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Calculation of the angle-resolved photoemission from copper

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Calculations of the angular photoemission from (100) and (111) copper have been made to explain the experimental data of Ilver and Nilsson, and to analyze the physical processes which produce these spectra. These *one-step* model calculations use low-energy-electron-diffraction (LEED) techniques to construct initial- and final-state wave functions properly matched at the surface. Inelastic scattering is included in the final state as in LEED. The wave functions and matrix elements are calculated exactly for a muffin-tin model with a planar gradual step between crystal and vacuum. Good agreement between theory and experiment is obtained.

I. INTRODUCTION

We give here theoretical calculations of angle-resolved photoemission to explain experimental intensities, in particular the angle-resolved measurements published by Ilver and Nilsson,[1] and to probe in detail the underlying processes producing the features seen in these data. Since the early work of Gobeli, Allen, and Kane,[2] it has been clear that angle-resolved photoemission could be capable of mapping out the electronic structure of crystalline solids, just as angular neutron scattering has been used to map out the phonon branches of solids. The work of Ref. 2 and other early work[3] showed that the angular dependence of the emitted electrons is not smeared away by phonon scattering and other effects. The experiments of Ilver and Nilsson, treated here, were some of the first in which only the electrons in a very narrow cone were measured. We hope to consider later work in future publications.

The noble-metal copper has played a prototype role in the development of the theoretical understanding of the photoemission process. Williams, Janak, and Moruzzi[4] were able to obtain good agreement between experiments on polycrystalline films and their calculations of angle-integrated photoemission, which included the calculation of the bulk bands and the matrix elements between them. However, Rowe and Smith[5] found that their angle-averaged experiments on clean Cu(100) and Cu(111) surfaces were not matched well by similar calculations (but with constant matrix elements) in which the transmission of the electron through the surface out of the given face of the crystal was also taken into account in a simple approximation. Following the simple formulation of photoemission theory using a plane-wave final state by Gadsuk,[6] a number of authors have attempted to interpret angle-resolved experiments using a plane-wave final state. For copper, Williams, Wehner, Stohr, and Shirley[7] found that their data did not fit this plane-wave model of the final state in the sense that unphysical values of the effective electron mass and/or the inner potential inside the crystal were required. Over a range of higher energies, Wagner, Hussain, and Fadley[8] were able to fit the positions of the peaks in their data using such a model, but found that matrix elements to a plane-wave final state gave much poorer agreement than assuming a simple constant form for the matrix elements.

Liebowitz, Sagurton, Colbert, and Shevchik[9] as well as Stohr, McFeely, Apai, Wehner, and Shirley[10] have suggested that the final state be represented by an orthogonalized plane wave (OPW). In their procedure a linear combination of atomic wave functions of energy below the final-state energy is added to the previously used plane wave to produce a wave properly orthogonalized to all of the states of the atom below the final-state energy. These additional components of the final-state wave function then are expected to give the principal contributions to the matrix element. Shevchik and co-workers[9] have assumed that the predominant contribution to the matrix element involved in transitions from the lower-state d bands arises from a final-state p wave in the direction of propagation of the final state, which results from this orthogonalization process.

Our work uses the correct lower- and upper-state bands as in the calculations of Williams *et al.*,[4] and further extends them by including an exact matching of wave functions through the surface. We find that in the region of the crystal between the atoms the final-state wave function is not a single plane wave, but rather that the expected plane wave is augmented by other plane waves differing by surface reciprocal-lattice vectors whose coefficients in the total wave function are about one third the size of the principal plane wave. We also find that the dominant contribution to the matrix element in the photoemission from the *d* bands are transitions between waves of *d* symmetry about the atoms to waves of *f* symmetry in the final state rather than to waves of *p* symmetry as suggested by Ref. 9. Our agreement with experiment is generally better than this earlier work but still leaves something to be desired considering the completeness and complexity of the model.

In this work we have attempted to carry through as accurate a calculation of the photoemission as possible short of finding a self-consistent electronic structure of the surface region. We follow the general one-step model of photoemission from crystal surfaces developed in large part by Mahan[11] and Adawi,[12] and elaborated by other authors.[13,14] It has not been clear how adequate this model of the photoemission process is in obtaining the detailed shape of experimental curves. Ilver and Nilsson themselves calculated the positions of direct transitions using the tabulated energies of a bulk band calculation, and compared them with the energies of their observed peaks. This calculation has been repeated and extended by Moruzzi, Marcus, and Knapp.[15] Both these calculations show that the positions in energy of the published peaks that do not have the behavior associated with surface-state emission can be explained in this way as the result of direct transitions. In contrast to the analyses of Refs. 1 and 15, we calculate in the present work not only the energy position of each photoemission peak, but its size and shape as well. We also attempt to assess the influence of a variety of physical factors involved in the photoemission process.

