the valence bands of solids over their entire widths. Difficulties arise in correcting for inelastic scattering and electron escape probability and in interpreting the data so corrected. Correction for scattering and escape probability seems to have been rather successfully done in a number of cases [2,3,4,5,6]. There are still detailed questions open in interpreting the data; however, as will be shown in this paper, it is clear that considerable information on the density of states can be obtained from photoemission data independent of these questions.

Let us look in more detail at the essence of optical excitation in solids and the photoemission experiment.

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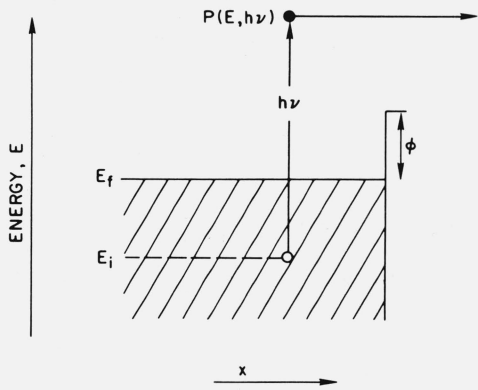


FIGURE 1. Energy diagram for a metal. $P(E, h\nu)$ is the probability of a photon of energy $h\nu$ exciting an electron to final energy E . ϕ is the work function, E_i is the initial energy of the excited electron, E_f is the Fermi energy.

Consider the probability, $P(E, h\nu)$, of a photon, of energy $h\nu$, exciting an electron to a final state of energy E (see fig. 1). The excitation spectrum in the solid is then given by the values of $P(E, h\nu)$ for all values of energy. The external photoemission energy distribution $N(E, h\nu)$ would correspond exactly to $P(E, h\nu)$ if all excited electrons escaped without inelastic scattering. Thus,

$$P(E, h\nu) \rightarrow N(E, h\nu). \quad (1)$$

In contrast, the optical constants $\omega\sigma$ or ϵ_2 (from which attempts are often made to determine the electronic structure) are related to the integral of $P(E, h\nu)$ over all possible final states

$$\epsilon_2 \rightarrow \int P(E, h\nu) dE. \quad (2)$$

ϵ_2 is the imaginary part of the frequency dependent dielectric constant and σ is the optical conductivity, $\sigma = \epsilon_2/\omega$. For the relations in eqs (1) and (2), it can be seen that photoemission contains much more detailed information than do the optical constants. This is illustrated by figure 2a, b, and c.

In figure 2a the imaginary part of the dielectric constant for Cu is plotted versus photon energy [7]. The arrows call attention to two values of photon energy, 5.0 and 10.2 eV. A maximum appears in ϵ_2 at $h\nu = 5.0$ eV. There has been considerable discussion [3,4,8,9,10] concerning the optical transition or transitions responsible for this peak. There is no measurable peak in ϵ_2 at 10.2 eV; rather, the curve is almost flat. In figure 2b and 2c, energy distribution curves, EDCs, are presented for $h\nu$ equal to 5.0 and 10.2 eV. The striking thing about these curves is the large amount of structure which is present in them. Whereas only one peak

was present in the ϵ_2 curve near 5.0 eV and none was present near 10.2 eV, several pieces of structure are present in the EDCs for each value of $h\nu$.

From the energy at which the structure appears, the initial and final states involved in the optical transition can be quickly identified. In the present case, the electrons within 2 eV of the high energy cutoff, E_{max} , are excited from the almost free-electron-like conduction states lying within 2 eV of the Fermi level; whereas, the sharp structure lying more than 2 eV below E_{max} is due to excitation from the d states.

By noting the manner in which EDC structure moves with $h\nu$, the relative importance of initial and final states can be determined and information can be obtained about selection rules and/or matrix elements. For example, it was possible to determine that the peak in figure 2b at about 2.7 eV was due to a direct transition from states near the Fermi level with a threshold at about 4.4 eV [3]. Examination of band calculations showed that the transition must be centered near the L symmetry point. We will return later to the discussion of the interpretation of photoemission data. In fact, such discussion will provide the central theme for this paper; however, it is first useful to briefly review experimental techniques and the effects of scattering on photoemission data.

2. Experimental Techniques

As was suggested in the Introduction, a large amount of information can be obtained from the photoemission energy distribution curves. A second useful measurement is that of the spectral distribution of quantum yield. Let us briefly review the experimental methods for obtaining such data. In so doing, we will not attempt an exhaustive list of references, but rather will attempt to refer to recent articles representative of the various techniques. Because of his closeness to the work at Stanford, the author will draw particularly heavily on this work.

For many years EDCs were obtained by measuring an I-V curve and differentiating it by hand. The most important modern advancement was the replacement of this tedious and demanding practice by various schemes which yield EDCs directly from the experiment. Most popular are methods which add a small alternating voltage to the retarding voltage so that the derivative is taken electronically [11,12]. By slowly (typically 1 volt/minute) sweeping out the retarding voltage, a complete derivative curve can be obtained. Recently [13,14], measurements have been made at the second harmonic of the alternating voltage to obtain

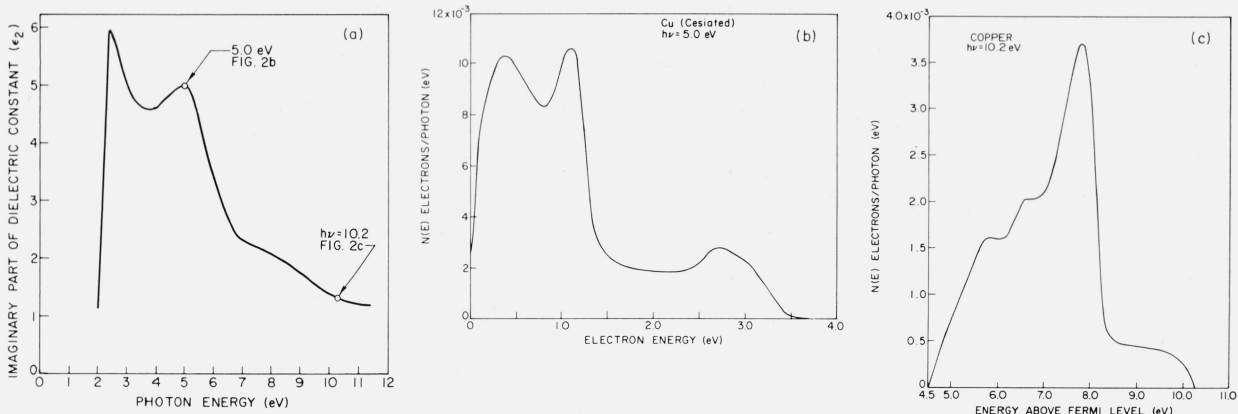


FIGURE 2. (a) ϵ_2 for Cu. (b) EDC obtained from Cu with Cs on the surface for $h\nu=5$ eV. Note that this curve has several pieces of structure in it, whereas the ϵ_2 curve had only one peak at 5 eV. (c) EDC for clean Cu. $h\nu=10.2$ eV. Note that several pieces of structure occur in the EDC, whereas there is no strong structure near 10.2 eV in the EDC.

the second derivative of the I-V curve. In this way weak structure in the EDCs can be detected and studied. A second approach is to take a I-V curve and then to either differentiate it electronically [15,16] or by means of a computer.

The geometry and other details of the energy analyzer are also of considerable importance. Because of ease of construction, wide use has been made of a cylindrical approximation [11] to the more ideal spherical geometry of the collector. This has given an energy resolution of between 0.1 and 0.3 eV, depending on the kinetic energy of the emitted electrons, the details of the emitter geometry, the uniformity of the collector work function, and other factors. Of particular importance for small electron kinetic energies are differences in work function between the face of the emitter and its sides. DiStefano and Pierce [17] have recently made an overall study of the factors limiting resolution. They conclude that a spherical collector with a spherical grid providing a field-free drift region should provide a significant increase in resolution provided that effects of the earth's magnetic field are properly minimized. Preliminary measurements with this geometry support these conclusions.

In principle, the measurement of the spectral distribution of quantum yield is much simpler than the energy distribution measurement. All that is needed is a standard detector of known response to which the emission of the sample under study can be compared. In the visible and near infrared spectral ranges, this is fairly easy to achieve because of the high light intensities available and the large number of suitable detectors. It is considerably more difficult in the ultraviolet where light intensity may be low and there are considerable problems with detectors [18]. Groups at the

National Bureau of Standards, Stanford University, and other laboratories are cooperating in an attempt to establish good standards on a national-wide basis.

Another very necessary condition for successful photoemission experiments is the ability to provide emitter surfaces which are atomically clean. One must be able to provide such surfaces and insure that they do not contaminate in the course of study (pressures better than 10^{-8} or 10^{-9} Torr are usually necessary). Depending on the material, surfaces may be provided by cleaving [19], evaporation [4,6,20], heating [21], sputtering [22], or a combination of these methods. In covalent semiconductors such as Ge, it is well known that care must be taken to preserve crystalline perfection; however, in metals such considerations seem much less important. In fact, for Cu and Ni, which have been studied both as single crystals and evaporated films, the evaporated samples have given to date as good or better results than have sputtered and/or heat-cleaned samples [21,23]. This is despite the fact that some evaporated samples may have very small crystallite sizes (for example, about 100 Å in the case of Ni [6,20]). The insensitivity to crystallite size is due to the escape length for photoexcited electrons often being much less than 100 Å.

