Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

To be presented at the International Conference on X-Ray Processes and Inner-Shell Ionization, Glasgow, Scotland, August 25-29, 1980

PHOTOEMISSION FROM SOLIDS: THE TRANSITION FROM SOLID-STATE TO ATOMIC PHYSICS

David A. Shirley

August 1980

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

PHOTOEMISSION FROM SOLIDS: THE TRANSITION FROM SOLID-STATE TO ATOMIC PHYSICS*

David A. Shirley

Lawrence Berkeley Laboratory
One Cyclotron Road
Berkeley, California 94720, U.S.A.

I. OVERVIEW

Interactions between solid-state and atomic physics are potentially very valuable, yet little studied as yet. Nowhere is this more true than in photoelectron spectroscopy, which has been developed quite independently in its applications to atomic and solid-state physics. In recent years, however, several phenomena attending photoemission have been specifically addressed in relation to their occurrence in both atoms and solids. Kunz and co-workers at DESY have compared total absorption in atoms and condensed phases, finding strong similarities and interesting differences. Focussing more explicitly on core-level photoemission per se, two groups at SSRL--Lindau, Spicer, et al., and our own--have found that total photoelectric cross-sections of core electrons in solids show interesting atomic behavior, including Cooper minima. Figure 1 illustrates this behavior.[1-3]

Another profitable comparison can be made around the binding energy, especially by considering the shift in atomic core-level binding energies brought about by solid-state effects. After the first clear realization that relaxation effects in solids generally lowered core-level binding energies,[4] a great deal of theoretical and experimental activity has ensued, yielding a very much higher level of understanding than that available ten years ago. Two recent papers, each deserving the designation of magnum opus, summarize our recent understanding of core-level line shapes[5] and binding energies[6] in solids. I cannot leave this subject without noting that a very simple model exists which even allows one to estimate the work function on the basis of atomic properties.[7]

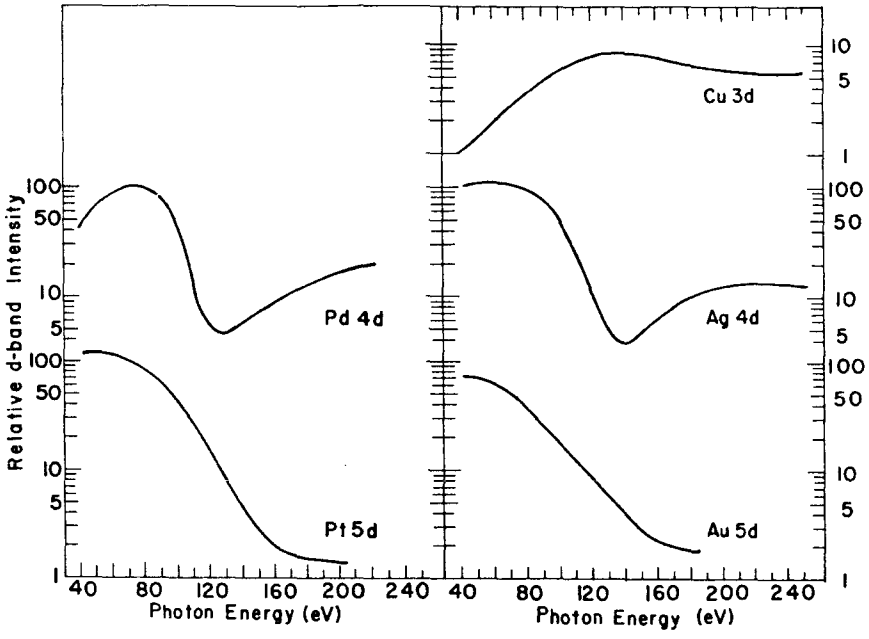

Fig. 1. D-band photoemission intensities of five metals as functions of photon energy. Note Cooper minima in Pd and Ag.