The theory upon which these calculations are based is worked out in detail in a previous paper.[14] The procedures used here were obtained by developing algorithms to obtain all of the quantities contained in Eq. (6) of that paper. Rather than restating the rather elaborate equations which occur in that treatment, we shall give a verbal description of the ingredients of the calculation in Sec. II. To make clear what is included in the present calculations and what is not included, we discuss a long list of minor points in that section. We can summarize the strengths and weaknesses of the present treatment by saying that it is essentially an exact calculation of the primary photoemission (omitting the possible production of phonons or other excitations in the photoemission process) for a model of the semi-infinite crystal consisting of muffin-tin atoms (even at the surface), and a flat smooth transition between crystal and vacuum, constant in planes parallel to the surface. The omitted excitation processes must be small, because they would lead to a blurring of the angular dependence of the emission which is not observed experimentally. The potential inside the surface atoms and the level of the potential between them are taken to be the same as in the bulk, rather than altered to obtain some form of surface self-consistency. The mean-free-path effects and the transmission through the surface are treated essentially in an exact manner for this model. In particular, full account is taken of the modification of the wave functions due to the scattering of Bloch (bulk) electrons by the surface of the crystal.

Our program has been operated for the same potential and surface matching as used by Pendry and Titterington[16] for a very similar theory, and very similar results have been obtained, with only slightly different relative peak heights. As yet, this slight difference is not understood. Pendry and Hopkinson[17] have also published comparisons between their calculations and some of the same experimental data as discussed here. Their results agree as well as can be expected with ours, taking into account that they used a different potential (Chodorov) and sharp step matching at the surface. The procedures developed by Pendry[18] are very similar to ours, but are developed from different low-energy-electron-diffraction (LEED) methods. Furthermore, Pendry begins his treatment from a formula for the photoemission derived by Caroli *et al.*[19] This formula includes many-body effects which can influence the photoemission process. Thus the advantage of Pendry's calculational procedure is that hole-lifetime effects are included which must be neglected in this work. The disadvantage with respect to the present method is that some of the physical interpretation which is given in the present paper cannot be obtained from the intermediate results in Pendry's calculational procedure. For a material like copper, where the hole-lifetime effects can be considered to be negligible, the two starting formulations of the problem can be reduced to the same equations.[13]

The computer program used in this work has been designed not only to calculate the photoemission from the crystal surface but also to obtain, in the process of calculation, a number of key intermediate quantities which are useful in interpreting the calculated results, and to print arbitrary selections of these quantities at the request of the user. Some of the quantities which are presently felt to be useful in this regard are the band structure [$E(k)$ surfaces] of the crystal involved in both the initial and final states of the photoemission transition, and the relative amplitudes of each of the Bloch wave components in the lower and upper states. We have also examined the contribution of the various spherical-wave components around an atom to the matrix element involved in the transition. Occasionally, we have also examined the factors indicating the relative contributions of different Bloch and evanescent waves to the matrix element, so that the relative importance of direct transition terms, i.e., terms involving two Bloch waves with nearly equal k_z values vis à vis other terms could be examined.

II. THEORY

This section gives a detailed description of the procedures used in the calculation and of the assumptions and approximations implied by them. This should enable the reader to see explicitly what can be inferred from the agreement, and, perhaps more important, what can be inferred from instances of poor agreement with experimental data. The comparison with the data is given in Sec. III.

Throughout this treatment we assume an atomically perfect planar surface on the crystal. For such a perfect surface, the components of the total reduced k vector in the plane of the surface, which we shall refer to as the parallel component of k, are good quantum numbers of the problem. Both LEED and directional-photoemission experiments show very sharp variations of measured intensities over angular variations as small as a half of a degree, which at typical energies and angles corresponds to a small fraction of the distance across the Brillouin zone. Thus a perfect planar surface appears to be a reasonable model for crystals without observable surface defects. This has the important implication that if we look at the elastic component of the photoemission the initial parallel k component of the electron below the Fermi level is the same as the parallel component in the upper state which describes the actual emission of the electron from the crystal. Thus, in this work, k parallel for both the initial and final states is determined from the angle and energy of emission of the electron detected outside the crystal.

The wave functions in the solid, both for the lower and upper states, are formed as coherent linear combinations of Bloch waves matching properly through the surface to vacuum waves at the vacuum-crystal interface as described below. These Bloch waves are obtained by procedures developed for calculating the intensities of the diffracted beams in low-energy-electron diffraction (LEED) and are closely related to the Korringa-Kohn-Rostoker (KKR) procedures commonly used in band-structure calculations. In the calculations discussed here, the LEED procedures give essentially the same numerical results as the KKR band-calculational procedures. These LEED procedures operate with the Fourier components of the wave function on planes parallel to the surface between the layers of atoms, and relate them mathematically to the spherical harmonic representation in a muffin tin around each atom. The wave function for a semi-infinite crystal in contact with vacuum is built up as combinations of the waves of the different layers of atoms by matching the wave function on these planes between layers. The upper state is a complex conjugate (time-reversed) LEED wave function, which represents a combination of Bloch waves in the crystal and incoming waves from vacuum, matching together in the surface region to give a single plane wave out of the crystal into vacuum propagating in the direction of the detector. Because of the complex conjugation, this upper-state wave function is a solution of the complex conjugate of the Schrödinger equation (really the Dyson equation; see the discussions of Ref. 20). This wave equation is complex because the inelastic scattering of the electrons to states of different energy introduces a negative imaginary contribution to the self-energy which is included with the potential. Since we neglect hole-lifetime effects, there is no imaginary part in the Schrödinger equation for the lower state.