It is often useful to reduce the threshold for photoemission by placing a layer of cesium on the surface of a material. Ideally the cesium will only form a monatomic layer which reduces the work function without affecting any other properties of the solid. However, since Cs may chemically combine, amalgamate, or interact in other ways with the material under study, one must take care. The best procedure is to obtain EDCs from clean material over a photon energy range of several eV or more before placing the cesium on the

surface. Then, after the cesium is placed on the surface, EDCs should be obtained from the same photon energy range. By comparison of the two sets of EDCs, an estimate can be obtained of any extraneous changes produced by the cesium.

3. Electron Scattering Phenomena

As mentioned in the Introduction, one must understand the effects of electron scattering in order to properly interpret photoemission data. Two principal scattering mechanisms are electron-electron and electron-phonon scattering. In the first type of event, the scattered electron loses a large fraction of its original energy to a second electron, which is thus excited. The electron-electron event is characterized by a mean-free path which decreases rapidly as the primary electron energy is increased in the range $E < 12$ eV. The energy loss in the phonon-scattering event is much smaller than that in the electron-electron event and, since this energy loss varies roughly as the Debye temperature, it will be much smaller for the material containing heavier atoms than for those with lighter atoms. There is no evidence that the phonon mean-free path is highly dependent on electron energy as is the case for electron-electron scattering. Kane [24] has pointed out that the electron-phonon scattering will be enhanced for final states having low group velocity (*i.e.*, states associated with a high density of states). Eastman [25] has made the same observation for the electron-electron event. However, it does not appear that massive distortion of the energy distributions are produced by these effects.

There is a threshold for pair production in semiconductors and insulators of about the forbidden band gap energy (*i.e.*, the electron must be above the conduction band minimum by this amount before it can produce a secondary). Thus, only phonon scattering is possible below this threshold. In a metal there is no such threshold. However, as mentioned previously, in both semiconductors above threshold and in metals the electron-electron scattering length decreases quite fast with increasing electron energy. In figure 3 we present values [5,26,27,28] for Au obtained by several different methods. Note that the mean-free path drops by two orders of magnitude within a few eV. The electron-electron scattering effects have been taken into account quantitatively in interpreting photoemission data [3,4,6]. In fact, photoemission measurements can be used to determine the electron-electron mean-free path. The solid curve in figure 3 was deduced from such measurements by Krolikowski and Spicer [4].

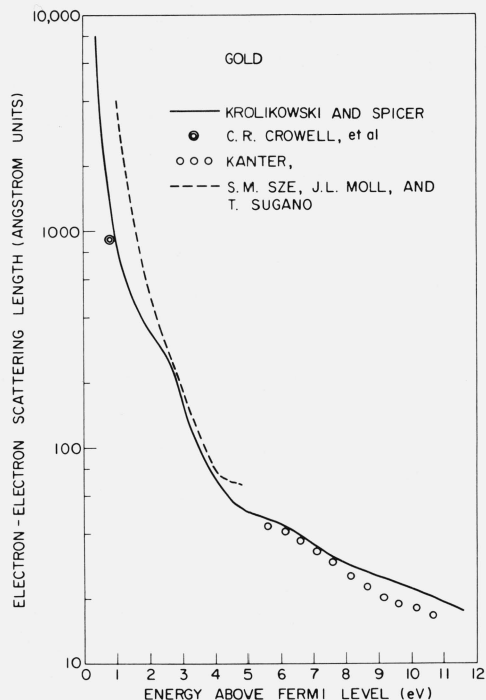


FIGURE 3. Electron-electron scattering length for Au as obtained by several workers [5,26,27,28].

More recently, Eastman [29] has developed a direct method for obtaining electron-electron mean-free paths from photoemission measurements. This is based on a variation of sample thickness.

For electron energies below the threshold for pair production in semiconductors, photoemission has been used extensively by James and Moll [30] to study the scattering of electrons by phonons in GaAs. This is of particular interest because of its importance in the Gunn effect. DiStefano and Spicer [31] have developed special photoemission techniques to study the scattering of hot electrons in alkali halides by phonons.

We give the examples listed above to illustrate the degree to which scattering of excited electrons in the photoemission experiment has been studied and is understood. This is not to say the processes are understood in all detail. This is not the case; however, a good, first-order understanding does seem to exist. There are other possible scattering phenomena which are less well understood. These include scattering from: (1) Bulk imperfections (such as grain boundaries), (2) the sample surface, and (3) scattering from oxide or other "crude" layers on the surface [19].

4. Interpretation of Photoemission Data: Direct and Nondirect Transitions

The present author and his coworkers have suggested [2,19,32] that, for excitation from *certain*

quantum states characterized by low mobility holes, conservation of \mathbf{k} may not provide an important selection rule and that only conservation of energy need be considered in interpreting the photoemission data. Such transitions were called nondirect.

The suggestion of nondirect transitions was prompted by the character of the photoemission data obtained from states of this character. Based on this data, it was further suggested that a measure of the density of states could be obtained directly from analysis of the photoemission data. Of course, such a strong departure from accepted theory was met with considerable skepticism. Recently, band calculations [25,33,34,35], as well as new photoemission data (much of which will be reported at this meeting), have shown that there are certain strong similarities between the experimental EDCs interpreted as nondirect and the EDCs calculated using band structure results and \mathbf{k} conservation when broadening effects were included in the calculation. However, other important systematic differences do remain, which may have considerable significance. In this paper, I will place particular emphasis on this discussion since it is central to the experimental determination of the density of states from uv photoemission.

Before proceeding further with this discussion, it should be recognized and emphasized that there were a number of materials in which direct transitions were clearly identified and many in which *only* direct transitions were seen; for example, the column IV and III-V semiconductors [36]. It should also be recognized that the criterion of peaks "moving with $h\nu$ " (or the criteria of peaks which are stationary independent of $h\nu$) has been considered a necessary, but not sufficient, condition for identifying a nondirect transition [36,37,38]. In particular, abrupt appearance or disappearance or strong modulation of *peaks* has been taken as suggestive of direct transitions even when peaks "move with $h\nu$ " [38]. PbTe [37], GaAs [36], CdTe, CdSe, and CdS [38] provide examples of this.

Another method for attempting to distinguish, experimentally, between direct and nondirect transitions is to examine the effects of reducing or destroying the periodicity of the lattice. Since \mathbf{k} conservation is imposed by the periodicity of the lattice, destroying that periodicity should remove any importance of \mathbf{k} conservation as an optical selection rule. Examples will be given of cases where periodicity is reduced or destroyed by alloying, melting, or forming an amorphous solid. Brust [39] has recently pointed out the possibility of explaining these changes by introduc-

ing an uncertainty in \mathbf{k} rather than removing it completely as a selection rule.

Neville Smith has played a key role in the development of calculations of photoemission from d bands at Stanford [33]. A paper describing some of his work is included in this conference as is work on indium and aluminum by Koyama and Spicer [40]. The group of Janak, Eastman, and Williams [41] has also completed calculations assuming direct transitions for Pd which they will report at this meeting. I will not attempt to summarize these papers; but rather I will attempt to emphasize certain points.

The nondirect transition model was developed empirically since it appeared to give a good first approximation to the behavior of experimental photoemission data in a number of cases, including Cu. This model has been described in detail elsewhere [2,3]. The essence of it is that the optical transition probability, $P(E, h\nu)$, is given by the product of the optical densities of states (ODS) at energies E and $E - h\nu$:

$$P(E, h\nu) \rightarrow \eta(E)\eta(E - h\nu). \quad (3)$$

Here $\eta(E)$ is the optical density of empty states at an energy, E ; and $\eta(E - h\nu)$ is the filled ODS at an energy $h\nu$ below E . The term "optical density of states" is used since this density of states is obtained from the optical transitions as seen in photoemission. It is also appropriate since the optical density of states may be modified from the true density of states by optical matrix elements.

Let us examine direct and nondirect models for Cu as well as the experimental data used most recently. Copper is most appropriate for a number of reasons. First, its band structure seems to be as firmly established as any of the noble or transition metals. Second, it possesses relatively narrow d bands which might provide nondirect transitions; and third, experimentally Cu has been studied as thoroughly or more thoroughly than any of the other noble and transition metals so that the experimental data now seems to be on a very good footing.