In the present paper we shall focus on the transition from the solid-state to the atomic physics regime in the context of the photoelectron angular distribution, an intrinsically more complicated--and probably ultimately more informative--subject. Angle-resolved photoemission (ARP) has begun to dominate the technique of photoelectron spectroscopy in the past five years, but ARP means different things to different investigators. In simple terms one can summarize the situation as follows. In randomly-oriented systems (free atoms and molecules) Yang's theorem[8] dictates the photoelectron angular distribution. In an ordered solid Bloch's theorem becomes dominant for valence bands at low photon energies, and Bragg's law for core levels at higher energies. Oriented molecules (or simply oriented orbitals) are the determining factor under some circumstances (e.g., shape resonances, or high energy). Finally, two or more of these factors are usually simultaneously present to influence the angular distribution. In the next three sections we shall attempt an orderly discussion of these effects under the headings of band-structure effects (Section II), photoelectron diffraction (Section III), and photoelectron asymmetry (Section IV). A brief summary is given in Section V.

II. BAND STRUCTURE EFFECTS

It is instructive to draw a formal analogy between the (scalar) energy-related properties in photoemission and the (vector)

momentum-related properties. In both cases the photoemission event can be represented by three participants: photon, system, and photoelectron. The energies related to each of these are, respectively, the photon energy $h\nu$, binding energy E_B, and electron kinetic energy K. They are related by the Einstein equation $h\nu = E_B + K$.

No analogous general relation exists for the momentum variables. In fact, the vector quantities that are relevant for describing a particular experiment will vary from case to case. In the most common situation, however, the following vectors are important: the vector potential $\vec{A}$ associated with the photon beam, the momentum $\vec{p}$ of the photoelectron, and a coordinate system (x,y,z) associated with the sample, illustrated in Figure 2. This coordinate system is the most common variation. It can even be as simple as a single vector $\vec{n}$: i.e., a surface normal or a molecular symmetry axis. In the other extreme six or more coordinate variables may be needed to describe the sample; e.g., a low-symmetry molecule adsorbed on a low-symmetry surface. Additional vectors may be relevant for the photon and electron as well; i.e., the photon momentum and the electron spin.

Turning now to our topic--band-structure effects--photoemission from a valence band in an unterminated solid is gov rned by an equation of the form[9]

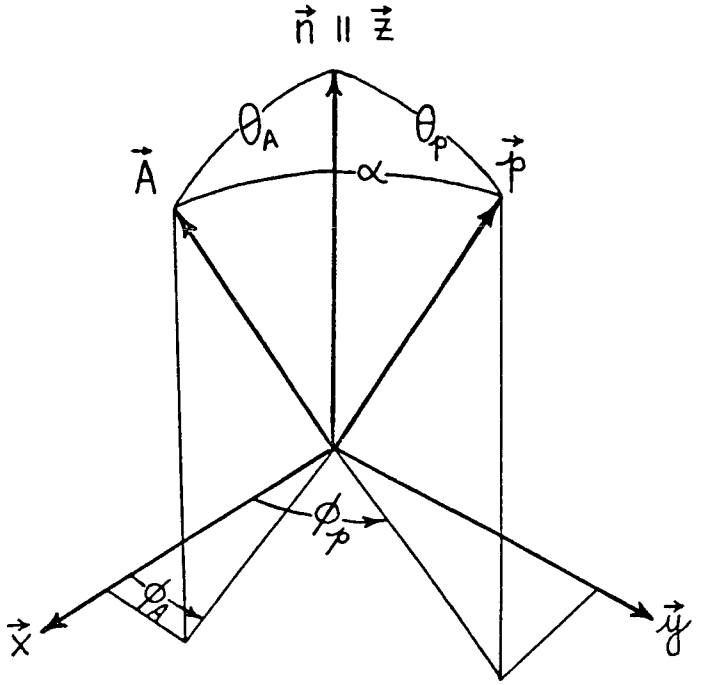

Fig. 2. Coordinate system for angular resolved photoemission.

$$N(E,h\nu) \propto \int_{BZ} d^3k_i \sum_{i,f} |\langle \phi^f(\vec{r}) | \vec{A}\cdot\vec{p} | \phi^i(\vec{r}) \rangle|^2 \delta(\vec{k}_f - \vec{k}_i - \vec{k}_{h\nu} - \vec{G})$$

$$\times \delta[E_f(\vec{k}_f) - E_i(\vec{k}_i) - h\nu] \delta[E - E_i(\vec{k}_i)]$$

where the delta functions express energy conservation and conservation of crystal momentum $\vec{k}$, the latter being the criterion for a direct transition. In the direct transition model (DTM) the photoelectron is excited into a conduction band vertically (in $\vec{k}$ space) as is the case for optical transitions in solids. It then propagates within the solid, with some probability of reaching the surface. At the surface it may propagate into vacuum, either with a change in direction or without, depending on whether it is scattered or refracted, or it may scatter back into the solid. If this were the whole story, the DTM would be complicated but always feasible in its application and "band-mapping", or the experimental determination of valence-band dispersion relations, would be straightforward, if tedious.