A typical lower-state wave function consists of a Bloch wave moving toward the surface from the bulk, as well as the reflected Bloch waves and the waves exponentially decreasing into vacuum needed to match it at the surface. All of the waves used in this matching process for one of these states have the same energy and the same reduced k parallel to the surface. At a given energy there may be several lower states corresponding to a number of Bloch waves in different bands moving toward the surface. All of these lower states (giving separate emission processes incoherent with each other) are included in the calculations. Matching both the upper- and lower-state wave functions at the surface also requires including evanescent waves, i.e., Bloch-like waves which decay, with or without oscillation, as one moves from the surface into the crystal.[21] All of these evanescent waves that do not decay to negligible values before reaching the first layer of atoms are included in the calculations.

The surface dipole region between the crystal and vacuum outside the first layer of atoms is assumed to be a gradual step transition which is independent of the coordinates parallel to the surface plane, and is intended to simulate the jellium-vacuum-interface potential calculated by Lang and Kohn.[22] The actual analytic form chosen was that of the curve

$$V(z) = (V_0/2)[\tanh(\pi z/\lambda) - 1],$$

because explicit solutions of the Schrödinger equation for this potential have been obtained by Eckart[23] in the form of hypergeometric functions. Here the zero of potential is taken to be the vacuum level, and V_0 is equal to the work function plus the Fermi energy relative to the muffin-tin zero. The parameter λ is a good measure of the width of the transition region. (See the curves in Eckart's paper.)

In real systems one expects the first layer of atoms in the surface to overlap this transition region. We have attempted to take some of this overlap into account in a crude way by adapting the overlapping-muffin-tin idea to this situation. This overlapping procedure has been developed by a number of authors[24] for multiple-scattering calculations of the electronic structure of molecules. The procedure was carried out as follows:

The phase shifts of a surface atom were obtained using muffin tins with a size typical of this atom in KKR or augmented plane wave (APW) calculations for a solid. However, in matching wave functions at the surface, these atoms were replaced by points in the potential background with the same phase shifts. (This procedure would have no effect in a standard KKR calculation.) Now the hypergeometric function solutions for the gradual-step potential in the region between the vacuum and the interior of the crystal were matched to the first terms of a beam expansion (see below) of the wave function on the plane containing the scattering points. We believe that this procedure is preferable to forcing the wave function to be a combination of plane waves in the region from the plane of the point scatterers used to represent the surface atoms to the plane which would be tangent to the outer edges of the surface-atom spheres. This latter procedure would be equivalent to the standard matching.

Each of the wave functions is resolved into spherical components about the atoms in each layer. Since, in its potential gradient form, the dipole matrix element of the electromagnetic field is nonzero only where the potential is nonzero, these matrix elements can be evaluated using their spherical components inside the muffin tins.[25] Computer code developed by Williams, Janak, and Moruzzi[4] was used for this purpose.

The term in the photoemission matrix element which contains the gradient of the potential step between the vacuum and the interior of the crystal has not been included in the calculations on the assumption that for transition and noble metals its contribution is smaller than the contribution from the potentials of the atoms inside the muffin tins. Since the gradient of the potential used here is perpendicular to the surface, only the component of the photon electric field E perpendicular to the surface can give a contribution to this part of the photoemission. In the experiments studied here this component is nominally zero.

The theory requires a knowledge of the local electric field inside the crystal. This was deduced from the known photon field outside the crystal using the Fresnel equations for matching the electromagnetic field through the surface.[26] In this way one obtains a general elliptically polarized field inside the crystal from each independent polarization mode outside the crystal. This procedure is a macroscopic model for the interaction between the electromagnetic wave fields and the shielding electrons in the interface that assumes the transition to the internal fields occurs outside the first layer of atoms. A more realistic but still macroscopic method for calculating the photoemission in the crystal taking the effects of plasmon motion into account has been given by Sauter[27] and Forstmann[28] and extended by Forstmann and Stenschke.[29] The procedures followed by these authors indirectly give a prescription for the effective photon electric field involved in photoemission including the effects due to plasma oscillations. This more general formalism tells us that our treatment of the s component is not changed by plasmon effects although a p component of the light wave would be enhanced inside the crystal by the existence of plasmons. Since the light was normal to the surface in the experiments discussed here, at least in this approximation, plasmon effects can be neglected.

Various authors[6-9] have considered the use of a single plane wave, either with or without a modification of the effective mass and background potential, to fit the expected characteristics of the final state. In the present work it is convenient to make explicit use of a representation of the wave function between the layers of the crystal in a Fourier series in the plane separating the layers, a representation which can be extended to plane waves and exponential waves describing the electron motion between the layers. These waves can be examined to evaluate the apparent plane-wave nature of the final state. Each one of these waves satisfies the Schrödinger equation outside the atoms for the energy of the state under consideration, and linear combinations of them can be joined to a solution inside the atoms. These waves differ from each other in the way the energy is shared between the in-plane and cross-plane motion. These waves are also used in standard dynamical diffraction theory and therefore will be called beams as in that theory. We are able to describe the diffraction of the electron coming out of the crystal in the upper state in terms of the behavior of these beam components, which are calculated explicitly as intermediate results in our calculations.