Let us now examine photoemission from clean Cu for $6.0 \leq h\nu \leq 11.6$ eV. In figure 4 we present EDCs for Cu from the work of Krolikowski and Spicer [4]. More recently, Eastman [42] and Smith [43] have reproduced these curves; thus, the experimental data seems quite reliable. This data has all of the characteristics which lead to the assumption of nondirect transitions. For one thing, the peaks superimpose when they are plotted against $E - h\nu$, *i.e.*, against the *initial* state energy. Thus, it is apparent that the EDC struc-

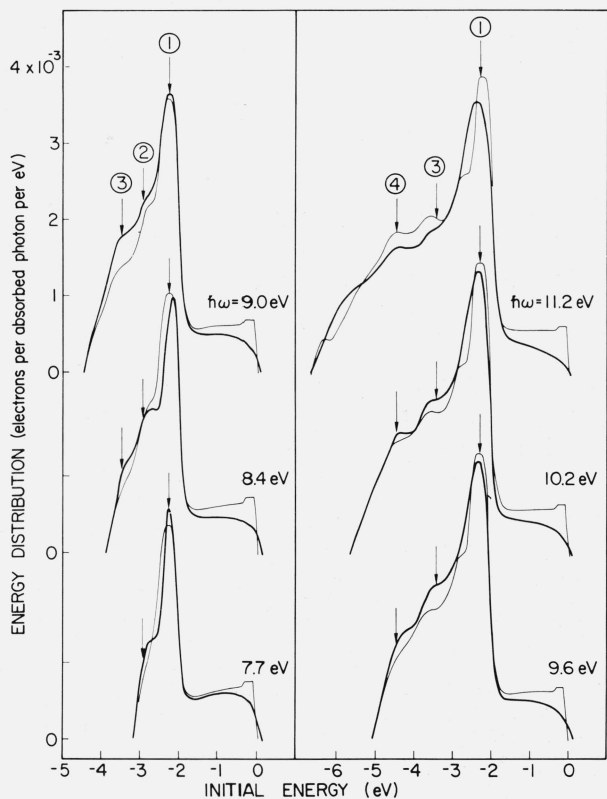


FIGURE 4. EDCs for clean Cu plotted versus the initial energy. The solid curve indicates the experimental curve and the thin full curve gives the energy distribution calculated using the nondirect model for the values of photon energy indicated. The arrows indicate the position in energy of structure in the ODS.

ture is due to the same structure in the initial ODS. Note also that the structure in the EDC varies very monotonically with photon energy. As we shall show later, a striking characteristic of the direct transitions calculations is the relatively larger amount of modulation which they predict in the peak strengths as a function of photon energy.

As described by Krolikowski and Spicer [4], the ODS was obtained from the photoemission and optical data. The ODS so obtained is presented in figure 5a and b. From this ODS, the thin full curves in figure 4 were obtained from this ODS using the nondirect, constant matrix element model. As can be seen, the agreement is rather good particularly since it is on an absolute basis. The notable difference is that the first peak broadens and the second peak appears to merge into it at higher photon energies.

In figure 5a and b, the ODS obtained from the photoemission studies is compared to the density of states from two band calculations [44,45]. As can be seen, rather good agreement is obtained between the locations of the major pieces of structure in the ODS and

the calculated density of states. However, there is no such agreement between the relative strengths of the structure. This may be due to the effects of optical matrix elements, to difficulties in the band calculations (note the difference between the two calculated density of states), or to other effects.

In figure 6, the results [33] of calculations based on the direct-transition model for clean Cu are presented. These calculated curves have strong similarities to the experimental data. However, in order to obtain such agreement it was necessary to include a Lorentzian broadening of 0.4 eV for the calculated curve. Other calculations [34,35] use broadenings of between 0.3 and 0.7 eV. If the broadening is not used, much too much sharp structure appears in the calculated EDCs and this structure is modulated much too strongly and fast. The use of the broadening function finds partial justification in several factors—the instrumental and lifetime broadening, the finite lifetime of the excited carriers, and the inaccuracy in the band calculations. However, it is important that we keep the broadening in mind since it tends to make the direct and nondirect calculations more similar and also since it may provide an empirical method of making correction for many body effects. In the limit of flat initial bands, the direct and nondirect models would be identical. As the bands become less flat, increased broadening will still tend to keep the agreement between EDCs calculated on the direct and nondirect models.

Let us now examine the EDCs calculated by the direct method. In figure 6 we show the results of the calculations of Smith and Spicer and in figure 7 we compare the results of these calculations to experimental data. Again, the comparison is on an absolute basis. Several things are noteworthy about these results: (1) The position in energy of peaks in the direct calculations is constant on the $E - h\nu$ plot, (2) the position of structure corresponds rather well with the position observed experimentally (the numbered lines correspond to the position of structure found experimentally and in the ODS), and (3) the modulation of peak heights and widths is much stronger than anything seen experimentally. If, in fact, such strong modulation was observed experimentally, this would have been attributed to the effects of direct transitions or matrix elements effects despite the constant position in $(E - h\nu)$ of the peaks. Such identification was made, for example, in the II-VI compounds [38], GaAs [36] and PbTe [37] where strong modulation was observed experimentally.

The constant position in energy of the direct structure in figure 6 and its agreement with experiment is

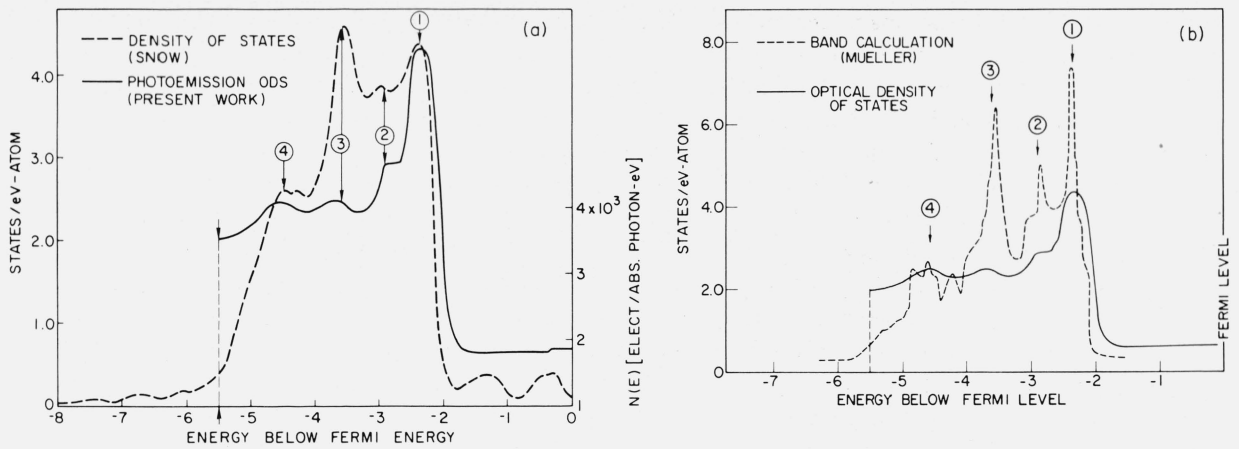


FIGURE 5. (a) Comparison of the ODS with the density of states calculated by Snow [44] using an $5/6 \rho^{1/3}$ exchange term. Snow's density of states have been shifted by 0.2 eV to place the Fermi level in exact agreement with experiment. The absolute scale was placed on the ODS by placing 11 electrons within 5.5 eV of the Fermi level. Note that the four pieces of numbered structure coincide rather well in energy. The numbered arrows correspond to those in figure 4. (b) Comparison of the ODS with the density of states calculated by Mueller [45].

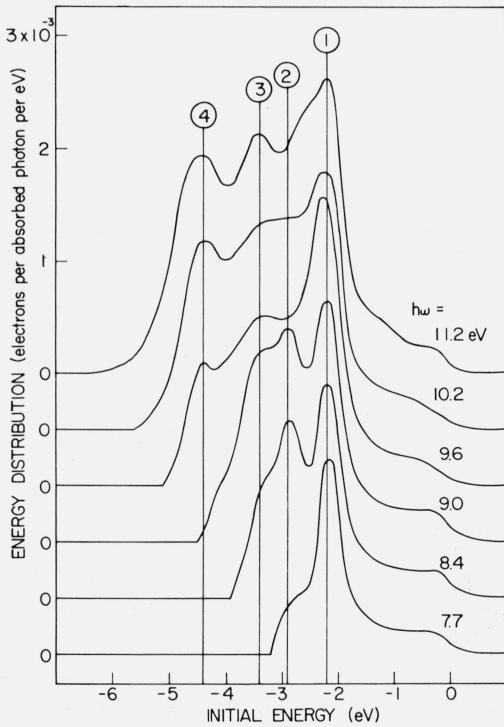


FIGURE 6. The EDCs calculated for Cu by Smith and Spicer assuming direct transitions.

not surprising in retrospect in view of the agreement between the ODS and band calculations shown in figure 5. It would appear, at least for the limited range of $h\nu$ covered by this study, that the Cu bands are sufficiently flat and that the broadening effects are sufficiently large so that the \mathbf{k} conservation condition does not impose overwhelming constraints on the optical excitation process. The fact that the nondirect model gives better detailed agreement with the experimental

data than the direct model, suggests that many body effects may still be important in bringing in a range of \mathbf{k} rather than a delta function in the optical absorption process.