In fact Nature is more complicated. The termination of an ordered solid at its surface will change the character of the electronic states near the surface, and $k_\perp$ will no longer be a good quantum number ($k_\parallel$ will, of course, because two-dimensional transverse order is still retained). There is then a tendency in the spectrum to average (or integrate) over $k_\perp$, and the result is a one-dimensional density of states (ODDOS). Although in some earlier work the ODDOS model was used exclusively to interpret spectra, it has now become apparent that in fact both the DTM and the ODDOS mechanisms are usually present in varying degrees. The spectra arising from valence-band photoemission are thus usually somewhat complicated composites of the ODDOS and DTM components, as well as contributions from inelastic processes, including thermal diffuse scattering.[9] The interpretation is correspondingly difficult, but the proper starting point is the electronic valence band-structure model, for relatively low photon energies ($h\nu \leq 50$ eV). A number of interesting bulk band-structure properties have been measured recently by ARP studies, using the DTM interpretation. For example, dispersion relations have been determined along the [111] directions of the face-centered cubic metals Ni, Cu, Pd, Ag, Pt, and Au.[10] In a recent study of the [100] direction in Pt, both DTM and ODDOS features were identified, yielding the dispersion relations shown in Figure 3.[11] Similar behavior has been observed in semiconductors.[12]

At higher photon energies the situation is less clear. Up to $h\nu \sim 200$ eV or higher, DTM effects are clearly present.[13] At x-ray photoemission energies, $h\nu \sim 10^3$ eV, there is strong evidence for effective integration over much or all of the Brillouin zone,[14] perhaps to a greater extent than expected on the basis of thermal

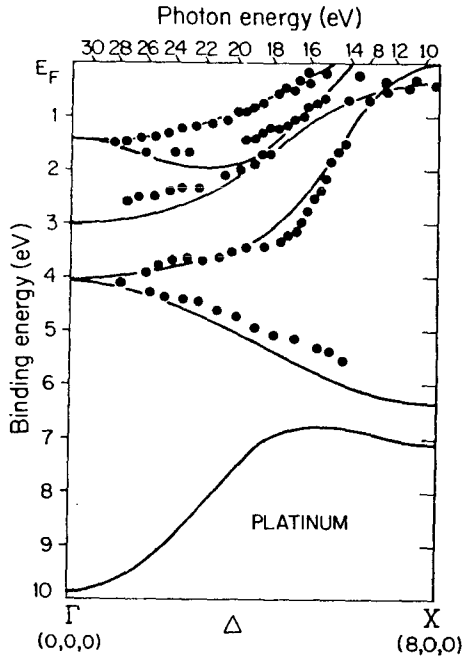

Fig. 3. Empirical dispersion relations (circles) and theoretical bands (lines) along Δ for platinum. The scale at the top gives the final state shifted down by the indicated photon energy. The final state crosses from the first to the second Brillouin zone at ca. $h\nu$ = 11 eV.

diffuse scattering,[15] in the noble metals. Recently, however, DTM effects have been observed in tungsten.[16]

In summary, angle-resolved photoemission from valence bands of ordered solids is governed by crystal symmetry. The crystal momentum $\vec{k}$ is conserved, and direct transitions are usually present and often dominant.

III. PHOTOELECTRON DIFFRACTION

As the energy is increased until the photoelectron's De Broglie wavelength is comparable to interatomic spacings, diffraction in the final state must be taken into account. Liebsch pointed out the possibility of using photoelectron diffraction as a structural tool in 1974,[17] and the effect was first observed in 1977.[18] During the past two years a considerable amount of work has been done on both azimuthal photoelectron diffraction (APD) and normal photoelectron diffraction (NPD), discussed separately below.