Because we assume that the initial state contains running Bloch waves, the photoemission from true surface states is not included. If included in our formalism, which omits processes involving the production of phonons or other excitations, and hole-lifetime effects, true surface states would give a photoemission into any particular set of angles which is concentrated (infinitely) at a single energy, isolated from any other emission because the surface state is in a gap. On the other hand, the surface states which exist in calculations along symmetry directions outside of gaps become resonances for angles near the symmetry directions. Resonances such as these are included in our formalism, since they manifest themselves as surface-reflected bulk states with high amplitudes near the surface. Although a surface state is known on Cu(111),[30] it does not appear in experimental data taken at the angles of these measurements.

The muffin-tin potential required for the calculations was obtained from self-consistant bulk band-structure calculations for copper metal by Williams, Janak, and Moruzzi.[4] The input data they used to obtain this potential were the atomic number of copper, the lattice type (fcc), the lattice constant, and the exchange correlation potential in $X\alpha$ form. These authors compared the optical absorption data, Fermi-surface properties, and angle-averaged photoemission spectra obtained experimentally from copper to their KKR calculations with this potential. They found that a best fit to the Fermi-surface data was obtained for a value of the exchange-correlation parameter $\alpha = 0.77$ which is also used here.

III. RESULTS OF THE CALCULATIONS

Figures 1–3 show a comparison between the results of our calculations and the experimental data. The thick curves are the experimental data, while the finer curves [two sets for the (100) face and two sets for some curves on the (111) face] are the results of our theoretical calculations. The theoretical curves for the (100) face drawn with the heavier lines are to be preferred, the difference will be discussed below. The theoretical curves for the (111) face drawn with the narrower lines will be discussed later in this section.

A background subtraction has been made from the experimental curves to eliminate the contribution of inelastic processes as much as possible.

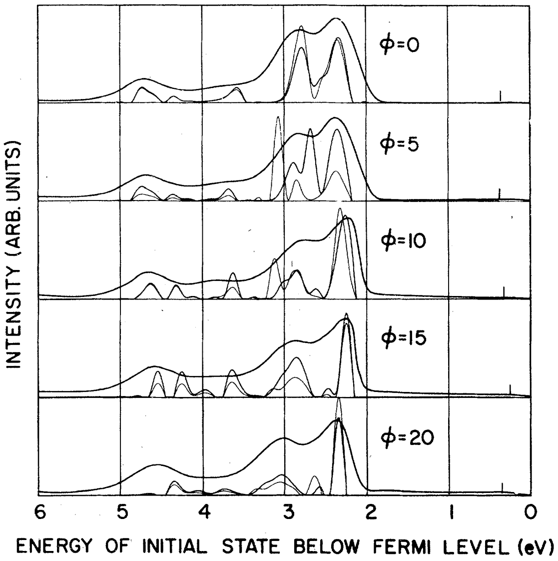

FIG. 1. Photoemission from Cu(100) for small azimuthal angles. The heaviest lines give the data of Ilver and Nilsson for various values of the azimuthal angle φ. The two sets of thinner lines are theoretical results, the thicker of these are calculated for a surface dipole layer with a thickness of about 0.6 bohr, and the thinner lines for a surface dipole layer with a thickness of about 0.3 bohr. The energy scale for the experimental data is given at the bottom, with the Fermi energy at zero at the right-hand end. The theoretical curves are shown to the same scale, but with the Fermi energy shifted down to the vertical bar at the right of each curve.

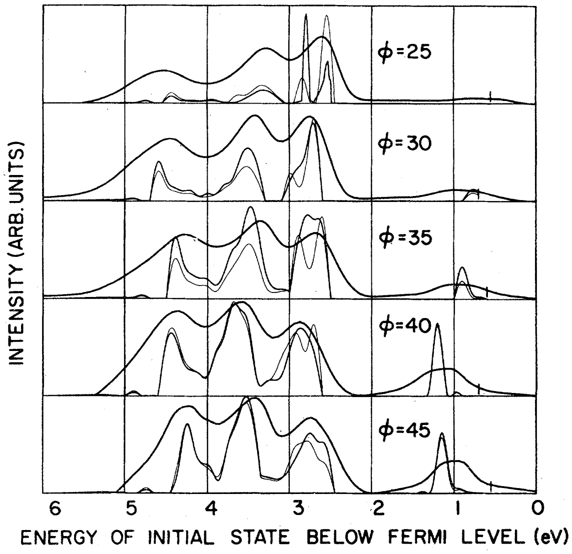

FIG. 2. Photoemission from Cu(100) for large azimuthal angles. Same as Fig. 1, except that larger azimuthal angles are shown.