In another paper, presented at this meeting, Neville Smith [34] will show new experimental data which give

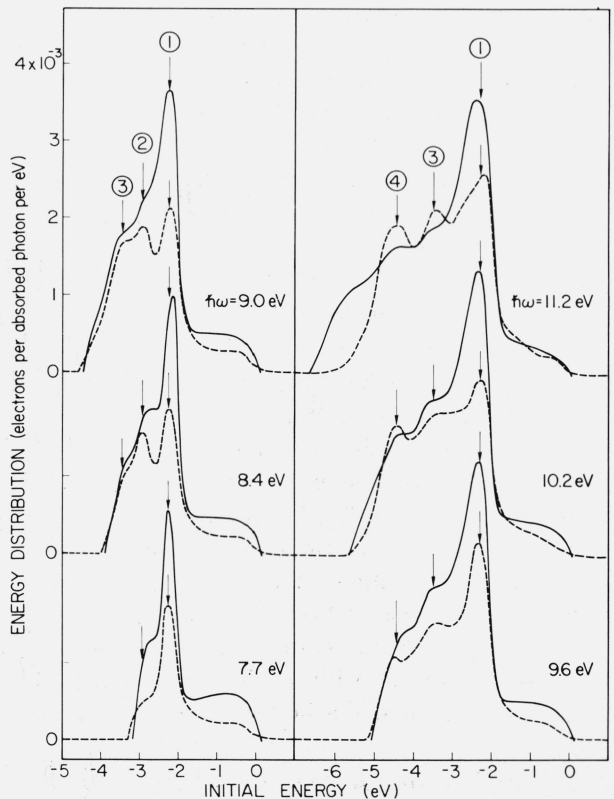


FIGURE 7. Comparison of the EDCs calculated for Cu using the direct transition model with the experimental EDCs. The full line gives experimental and the dashed line calculated EDCs.

clear evidence of direct transitions in cesiated Cu. The transitions originate from states 2.8 to 3.8 eV below the Fermi level. It is in this region that the d bands have greatest curvature. Recognizing that this curvature should provide the most easily detectable evidence for direct transitions, Berglund and Spicer [3] looked especially for direct transitions in this region. Apparently poorer sample preparation conditions prevented them from seeing the transitions. The success of Smith is a tribute to him and to the advances in vacuum and preparation techniques made at Stanford and elsewhere in recent years.

Smith has also made direct transition calculations of the EDC for cesiated Cu. These show the effects found experimentally; however, despite the inclusion of a 0.3 eV broadening factor, the predicted modulation is considerably stronger than that observed experimentally.

There is perhaps a good analogy between the present situation in this matter and that with regard to x-ray emission spectroscopy for many years. The simple and popular view of the latter field was that one could always explain the x-ray emission spectra just in terms of single particle transitions so that the valence band density of states could be obtained directly from the emission spectra if "atomic-like" matrix elements were properly taken into account. With the simple metals fair agreement was obtained between experiment and theory on this model, although certain nagging inconsistencies remained. The situation has changed drastically in the last few years since theorists have had success in treating the many body effects of the hole in the core state. I will not attempt to review this work since it will be discussed in some detail at this conference. However, there may be a parallel with regard to the uv photoemission work.

At Stanford, Doniach [46] has been expanding his investigation of many body effects in the x-ray photoemission effect to include the many body effects associated with screening of the valence band hole in the uv optical excitation process [32]. Preliminary results suggest that such effects exist, producing a spread in possible \mathbf{k} in the optical transitions, and increase in importance as the effective mass of the hole increases. Thus, the flatter the valence band is, the larger the effect. If one looks at the Cu results with this in mind, one notes that the flatter the bands, the better the nondirect model works.

In concluding this section, I would like to remark that the direct transition model is based on a rather idealistic assumption which applies best where the bands have good curvature; empirically, this model

seems to work very well for a wide range of materials of this type. On the other hand, the nondirect, ODS, model should work best in materials with quite flat bands. It may never be completely correct (we must understand the physics better before it is possible to pass quantitative judgment); however, its great simplicity may make it a good first approximation when it can be successfully applied, *i.e.*, when the EDCs based on the ODS are in relatively good agreement with experiment. Certainly the success with Cu, Ni, and similar material, suggests that it may give us the best first approximation to the densities of states of these materials which can be obtained solely from experiment.

There may be an intermediate range of bands and materials in which neither the direct nor the nondirect model applies with great accuracy. In this case, detailed understanding can only be obtained when theories such as that of Doniach are fully developed. In the meantime, it is probably well to keep open the possibility of transitions occurring over a range of \mathbf{k} and not just at a given value. It would be extremely nice if in the direct calculations, a broadening could be put in by a distribution in \mathbf{k} before searching the zone rather than over energy after the vertical transitions have been tabulated.

Experimentally, it is important to obtain data over a wider range in energy to test the selection rules with more rigor. Eastman [29] has already begun to do this with very interesting results.

5. Effect of Reducing or Destroying Crystal Periodicity: Liquid In, Alloys, and Amorphous Ge

Another way of testing for the importance of \mathbf{k} as an optical selection rule is to reduce or destroy the long-range order of a crystal. Clearly as the solid becomes increasingly disordered, any dependence of \mathbf{k} must become less and less well defined, *i.e.*, a single value of \mathbf{k} can no longer be used to define a quantum state. Rather, if a description in terms of \mathbf{k} is used, it must contain a distribution of \mathbf{k} ; a single \mathbf{k} will be insufficient. In the limit of complete disorder, \mathbf{k} will lose meaning as a quantum number.

5.1. Indium

Indium has been studied experimentally by Koyama [18] in the crystalline, amorphous and liquid forms. Note that, since it contains no d electrons, In would not be expected to fall within the class of nondirect materials. In addition, Koyama has made calculations based

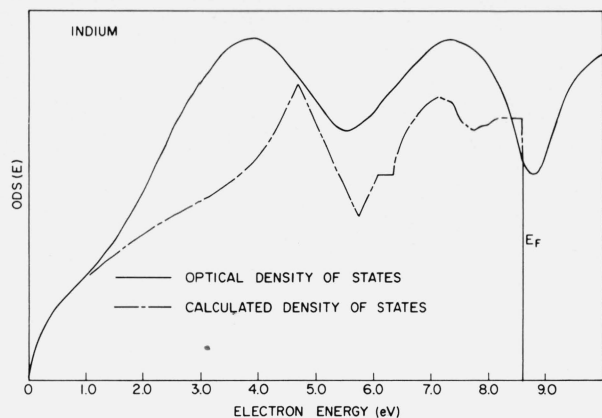


FIGURE 8. Comparison of the ODS for In with the density of states obtained from band calculations [40].

on direct as well as nondirect models. These calculations will be described in detail in a separate paper of this conference [40]. Koyama's findings for crystalline indium are quite interesting: (1) Both the direct and nondirect transition models fit the experimental data fairly well (as they do for Al), (2) the EDCs for In are characterized by two broad peaks separated by a minimum which correlates [47] well (in either model) with a large band gap in the band structure of Ashcroft and Lawrence [48] (see fig. 8), and (3) the principal features of the EDC (the two peaks) were seen to persist in liquid indium despite highly increased electron scattering. Since there seems, at least at present, to be less physical justification for the nondirect model in In than in Cu, it is tempting to assume for this material that direct transitions dominate in the crystalline material and that nondirect transitions occur in the liquid. Even then a question would arise as to why the density of states structure due to crystalline potentials persists into the liquid. (Shaw and Smith [49] have found theoretical evidence of such effects in Li.) Koyama [18] has suggested that this is due to the dominance of short-range interactions in determining the electronic structure and thus the density of states of both liquid and crystalline In. Clearly studies of In at higher resolution and for a wider range in $h\nu$ should prove very worthwhile.

In any case for both Al and In, the density of states obtained by the nondirect analysis seems to be in fair agreement with the results of band calculations. As the direct transition calculations show, this may be due to the large range in \mathbf{k} space from which direct transitions can take place and thus not be a true indication that \mathbf{k} vector is unimportant (although, again, some uncertainty in \mathbf{k} is probably important in bringing the direct and nondirect models into agreement). The sensitivity of

the calculated EDCs to the electronic structure is illustrated by the fact that, whereas Ashcroft and Lawrence's band structure for In agreed with experiment, other proposed band structures [49] did not give agreement with the ODS.

Mosteller, Huen and Wooten [50] have recently studied the photoemission from Zn as a function of temperature and found that the quantum yield decreased significantly on cooling the sample from room to liquid N_2 temperature. Based on this, they note the possibility that in Zn the ultraviolet optical transitions may be indirect, *i.e.*, phonons conserve \mathbf{k} . Such temperature dependence has not been observed for other semiconductors and metals such as Cu, Gd [51] and Cr [52] which have been studied as a function of temperature. The Zn results are mentioned here because of the similarity between the In and Al band structure and that of Zn and because In and Al have not been measured below room temperature.

5.2. Amorphous and Crystalline Ge

In contrast to In, Ge provides a striking case of a material whose optical properties and uv EDCs change drastically when the long-range order is destroyed by forming amorphous Ge. Photoemission studies show clearly the direct nature of the transitions in crystalline Ge [36] in agreement with analysis of optical data [53]. Thus, differences between crystalline and amorphous Ge are of considerable importance.