In azimuthal photoelectron diffraction the photon energy $h\nu$ and the photoelectron polar angle θ are treated as parameters (i.e., are held constant for a particular experiment) and the photoelectron's

azimuthal angle ϕ is varied through the range $0 \leq \phi \leq 2\pi$. An angular distribution pattern $I_{\theta,h\nu}(\phi)$ is thus produced for each θ, $h\nu$ combination. Data-enhancement techniques lead to "flower patterns" which are characteristic of the adsorbate-substrate structure under study. Comparison with LEED-style multiple-scattering calculations for low $h\nu$--or single scattering calculations in the high-energy regime--can lead to a structure determination.

Two groups have studied APD in considerable detail. Smith and co-workers[19] have used synchrotron radiation in the $h\nu$ = 100 eV range to study several adsorbate-substrate systems. They have found large effects in $I(\phi)$ and have made detailed analyses using LEED theory. Because past LEED analyses have not been very convincing, the efficacy of low-energy APD for structural determinations has been unclear. In the author's opinion the technique now shows considerable promise in this regard.

High-energy APD, pioneered by Fadley, et al.[20] with a fixed-energy laboratory source, has shown promise as a structural tool from the start. It yielded a "coplanar" geometry for oxygen atoms adsorbed on copper in the c(2x2)O/Cu(001) system. At high energies APD has the advantages of theoretical simplicity and the requirement of only a laboratory source. Furthermore, it appears to be a technique of considerable generality.

Normal photoelectron diffraction is qualitatively different, both in its experimental format and apparently also in the physical parameters to which it is most sensitive. In NPD photoelectrons from a given core level are detected along the normal direction as the photon energy is varied. The photoelectron intensity is found to be modulated, showing several maxima and minima as a function of photon energy (Figure 4).[21] The first structure analysis by NPD was done on the system c(2x2)Se(3d)/Ni(001), in which the Se3d line showed a factor of two intensity modulation. By fitting a LEED-style theoretical curve to the data, a distance $d_\perp$ = 1.55Å was derived for the overlayer-substrate spacing.[22] A number of systems have subsequently been studied, including c(2x2)C(1s)O/Ni(001), in which the C-Ni distance was found to be 1.3Å. A preliminary fit of peak positions to theory for this case is shown in Figure 5.

It has recently become apparent that NPD, which has been compared with LEED, can equally well be compared with EXAFS.[23] The argument is quite simple. In NPD, $d_\perp$ values are derived from the positions of peaks in the intensity-versus-energy curve, as in EXAFS. The modulation pattern depends largely on single scattering; this is especially true as the energy is increased. In fact Tong and Li[24] showed that only a single back-scattering event need be considered to calculate NPD curves for kinetic energies in the 100-400 eV range. Finally, these curves look, upon inspection, like sine-wave modulations. In fact we have found[25] that Fourier transforms of the

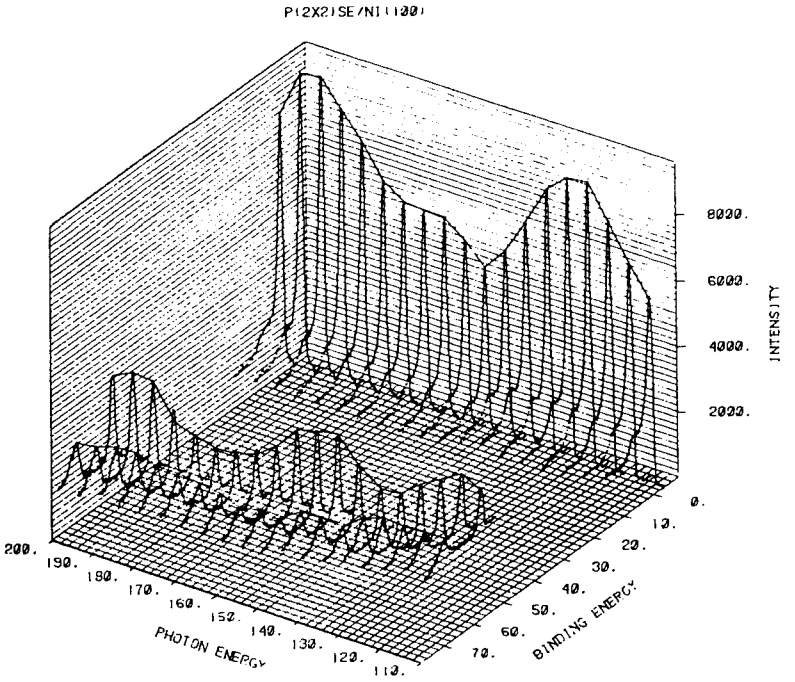

Fig. 4. 3-dimensional plot of the NPD effect.