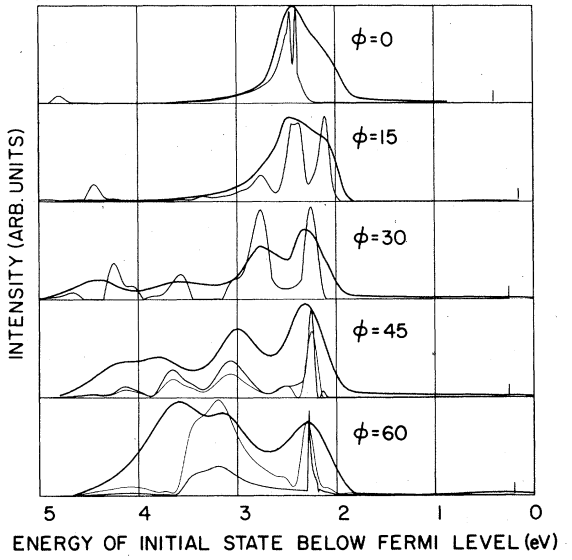

FIG. 3. Photoemission from Cu(111). The heaviest lines give the data of Ilver and Nilsson for various values of the azimuthal angle φ. The lines of medium thickness give our calculations at the nominal angles of the experiment. The very thin lines for the bottom two curves give the weighted average of calculations of five points at different angles chosen to sample the acceptance cone of the experiment. The energy scale for the experimental data is given at the bottom, with the Fermi energy at zero at the right end. The theoretical curves are shown to the same scale, but with the Fermi energy shifted down to the vertical bar at the right of each curve.

A simple parabola centered at the Fermi energy with an empirically chosen coefficient was used for this purpose. The same subtraction was used for all curves. In some figures the inaccuracy of this simple procedure leaves a slightly rising tail at the left end of the graph; in others it causes a premature drop to zero in this same region. The experimental results contain an instrumental broadening of about 0.1 eV which has not been put into the theoretical curves.

The agreement between our calculations and the experimental curves is generally good, which justifies the determination of the important physical factors involved in producing the shapes of the experimental curves from the behavior of various intermediate results produced in the calculations.

As stated before, the muffin-tin potential required for the calculations was obtained from self-consistant bulk band-structure calculations for copper metal by Williams, Janak, and Moruzzi.[4] They introduced a uniform stretching of the energy scale of 8% from a zero taken at the Fermi level, in the manner of an increased effective mass to move the d bands down to the observed distance from the Fermi level. This stretching procedure is suggested by the work of Sham and Kohn.[31] Since an 8% effective-mass enhancement, even if produced by combining both phonon and many-body effects, still seems unphysically large,[32] this factor has not been included in the present work. Instead, we have tried to match the positions of the principal experimental peaks by a rigid shift of the energy axis, performed spearately for each of the experimental curves. We find we must move both the d and the s-p bands down to match the photoemission data and therefore this rigid shift has the proper effect. The shift is 0.2–0.3 eV for all curves on the (111) face except $\varphi = 0°$, but becomes as large as 0.5–0.6 eV for the other curves. The position of the experimental Fermi energy is the right end of the box in each figure. The theoretical Fermi energy is indicated by the vertical bar to the right of the photoemission curves in each figure. This disagreement between the experimental displacement of the peaks from the Fermi level and the corresponding displacement of the theoretical peaks remains unexplained, but could arise from inadequacies in the procedure for specifying a one-electron potential, from relaxation effects, from experimental error in determining the Fermi level, or most probably, a combination of these.

The agreement between theory and experiment can be affected by the width of the dipole layer region in the surface. The fine-line theoretical results in Figs. 1 and 2 for Cu(100) contain peaks around −3.0 eV which are not found in the experimental data. The heavier theoretical curves, which do not show these features, result from an identical calculation except that the thickness of the transition region between crystal and vacuum has been increased from a value of 0.1π to a value of 0.2π. This additional structure found in the first set of calculated curves and not in the second can be traced to surface resonances which exist for the sharper surface barrier but which are less strong and more hidden under direct transition peaks for the more diffuse surface barrier. Actually, such a resonance does appear in the $\lambda = 0.2\pi$ data for $\varphi = 5°$ at an energy corresponding to the experimental energy of −2.8 eV in Fig. 2. If this resonance did not exist the agreement of this theoretical curve with experiment would be better. Other very narrow resonances may actually exist that were missed between the points of the theoretical calculation. The points were spaced at 0.1-eV intervals in most regions of the curves; points were more closely spaced in regions around some of the peaks.

No surface states are known experimentally to be involved in this data; however, it is quite possible that surface states do occur in the small gaps between the *d* bands. For example, we find in separate calculations using the methods of a previous publication[33] that a surface state exists in the calculated gap at −4.5 eV in the spectrum for $\varphi = 20°$ in Fig. 1. It is reasonable to assume that such a state contributes to the middle of the experimental peak which lies over this gap in this and neighboring curves. As stated before, no such surface states are included in the present photoemission calculations.