Figure 9 indicates ϵ_2 for the amorphous and crystalline material [54,55] and figure 10 indicates EDCs for

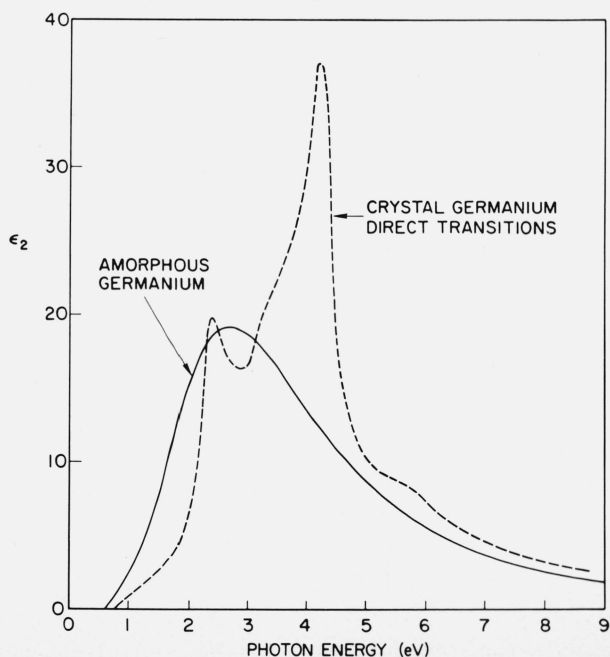


FIGURE 9. ϵ_2 for amorphous and crystalline Ge.

5.3. Cu-Ni Alloys

A third example of the effect of disorder is in the alloys such as those between the noble and transition metals. Here the lattice periodicity is not destroyed. Rather, atoms with two different potentials are arranged at random, or almost at random (it appears that clustering effects are negligible [21]) within the periodic lattice. Since the potentials are quite different (for example the transition metal typically produces a virtual-bound state when dissolved in a noble metal), the effect on the periodicity should be considerable. Despite this, the effect on the ϵ_2 and on the EDCs of the host metal does not appear to be drastic. The principal effect is in the production of a virtual-bound state under the proper circumstances. Such states have been and are being qualitatively studied through the use of photoemission [21,23,60,61,62,63].

In figure 12, the optical parameter $\omega\sigma$ is presented for the Cu-Ni alloys studied by Seib and Spicer [21,23]. Except for $h\nu < 2$ eV in the Cu-rich alloys where the change is due to the formation of a virtual-bound Ni state, the changes are much less than those found in the crystalline to amorphous transformation of Ge.

As outlined in the Introduction, photoemission can give a more detailed look at the optical transition than can the optical data. Examination of EDC data from the alloys shows that the direct transition from the s - p -derived bands near the Fermi surface at L is not detectable in the alloys [21]. However, the transitions from the d states are much less affected. In fact, the EDCs from Ni and Ni-Cu alloys with up to 19 percent

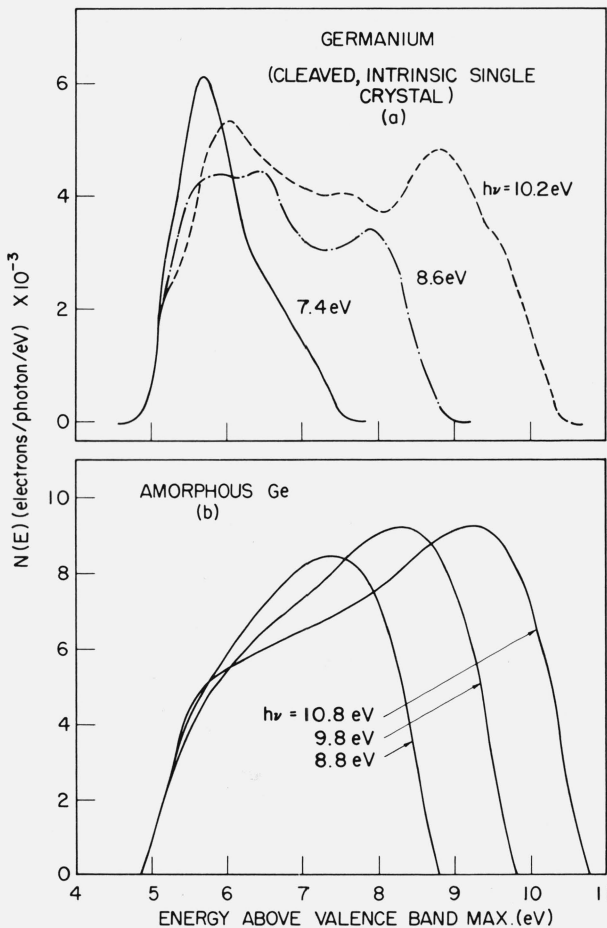


FIGURE 10. Photoelectron energy distributions for Ge surfaces. (a) Cleaved, intrinsic, single crystal. (b) Amorphous film. The vertical axis gives the number of electrons per absorbed photon per eV. The horizontal axis gives the electron energy relative to the maximum in the valence band. The sharp structure in (a) is due to direct transitions in specific regions of the zone. The single broad peak in (b) is due to a peak in the valence-band optical density of states.

crystalline and amorphous Ge [54,55,56,57]. As can be seen, the changes in ϵ_2 and the EDCs which accompany the change in form of Ge are first order. The loss of sharp structure is clearly due to the loss of long-range order. In their studies of amorphous Ge, Donovan and Spicer have used a nondirect analysis with considerable success to treat data from the amorphous material. In figure 11 the ODS obtained from these studies is compared to the density of states obtained from band calculations [58]. Brust is approaching the problem of amorphous Ge from calculated band structures by a method in which there is a spread in \mathbf{k} associated with the optical transitions and thus is intermediate between the direct and nondirect models [59]. Because of its flexibility due to the possibility of assigning various values to the spread in \mathbf{k} , this approach clearly has certain advantages over the pure nondirect approach.

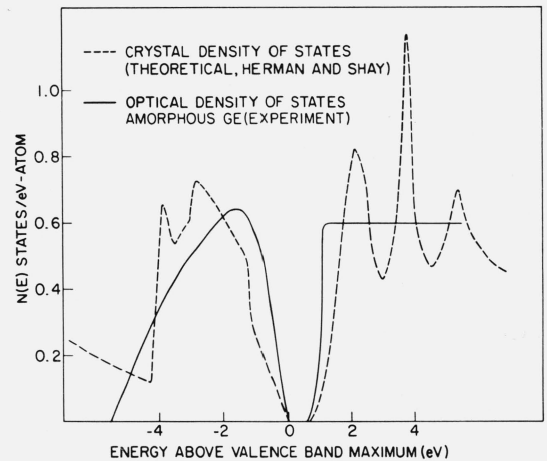


FIGURE 11. Optical density of states for amorphous Ge as determined by photoemission compared with the electronic density of states for crystalline Ge calculated by Herman and Shay. The vertical axis is in units of states per eV per atom for the crystal density of states and in arbitrary units for the optical density of states. The energy zero in both cases is taken at the maximum of the valence band.

6. Methods of Determining the Density of States from Ultraviolet Photoemission Data

Two extreme approaches can be taken in using photoemission data to determine the density of states of solids. One is to use the photoemission results to provide input into band calculations. This approach is not necessary if first-principles band calculations give exact results. If this is not the case, the band calculations can be adjusted to give agreement with the experimental data. Such correction is often necessary and, in addition to overcoming uncertainty in the potential used in the band calculation, the empirical correction may correct for departures from Koopmans' theorem as, for example, suggested by Herman [66]. One approach is to parameterize the calculation and use experimental data. de Haas-van Alphen data or optical data could also be used for adjusting the band calculations. Since the de Haas-van Alphen data give experimental data only at the Fermi surface, it is not very sensitive to energy shifts from the Fermi level. Unambiguous interpretation of structure in the optical constants, such as ϵ_2 , has proven very difficult. Piezoreflection has proven to be very powerful in Cu [10] but despite considerable effort, so far has not been successfully applied to Ni [67]. A difficulty in piezoreflection also lies in estimating the absolute or relative strength of optical transitions whose symmetry is determined by these measurements.

If first-principles band calculations were thought to be sufficiently good, the photoemission studies would

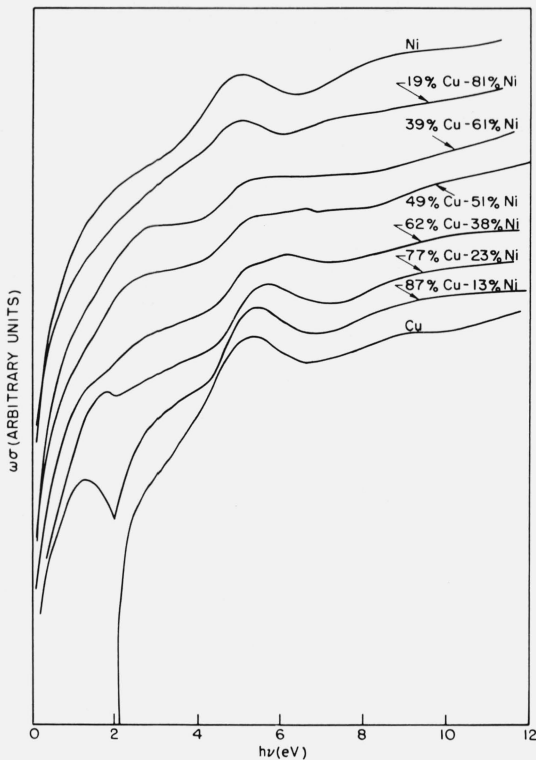


FIGURE 12. The optical constant $\omega\sigma$ for pure Ni and Cu and a series of Ni-Cu alloys.