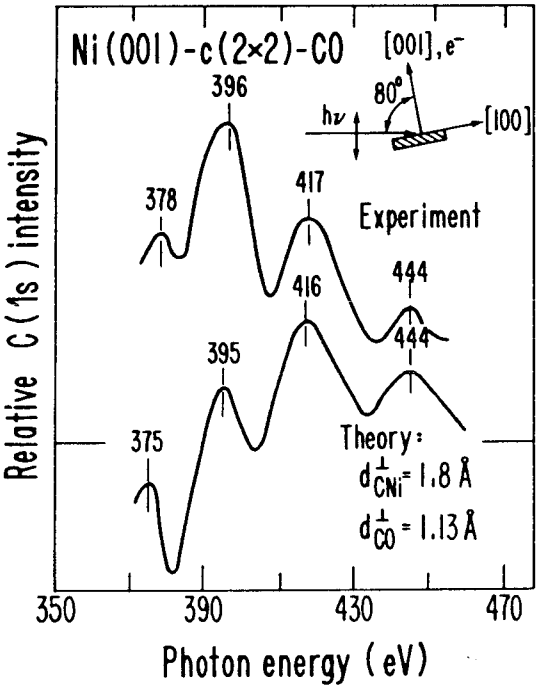

Fig. 5. NPD experimental and theoretical results for the Carbon (1s) level in CO/Ni(001).

theoretical NPD curve actually yield peaks at the distances $d_\perp$, $d_\perp + b$, $d_\perp + 2b$, etc., where b is the substrate interlayer spacing, in the Se/Ni system. A preliminary result is shown in Figure 6. The implication of this result is that Fourier analysis of sufficiently accurate NPD data should suffice to yield a geometry, by analogy with EXAFS.

IV. PHOTOELECTRON ASYMMETRY

It is well known, following Yang's theorem,[8] that dipole excitation of a photoelectron transition in a randomly-oriented system yields an angular distribution of the form

$$\frac{d\sigma(\varepsilon,\alpha)}{d\Omega} = \frac{\sigma(\varepsilon)}{4\pi}\,[1 + \beta(\varepsilon)P_2(\cos\alpha)].$$

Here ε and α are, respectively, the electron kinetic energy and the angle between $\vec{A}$ and $\vec{p}$, $\sigma(\varepsilon)$ is the total cross-section for photoemission, and $\beta(\varepsilon)$ is the photoelectron asymmetry. Calculations and measurements of $\sigma(\varepsilon)$ and $\beta(\varepsilon)$ for atomic gases are fairly abundant, but very little work exists that is related to $\beta(\varepsilon)$ in solids. In fact until a recent investigation by our group, the question of whether the above equation is even applicable to solids had not been addressed systematically.