In Figs. 4–6 we show the parts of the bulk band

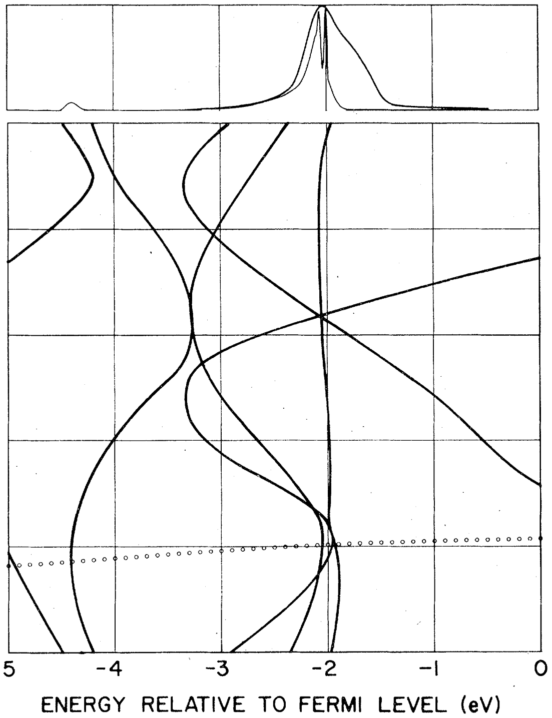

FIG. 4. Photoemission and band structure for Cu(111) at $\varphi=0°$. The experimental and calculated photoemission at top (repeated from Fig. 3) is related to the energy bands in the crystal shown below them. The band plot has been turned on its side so that the energy scale at the bottom also gives the energies of the photoemission spectrum. The top of the band plot is at 1/2 reciprocal-lattice vector toward the surface and the bottom is at 1/2 reciprocal-lattice vector into the crystal away from the surface. The lower-state bands are shown as solid lines in the band plot. The upper-state band involved in the photoemission process is also shown as a line of circles shifted down in energy by the energy of the photon. Because of this shift, the positions of direct transitions are indicated by the points of crossing of this line of circles representing the upper-state band with the solid curves representing the lower-state bands. Here the Fermi energy of the theory is at the right side of the diagram, and the experimental curve has been shifted to the right to bring its peaks in correspondence with those of the theory.

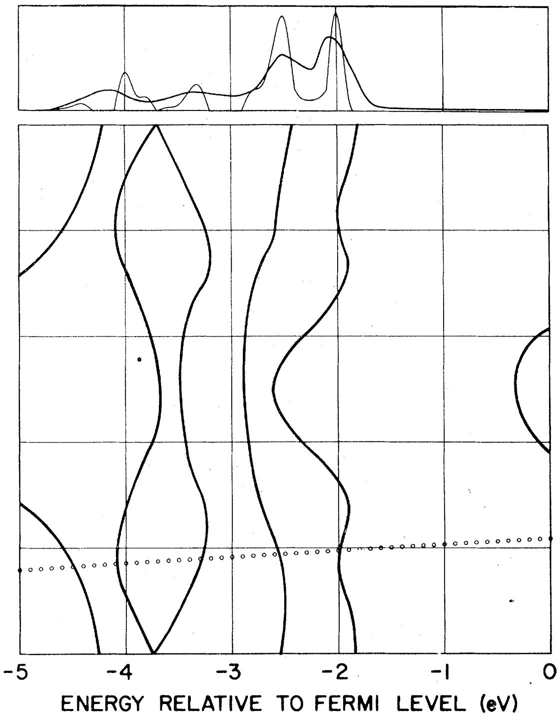

FIG. 5. Photoemission and band structure for Cu(111) at $\varphi=30°$. Similar to Fig. 4, but with $\varphi=30°$.

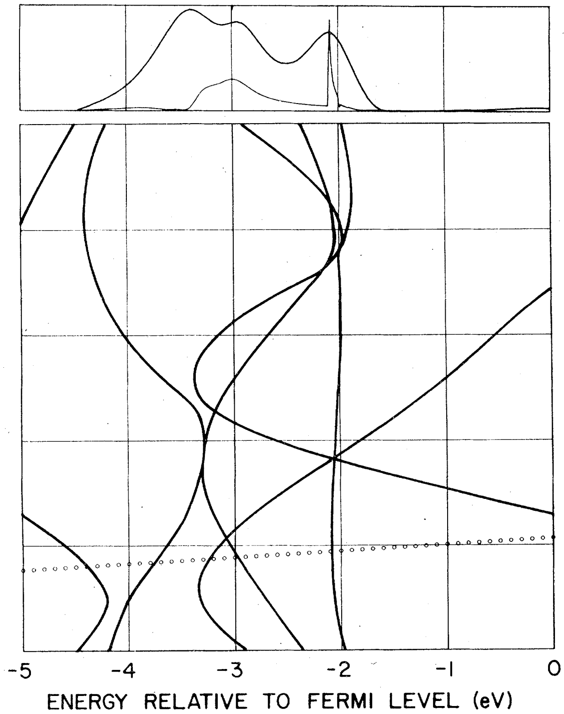

FIG. 6. Photoemission and band structure for Cu(111) at $\varphi=60°$. Similar to Fig. 4, but with $\varphi=60°$.

structure which are involved in producing some of the spectra calculated for the (111) face. The previously shown photoemission spectra are given again above the appropriate sections of the band structure. The band-structure curves in these boxes are a by-product of the calculation of the theoretical photoemission curves given above them. The solid curves give the lower-state bands and the lines of circles give the most important (see below) of the upper-state bands involved in the photoemission process. For each energy abscissa, the ordinates of the points on the solid curves are the reduced-wave-vector components k_z, perpendicular to the surface, of the Bloch waves in the crystal at this energy. All waves considered have the k parallel value determined by the geometry of the experiment. Since the band energies are periodic in k_z, each band energy at the upper edge of this plot is equal to its energy at the lower edge, and each band must return to its initial value when followed down across the graph. The corresponding points on the line of circles give the k_z values for the most important upper-state band at energy $E+h\nu$, where $h\nu$ is the energy of the photon, again with k parallel determined by the collection angles of the experiment. Only upper Bloch waves with this k parallel are involved in the photoemission process.