Cu (atomic present) are almost indistinguishable except for effects due to the change in work function. This is shown by the data in figure 13. Even for 39 percent Cu, the position of the two strong peaks in the EDC were unchanged [23].

Let us next examine the Cu-rich alloys. In figure 14 we present data for pure Cu and Cu containing 13 and 23 percent Ni [21]. As can be seen, the Cu d edge is little changed and the position in energy of structure from the d bands is similar to that in the pure material; however, the relative strengths of the peaks are changed.

The contrast in optical properties and EDCs between these alloys and Ge in its crystalline and amorphous forms is striking. For the alloys, the changes are relatively small whereas, for Ge, they are much larger. \mathbf{k} conservation clearly plays the dominant role in determining the optical transition probabilities in crystalline Ge; thus, destroying the long-range order completely changes the optical properties. The insensitivity of Cu and Ni to disruption of the long-range order suggests that the optical transitions from the d states of pure Cu and Ni are, on the average, much less strongly affected by the \mathbf{k} conservation condition; however, the L transition from the s - and p -derived states is clearly a direct transition and this disappears in the alloys studied.

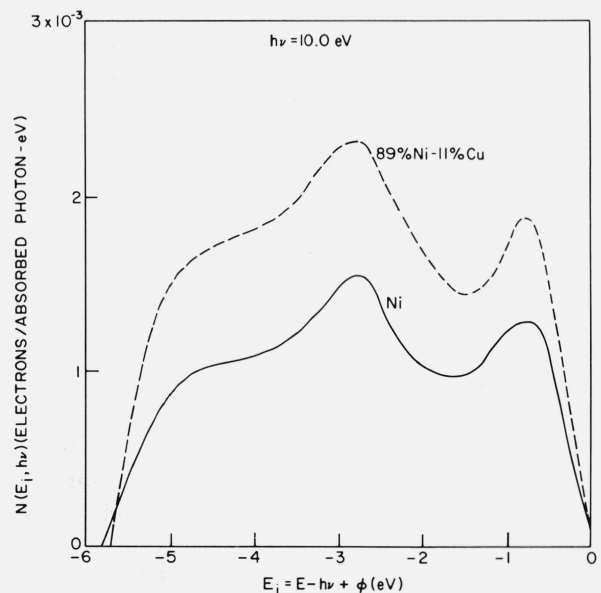


FIGURE 13. The EDCs at $h\nu = 10$ eV obtained from pure Ni and a Cu-Ni alloy containing 11 atomic percent Ni.

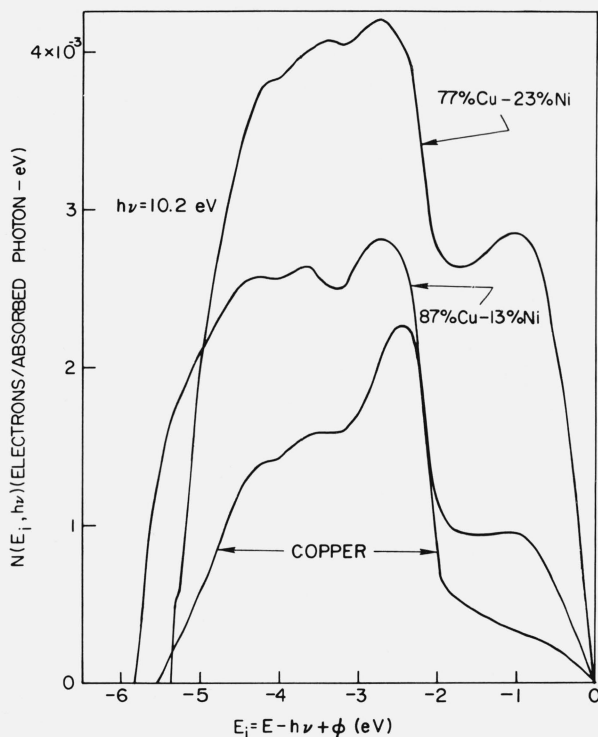


FIGURE 14. EDCs from pure Cu and two different Cu-Ni alloys. Note that the Cu d edge and the position in energy of the d peaks is essentially unaffected by the alloy.

simply serve as a check. For best results, this approach requires two conditions. First is a fairly accurate and well-advanced band theory. Without this, it is difficult to relate the photoemission data to the band structure in a meaningful way. Second is photoemission data which shows dramatic band structure effects such as the onset of the L transition in copper or the Γ transition in CdTe [38]. For materials like GaAs in which \mathbf{k} conservation dominates the optical transition probability, Eden has developed a systematic method for comparing photoemission results and the results of band calculations. This will be reviewed briefly in the next section.

A second approach is to attempt to obtain density of states information directly from the photoemission data. The more apparent the connection between the photoemission data (*i.e.*, the optical transition probability) and the density of states, the more efficient is this approach. As we will see in the next section, it is very difficult to obtain density of states information from photoemission data for a material such as GaAs where \mathbf{k} conservation provides a dominant optical selection rule; however, in a case such as copper where \mathbf{k} conservation does not play such a dominant role, the nondirect method of analysis gives a good mechanism

for obtaining the principal features of the density of states from experimental data.

The nondirect transition [3,4] model provides a simple way to analyse the photoemission data to obtain an ODS. Once this is done, EDCs can be calculated and compared with experiment. In this way, the consistency of the nondirect approach can be judged. Only where reasonable consistency is obtained can the nondirect approach be used in a meaningful way. However, even when clear evidence is obtained that some structure is due to direct transitions, useful density of states information can apparently be obtained from the nondirect approach when EDCs calculated using the ODS reproduce closely enough the major strengths in the experimental EDCs. (Cu [3,33,34] and Au [5] appear to be examples of this.) By major strengths, we mean attention should not be focused on relatively weak structure which is clearly direct, but on the overall amplitudes in the EDCs.

7. A Sampling of Experimental Data

Since this paper is already lengthy, we will not attempt a comprehensive survey of the photoemission literature; rather, we will attempt to present only a few representative results which have not been presented previously in this paper in order to illustrate and amplify the remarks made earlier.

Photoemission measurements and the nondirect analysis has been made on a fairly large number of transition and noble metals other than those mentioned earlier. Eastman, in particular, has obtained the ODS for a wide range of transition metals [6,20,29]. In figure 15 we present the ODS obtained by Eastman for ten metals [68]. For the sake of comparison, the density of states from band calculations are also given [68,69]. Although the agreement between experiment and calculation is not perfect, it is encouraging, particularly when one realizes that the band calculations were not highly refined and in some cases were just obtained from the calculation for a different material using a rigid-band approximation. The agreement obtained suggests that there is a meaningful relationship between the ODS and density of states obtained from band calculations, as does the agreement found for Cu [3,4], Ag [3,62,70], Ni and other transition [6,52] and rare earth metals [71].

In section 4, it was suggested that the narrower the bands the more valid the nondirect approach and thus the ODS of the correct density of states. If this is true, the situation within the transition metals should become less favorable as the atomic weight of the metal