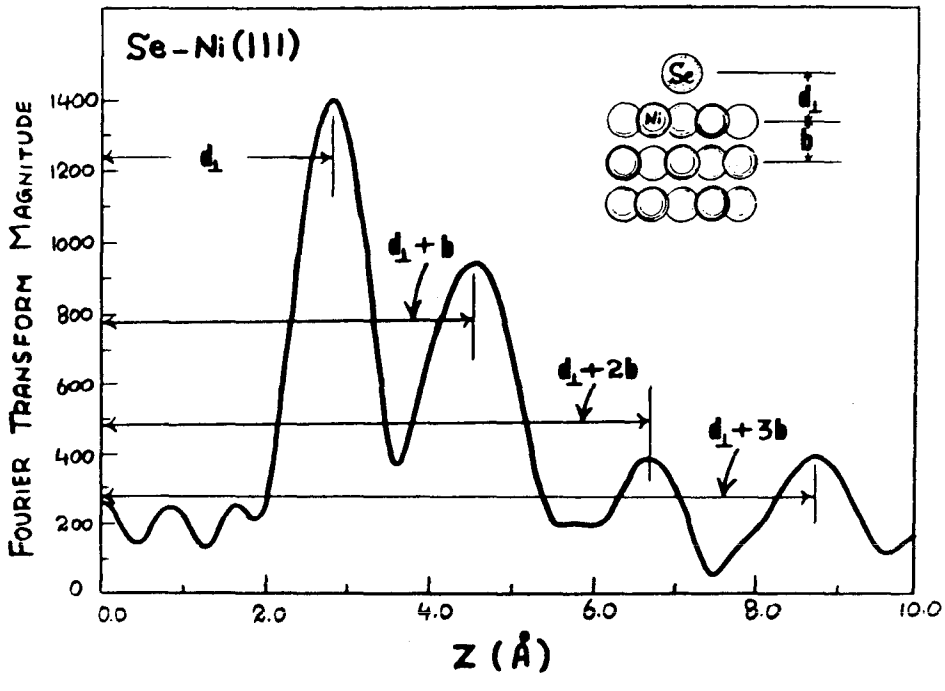

Fig. 6. Fourier transform by Z. Hussain of photoelectron diffraction pattern for Se/Ni(111) computed by S.Y. Tong, et al. Note peaks at interlayer spacings.

In experiments at SSRL, R.F. Davis, et al.,[26] have discovered very large anisotropies associated with photoemission from both core levels and valence levels in solids. Intensities changed by up to a factor of 25 as the angle α was varied. Figure 7 shows both $\sigma(\varepsilon)$ and $\beta(\varepsilon)$ for the Ag 4s and Ag(4d) "levels": the 4d shell of course forms the valence bands, which show dispersion and follow the DTM at lower photoemission energies. These results are compared with the calculations of Kennedy and Manson[27] for the Xe 4s and Xe 4d levels. At the time of the measurements by Davis, et al., no experimental confirmation was available of the detailed variation of $\beta(\varepsilon)$ for the Xe 4d level. However, a recent experimental study by S. Southworth, et al.,[28] in our group supports this theory.

It thus appears that core levels in solids--and valence levels as well--do show substantial photoelectron asymmetry. This asymmetry is similar, but not identical, to the predictions of atomic theory. In a "muffin tin" potential picture, one would expect the outgoing photoelectron's wave function to show phase shifts characteristic of the atomic potential for about one atomic radius, then to show behavior characteristic of a screened Coulomb potential plus a periodic potential. A quantitative development of this picture might yield incisive information about the final state.

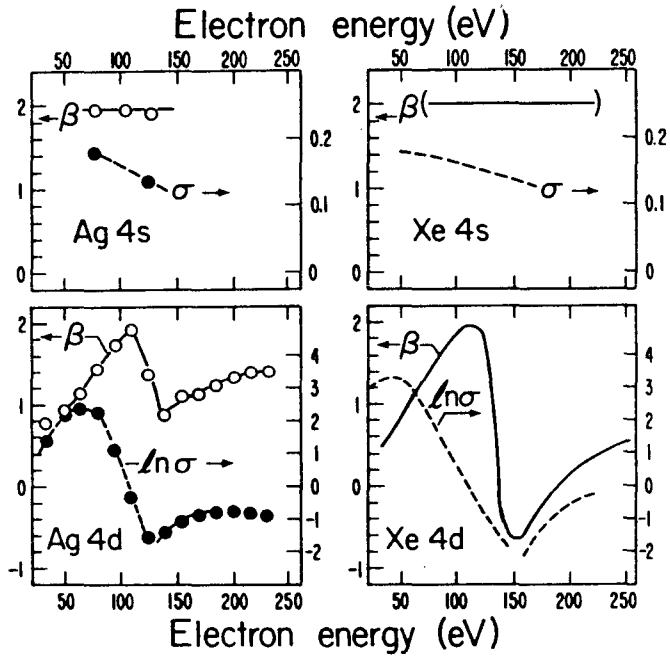

Fig. 7. A comparison of $\sigma(\varepsilon)$ and $\beta(\varepsilon)$ results from Ref. 26 for the 4s and 4d shells of silver (Z = 47) with calculated values for atomic xenon (Z = 54), from Ref. 27. The experimental σ scale is only relative. The 4s shell shows $\beta \sim 2$, while for the 4d case both the Cooper minimum in $\sigma(\varepsilon)$ and the modulation in $\beta(\varepsilon)$ are qualitatively reproduced.