It is simple to pick out all of the Bloch waves involved in the photoemission process from the band diagram. Band lines with positive slope correspond to Bloch waves moving toward the surface and band lines with negative slope correspond to Bloch waves moving into the crystal, because of the relation between dE/dk_z and the group velocity. The upper state contains only waves moving toward the surface; however, the lower state, which is a wave in the crystal reflected by the surface, must contain Bloch waves moving in both directions. For example, Fig. 5 shows four Bloch waves at −4 eV. Of the four, the two with positive slope correspond to electrons moving toward the surface, while the other two with negative slope describe electrons moving away from the surface. A typical lower state at −4 eV could be formed from the Bloch wave moving toward the surface corresponding to the crossing of the solid curve in Fig. 5 with the −4-eV vertical line which lies just above the line of circles which represent the upper state. This would be combined with both the lower-state Bloch waves moving back from the surface. There are an equal number of Bloch waves moving in each direction at any given energy E_0, because any band line which crosses the vertical line $E=E_0$ left to right must cross it again right to left, and vice versa, in order to repeat the period.[34]

Similar band plots are given in Figs. 7–9 for certain of the photoemission spectra obtained from the (100) face, but only half of the relevant section of the Brillouin zone is shown. Since there is reflection symmetry in the bulk for a plane parallel to the surface, each Bloch wave and its k_z are carried into a similar wave moving

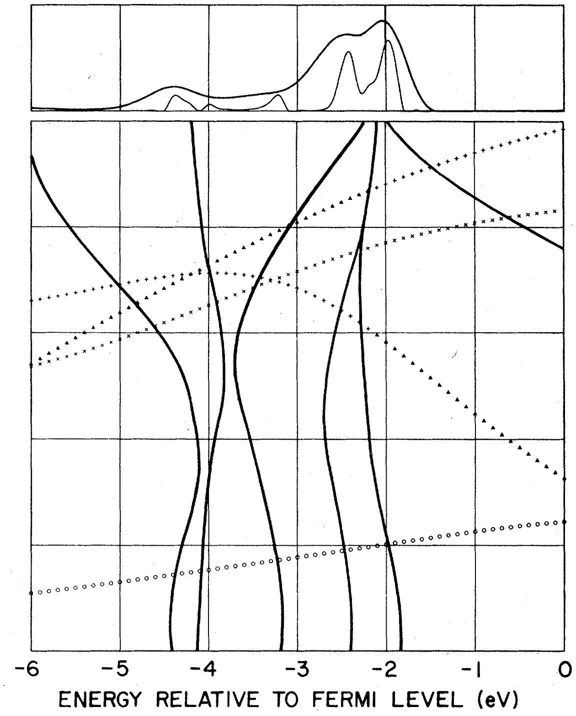

FIG. 7. Photoemission and band structure for Cu(100) at $\varphi=0°$. The experimental and calculated photoemission at top (repeated from Fig. 1) is related to the energy bands in the crystal shown below them. The band plot has been turned on its side so that the energy scale at the bottom also gives the energies of the photoemission spectrum. The component of reduced k in the direction of the surface is equal to zero at the top of this diagram, and equal to one half of a reciprocal-lattice vector at the bottom. The lower-state bands are shown as solid lines in the band plot. The upper-state bands involved in the photoemission process are also shown as lines of symbols shifted down in energy by the energy of the photon. Because of this shift, the positions of direct transitions are indicated by the points of crossing of this line of symbols representing the upper-state band with the solid curves representing the lower-state bands. The upper-state band contributing the largest flux to the wave to the detector is indicated by a line of circles. The triangles indicate the next largest contribution, followed by the plusses and then the ×'s. We find that only the band indicated by circles need actually be considered. Here the Fermi energy of the theory is at the right side of the diagram, and the experimental curve has been shifted to the right to bring its peaks in correspondence with those of the theory.

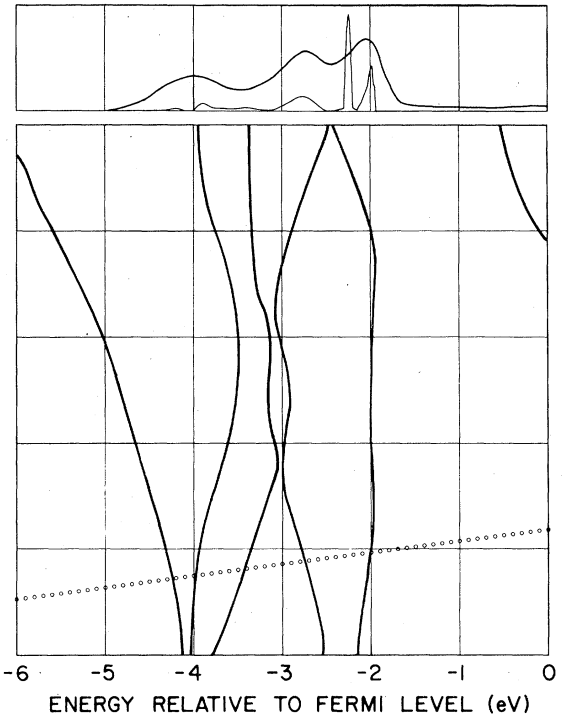

FIG. 8. Photoemission and band structure for Cu(100) at $\varphi = 25°$. The experimental and calculated photoemission at top (repeated from Fig. 2) is related to the energy bands in the crystal shown below them. This is similar to Fig. 7, except that $\varphi = 30$, and only the most important upper-state band is shown. Note that there is a surface resonance peak which does not correspond to a band crossing.