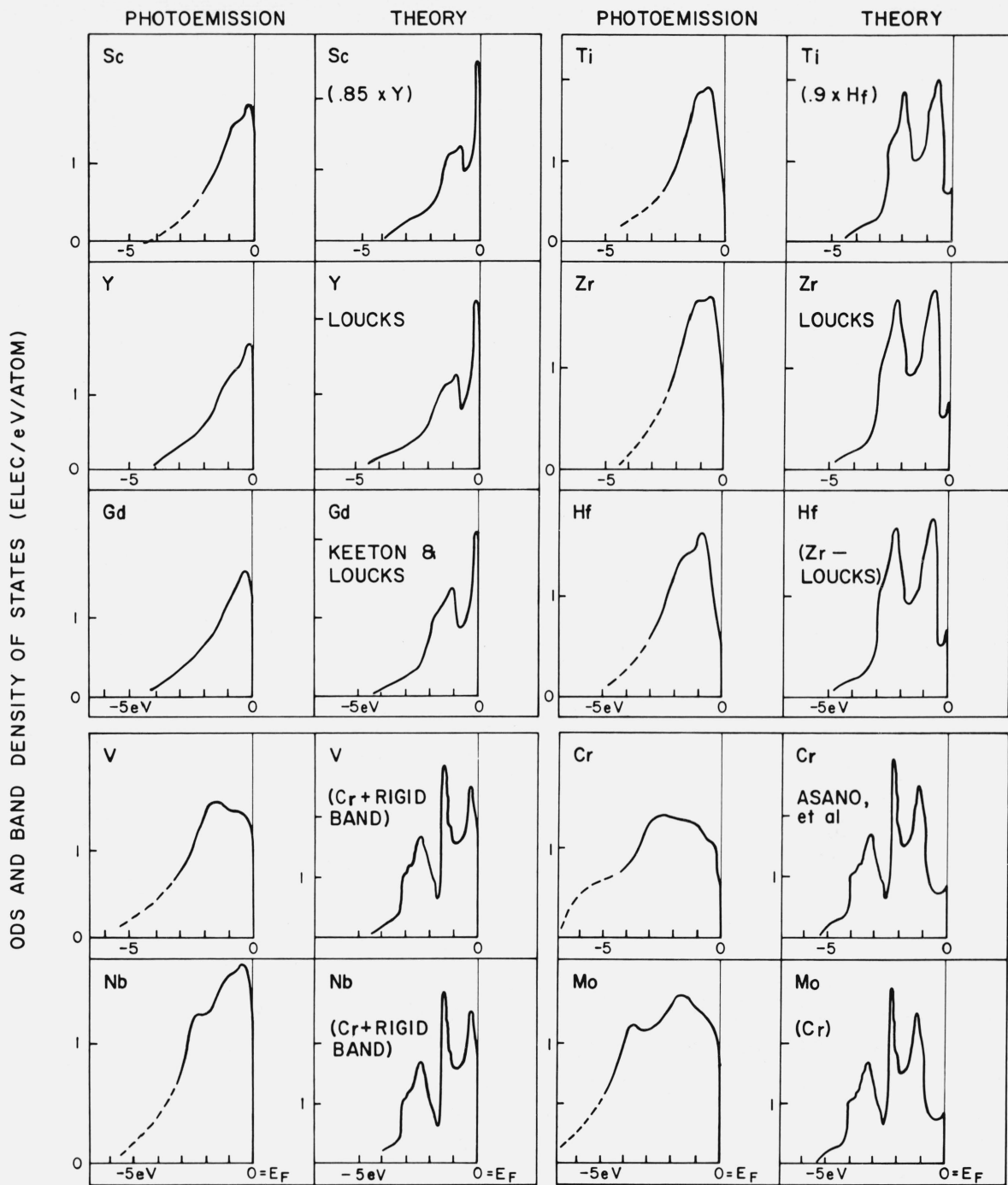


FIGURE 15. Optical density of states obtained by Eastman as compared to the density of states obtained from band calculations. This figure is taken from ref. 68.

increases since relativistic effects will broaden the bands. For example, the d -band width of Au is about twice that of Cu. Krolikowski and Spicer [5] have also studied clean Au in good vacuum for $5.4 \leq h\nu \leq 11.6$ eV and in poor vacuum for $h\nu$ values of 16.8 and 21.2 eV. From this work the ODS presented in figure 16 was obtained. As can be seen in figure 16, the ODS is in

rather good agreement with the EDCs obtained from soft x-ray photoemission work [72]. The photoemission results also have been found by Ballinger and Marshall [73] to correlate rather well with their band calculations. On the other hand, work by Eastman at photon energies of 16.8 and 21.2 eV in good vacuum gives strong evidence that direct transitions are important in

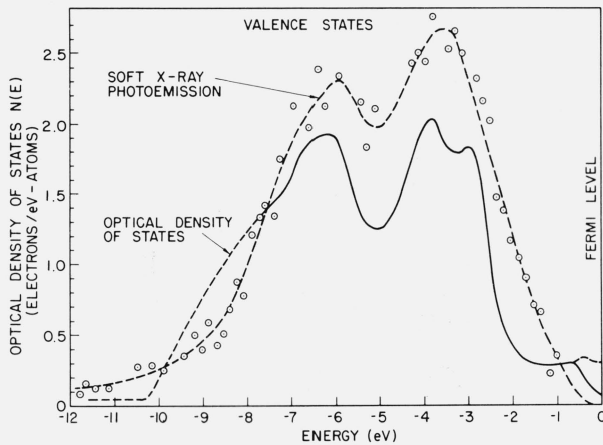


FIGURE 16. Comparison of the ODS and the soft x-ray photoemission results of Siegbahn, et al. [72]. The x-ray results have been shifted to lower energy by 0.6 eV to obtain the best fit. (It is difficult to set the absolute zero of energy in the x-ray experiment.)

Au. This series of results suggest that quite useful density of states information can be obtained from the relatively narrow bands of noble and transition metals by the ODS type of analysis even when direct transitions are important and that the broadening of the d band in going to Au does not make the ODS approach useless.

Up to this point we have concentrated to a large extent on materials for which the nondirect analysis can be used. In order to give perspective, let us now examine GaAs in which \mathbf{k} conservation has been found to provide a dominant optical selection rule as it has been found for Ge, Si, and other III-V compounds [36]. If structure in the EDCs is due to peaks in the initial or final density of states, this can be detected by plotting the EDCs against initial energy ($E - h\nu$) or final energy (E) respectively. This argument holds even if the transitions are direct. The distinction between direct and nondirect transitions is made on the basis of modulation of the strengths of the peaks with particular atten-

tion being paid to evidence for them appearing or disappearing as photon energy is varied [36,37].

With this in mind, let us examine figure 17a and b where two typical EDCs for GaAs [36,74,75] are plotted versus final, figure 17a, and initial state energy, figure 17b. As can be seen, these EDCs are particularly strong in structure. Despite this, there is little tendency for the structure to fall at the same energy either on initial ($E - h\nu$) or final, energy plot. This shows clearly that \mathbf{k} conservation provides an important selection rule. As a result, it is difficult to obtain density of states information directly from such plots. Eden [74] and Eden and Spicer [75] have derived a reasonable way of analyzing such data. This is done by making a plot of the final state energy of structure in the EDC, E , of structure versus the photon energy. Such a plot is shown in figure 18 for cesiated GaAs. One can obtain from band calculations theoretical plots of the same type for the symmetry directions of the crystal. By superimposing the two plots, it is possible to make identifications of the structure in the EDC. Such identification is indicated in figure 18. Further details are available elsewhere [36,74,75]. To obtain information on the density of states, it is sufficient to note two features: (1) A horizontal set of points for $E \approx 5$ eV labeled, "Final States Near L_3, W ;" and (2) the 45° line between final state energies of about 4.5 and 8 eV labeled, "Transition II from Band 3 Minimum." Since (1) is a fixed, final state, it would suggest a peak in the final density of states at about 5 eV. In figure 19 we present a band structure for GaAs by Cohen and Bergstresser [76] along with the density of states calculated from it by Shay and Herman [77]. As can be seen, there is a very sharp peak in the final density of states at about 5 eV.

The 45° line in figure 18 indicates a transition from initial states at a fixed energy E_i since $E = E_i + h\nu$.

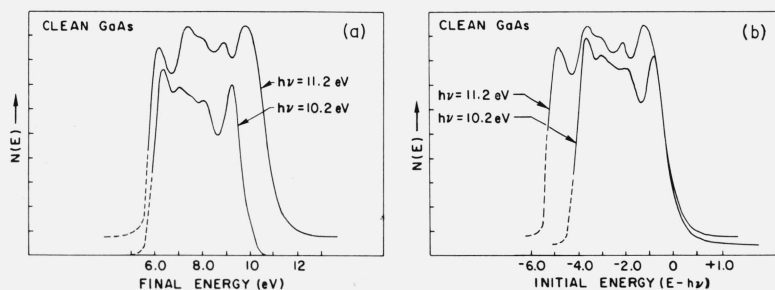


FIGURE 17. (a) EDCs from GaAs for photon energies of 10.2 and 11.2 eV plotted as a function of final state energy. (b) EDCs for GaAs plotted vs $E - h\nu$ to refer the energy distributions to the initial states. Note that the structure in the EDCs does not coincide on either a final energy plot (fig. 17a) or an initial energy plot as in this figure. This gives clear evidence that the transitions are direct.

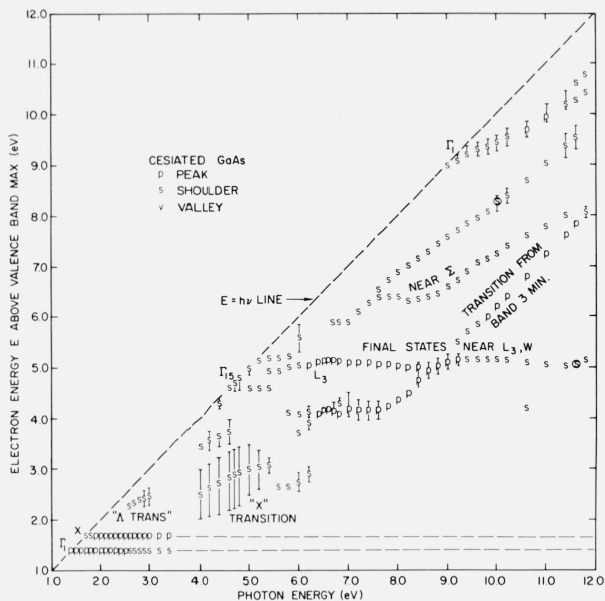


FIGURE 18. A structure plot for the photoemission from cesiated GaAs. In such a plot the final energy of structure in the EDCs is plotted vs the photon energy. Such plots can be compared to predictions from band theories. They also provide at a glance certain information on the nature of the source of the structure in the EDCs, i.e., a horizontal line indicates transitions from flat portion of the valence band.

Since the 45° line is located about 3.7 eV behind the $E = h\nu$ line, the initial states must be located this distance below the top of the valence band. As can be seen in the density of states plot of figure 19, there is a sharp density of states peak at just about this energy. Thus the two density of states peaks which are perhaps strongest and sharpest can be identified directly from the photoemission data; however, other strong structure which is not so narrow was not immediately detected from the photoemission data. This was because the curvatures were not sufficiently small so that a clear distinction could be made between the effects of initial and final density of states.