V. SUMMARY

As the photon energy is increased, photoemission from solids undergoes a slow transition from solid-state to atomic behavior. However, throughout the energy range $h\nu$ = 10-1000 eV or higher both types of phenomena are present. Thus angle-resolved photoemission can only be understood quantitatively if each experimenter recognizes the presence of band-structure, photoelectron diffraction, and photoelectron asymmetry effects. The quest for this understanding will build some interesting bridges between solid-state and atomic physics and should also yield important new insights about the phenomena associated with photoemission.

REFERENCES

*This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-7405-Eng-48. It was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the NSF Grant No. DMR 77-27489, in cooperation with the Stanford Linear Accelerator Center.

1. I. Lindau, P. Pianetta, and W.E. Spicer, Phys. Lett. 54A:225 (1976).
2. G. Apai, P.S. Wehner, J. Stöhr, R.S. Williams, and D.A. Shirley, Solid State Commun. 20:1141 (1976).
3. P.S. Wehner, S.D. Kevan, R.F. Williams, R.F. Davis, and D.A. Shirley, Chem. Phys. Lett. 57:334 (1978).
4. D.A. Shirley, Chem. Phys. Lett. 16:220 (1972).
5. P.H. Citrin, G.K. Wertheim, and M. Schlüter, Phys. Rev. B20:3067 (1979).
6. B. Johansson and N. Martensson, Phys. Rev. B21:4427 (1980).
7. L. Ley, F.R. McFeely, S.P. Kowalczyk, J.G. Jenkin, and D.A. Shirley, Phys. Rev. B11:600 (1974).
8. C.N. Yang, Phys. Rev. 74:764 (1948).
9. D.A. Shirley, J. Stöhr, P.S. Wehner, R.S. Williams, and G. Apai, Physica Scripta 16:398 (1977), and references therein.
10. K.A. Mills, R.F. Davis, S.D. Kevan, G. Thornton, and D.A. Shirley, Phys. Rev. B22:XXX (1980), and references 1-4 therein.
11. G. Thornton, R.F. Davis, K.A. Mills, and D.A. Shirley, Solid State Commun. 34:87 (1980).
12. T. Grandke, L. Ley, and M. Cardona, Phys. Rev. B18:3847 (1978).
13. J. Stöhr, G. Apai, P.S. Wehner, F.R. McFeely, R.S. Williams, and D.A. Shirley, Phys. Rev. B14:5144 (1976).
14. P.S. Wehner, J. Stöhr, G. Apai, F.R. McFeely, and D.A. Shirley, Phys. Rev. Lett. 38:169 (1977).
15. R.S. Williams, P.S. Wehner, J. Stöhr, and D.A. Shirley, Phys. Rev. Lett. 39:302 (1977).
16. Z. Hussain, S. Kono, R.E. Connelly, and C.S. Fadley, Phys. Rev. Lett. 44:895 (1980).

17. A. Liebsch, Phys. Rev. Lett. 32:1203 (1974); Phys. Rev. B15:544 (1976).
18. Reference 9, pages 411-412.
19. D.P. Woodruff, D. Norman, B.W. Holland, N.V. Smith. H.H. Farrell, and M.M. Traum, Phys. Rev. Lett. 41:1130 (1978).
20. S.Kono, C.S. Fadley, N.F.T. Hall, and Z. Hussain, Phys. Rev. Lett. 41:117 (1978).
21. D.H. Rosenblatt, private communication, August, 1979.
22. S.D. Kevan, D.H. Rosenblatt, D. Denley, B.-C. Lu, and D.A. Shirley, Phys. Rev. Lett. 41:1565 (1978).
23. S.D. Kevan, J.G. Tobin, D.H. Rosenblatt, R.F. Davis, and D.A. Shirley, submitted to Physical Review.
24. C.H. Li and S.Y. Tong, Phys. Rev. Lett. 43:526 (1979).
25. Z. Hussain, private communication, July, 1980. A manuscript on this result is in preparation.
26. R.F. Davis, S.D. Kevan, B.-C. Lu, J.G. Tobin, and D.A. Shirley, Chem. Phys. Lett. 71:448 (1980).
27. D.J. Kennedy and S.T. Manson, Phys. Rev. A5:227 (1970).
28. S. Southworth, private communication, July, 1980.