As is reported in a paper by Buss and Shirf [78] at this meeting, work by Spicer and Lapeyre [37] on PbTe seemed to have been successful in determining peaks in the density of states which correlate well with their band calculations. This occurred despite the fact that direct transitions are clearly important in these materials.

8. Comparison of Density of States Determinations Using Various Experimental Methods

In addition to uv photoemission spectroscopy, three other experimental techniques exist which can give direct information on the density of states of solids. In

this section we will compare the density of states obtained by these methods for Cu with that obtained from our measurements.

8.1. Comparison with Results of Ion Neutralization Spectroscopy

In figure 20 the ODS for Cu is compared to the density of states obtained by Hagstrum [79] from Cu via the ion neutralization spectroscopy (INS) technique which he has developed. The peak between -2 and -4 eV is associated with the d states. As can be seen, the width of this peak is considerably greater than the d width indicated by the ODS or calculated band structure. In addition, there is no detailed structure in the ion neutralization results even though the instrumental resolution is sufficient to resolve structure such as that seen in the ODS or calculated density of states. Hagstrum has noted [80] that since his technique depends on electrons tunneling from the surface of the metal, it is sensitive to the electronic structure just at the surface and that for d electrons this structure may be different from that in the bulk of the material.

If it is suggested that a change of the electronic structure can take place at the surface, one must ask whether this can also affect photoemission studies. In principle, the photoemission is a bulk effect and thus would not be changed by variations in the electronic structure associated with the last atomic layer or so of the solid. However, the fast electron-energy dependency of the electron-electron scattering length (see fig. 3) and the low scattering length at high energies (as low as 10 Å in some materials) must be taken into account. Thus, as photon energy is increased up to 12 eV, the escaping electrons will come from regions closer and closer to the surface and it is possible that measurable changes in the EDCs might be due to changes in the electron structure at the surface. Comparison of the EDCs from cesiated [34] and uncesiated [4] Cu show that changes occur on cesiation in the relative strengths of the two leading d band peaks in Cu. Similar results are found in the Ni-Cu alloys [21]. These results are not understood, but are mentioned to indicate that the d band transitions appear to be sensitive to changes in the details of the conduction band electrons. If this is the case, changes of spatial distribution of conduction electrons at the surface might affect transitions from the d states. This could for example, contribute to the broadening of the first d peak from clean Cu which occurs as photon energy is increased (see fig. 4). The purpose of this discussion was to point out effects which might be important in photoemission but which have

cant that there is little evidence for the s - and p -derived states lying within 2 eV of the Fermi surface (see figure 5a and b). This effect can also be seen in the Au XPS data presented in figure 16. The s - and p -derived states can be clearly seen in the photoemission and INS work. The lack of any detailed structure in the excitation from the d states would also seem to be significant since such detailed structure does appear in the ODS as well as in the calculated band structure. However, it should be noted that substructure has been obtained in XPS results from Pt [81], Ag and Au [72] (see fig. 16) and that the position in energy of this structure is in reasonable agreement with structure in the ultraviolet photoemission work.

The reason for the lack of structure in the XPS for Cu is not clear at this time; however, it is interesting to note, as will be shown in the next section, that almost the same symmetric curve is obtained in soft x-ray emission spectroscopy as in the XPS results.

8.3. Comparison with Results of Soft X-Ray Emission Spectroscopy

A fourth experimental method used to investigate the filled states solids is that of soft x-ray emission spectroscopy (SXS). The results of such investigations [82,83] for Cu are compared in figure 22 with the ODS. As mentioned in the last section, the SXS curve is very similar to the XPS curve in that it contains a single almost symmetric peak and shows no evidence of the s - and p -derived states lying between the Fermi level and the top of the d band.

Cuthill, McAlister, Williams, and Watson [85] have reported structure in the SXS from Ni. However, it is not nearly as pronounced as that seen in the ODS of Eastman. There are some similarities between the ODS and the SXS results for Ni; however, the correlations do not seem to be strong.

Cu-Ni alloys have been studied both by SXS [86] and ultraviolet photoemission [21,23]. It is interesting to note that in the photoemission and optical work it has been possible to clearly identify a Ni virtual-bound state in the Cu-rich alloy and that these virtual-bound states are much different than Ni states in pure Ni. For example, their width at half maximum appears to be less than half of that of pure Ni for Ni concentrations up to about 25 atomic percent in Cu.

In contrast, in the x-ray work the spectrum obtained for Ni in Cu down to 10 percent concentrations was indistinguishable from that of pure Ni [86]. These results suggest that interactions with the deep hole override valence band structure in determining the SXS from

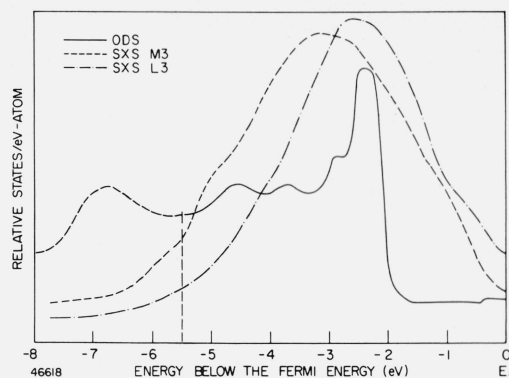


FIGURE 22. Comparison between the ODS and results obtained from soft x-ray emission spectroscopy. The curve labeled M3 was obtained using M_3 radiation [83] and that labeled L3 using L_3 radiation [84].

Ni; if this is so, the SXS would yield more information on the interaction between the deep hole and the valence electrons than on the valence band density of states.

9. Conclusions

The ultraviolet photoemission work done to date shows that density of states data can be obtained from such measurements. Because of the high resolution available in such measurements (0.05 to 0.3 eV), more detailed information can presently be obtained than by any other experimental method used to determine experimentally the density of states. In materials such as Cu where the most extensive work has been done, both experimentally and in theoretical calculations of the density of states, relatively good agreement is obtained between the position in energy of structure in the density of states. No other experimental method has given such clear-cut results or impressive agreement; however, good agreement is not obtained in the relative strengths of structure in the experimental and theoretical density of states. There are still fundamental questions which must be answered both with regard to the photoemission experiment and its interpretation and with regard to the band calculations and their relation to optical excitation spectra.

The photoemission data as well as calculations on Cu are probably the most complete available for any metal. The work of Smith [34] on Cu shows clear evidence of direct transitions from the regions of the d bands having large curvature. The calculations of Smith [34] and Smith and Spicer [33] show strong similarities between measurements and calculations based on direct transitions; however, the direct calculations predict much stronger modulation of the intensities of peaks than is seen experimentally. It should also be

noted that a broadening of 0.3 to 0.4 eV is used in the calculations to bring them into closer agreement with experiment. It is suggested that the experimental data is consistent with a model (suggested by Doniach's [46] theoretical work) which assumes that the delta function \mathbf{k} selection rule be replaced by a selection distribution of \mathbf{k} 's, with the width of the distribution increasing as the curvature of the bands decrease (*i.e.*, as the group velocity decreases). Thus, one would move in a continuous fashion from a completely direct transition model for a material with sufficiently wide bands to a non-direct-type of model for sufficiently narrow bands. The band widths at which such transitions take place would depend on the detailed characteristics of individual materials.

It appears that some density of states information can be obtained from photoemission data even when the transitions are completely direct. This can occur because peaks in the valence band density of states may produce EDC peaks which move with photon energy over a limited range of $h\nu$. Likewise, density of states peaks in the final states may produce peaks which fall at a constant energy over a limited range of $h\nu$. All of this is just a consequence of the fact that a large volume in \mathbf{k} space must lie near a single energy to give a peak in the density of states. Such behavior has been pointed out at this meeting in, for example, GaAs and PbTe where the density of states peaks so identified have been found to correlate well with density of states peaks in the calculated band structure. However, other peaks in the density of states in GaAs were not identified. This may have been due to the fact that the $h\nu$ range used was not sufficiently large or that too crude a method is being used to identify density of states structure.

In a different type of approach, photoemission studies can also be used in direct collaboration with band calculations by providing empirical data on the band structure. This data can then be used to refine the band structure and the density of states can be calculated from the refined band structure.

10. Acknowledgment

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- [1] Koopmans' theorem states that the one-electron energy eigenvalue ϵ_j in the Fock equation for a solid is the negative of the energy to remove the electron in state ϕ_j from the solid. The proof of Koopmans' theorem depends on the spatial part of the wave function being of the Bloch type and on all other wave functions being unchanged when one electron is removed. If Koopmans' theorem holds, it follows that the photon energy necessary to excite an electron from state ϕ_j to state ϕ_k is just the difference between the one-electron energies of the two states. However, if the eigenfunctions of other states are modified in the excitation, Koopmans' theorem will not hold, and many-body effects must be taken into account. See also: F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 313; J. Callaway, *Energy Band Theory* (Academic Press, Inc., New York, 1964), p. 117; J. C. Phillips, *Phys. Rev.* **123**, 420 (1961); L. G. Parratt, *Rev. Mod. Phys.* **31**, 616 (1959).
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