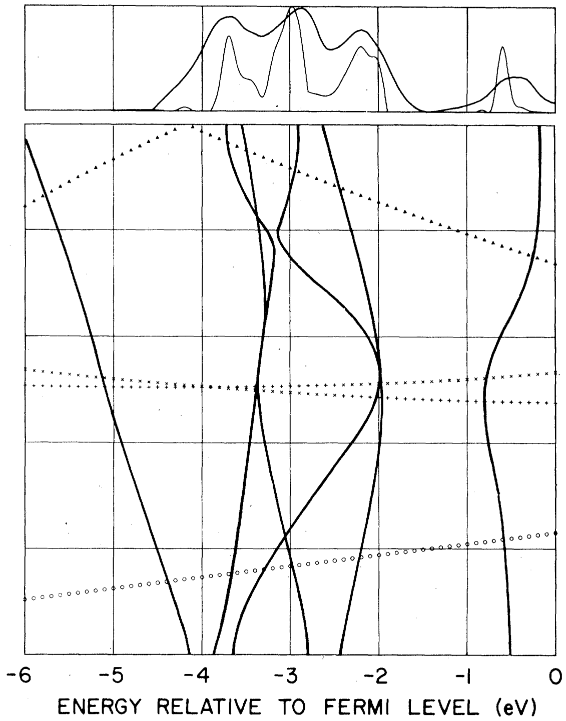

FIG. 9. Photoemission and band structure for Cu(100) at $\varphi = 45°$. The experimental and calculated photoemission at top (repeated from Fig. 2) is related to the energy bands in the crystal shown below them. This is similar to Fig. 7, except that $\varphi = 45°$.

in the opposite direction with opposite k_z by this symmetry. The values of k_z for which curves are shown extend from zero at the top to half a reciprocal-lattice vector at the bottom, so that the usual band plot is obtained by turning the figure on its side. Figures 7 and 9 show four of the upper bands with the proper k parallel as curves made up of various symbols.

Where the lines of symbols cross the solid curves in the band plots for either the (100) or (111) faces, all three components of the k for the initial state equal the corresponding components of the final state. Such points mark the positions where direct transitions may occur. At such points a Bloch wave of the lower state remains in phase with a Bloch wave of the upper state throughout the crystal. Thus the contributions to the photoemission from the various layers of the crystal below the surface add constructively. In a bulk theory of the photoemission process, emission can only occur at one of these points, where coherence is maintained, giving rise to the momentum conservation selection rule. When inelastic scattering is present, only transitions in the region of the crystal near the surface, from which the electron can escape into vacuum without inelastic scattering, produce the primary photoemission spectrum. If this region is sufficiently shallow the coherence of the two states at such a point in the band structure loses its importance. From the fact that the experimentally observed peaks are found around these points we find, as previous investigators[1,15] have concluded, that direct transitions are responsible for most of the experimentally observed peaks. The region producing the spectra is from two to four layers into the crystal.

In the work done here on copper, we find that the upper-state wave function consists mainly of only one Bloch wave, with all other Bloch waves giving contributions of less than 5% to the flux carried out of the crystal by the upper state. Only this wave is shown in the figures for the (111) face, because only it influences the observed photoemission. The concentration of flux in one Bloch wave is an expression of the fact that an electron in one of these Bloch waves passes through the surface in the direction of the detector, while an electron in one of the others either leaves the crystal outside the acceptance cone of the detector, or, if this Bloch wave has a low group velocity toward the surface, is reflected back into the crystal at the interface. This can be summarized by saying that the electron passes through the surface without umklapp. However, it is difficult to define which Bloch wave is in any given extended zone when the potential is strong. Perhaps one can establish extended zone assignments from the way calculated bands match to vacuum. Figures 7 and 9 show the four upper-state bands most important for the matching in the calculations of the photoemission intensity curves shown above them. At $\varphi = 0°$, for initial state energies below about -2 eV, three of these bands would correspond to ordinary Bloch waves and one would be an evanescent wave, if there were no inelastic scattering of upper-state electrons in the crystal. Inelastic scattering produces an extra decay in all these waves. Similarly, at $\varphi = 45°$, with no absorption, there would be two ordinary upper-state Bloch waves and two evanescent waves at all energies. In all our diagrams the upper Bloch wave represented by circles carries 95% of the flux which reaches the detector.

On the basis of limited experience we find that essentially only one Bloch wave carries flux to the detector, not only in copper but also in iron, nickel, and silver. On the other hand, again based on limited experience, two or more Bloch waves usually seem to be involved in the photoemission from tungsten and molybdenum.

It appears that the dominant Bloch wave is the one which has a k_z value nearest to that of the plane wave outside the crystal going to the detector and, being similar, couples strongly to it. This wave appears to be the most free-electron-like and therefore has an energy dependence which resembles the free-electron parabola at this energy, moving toward the detector, with a large value of dE/dk_z. We find, on the other hand, that Bloch waves which correspond to flatter upper-state bands as viewed in our graphs have larger components on the part of a basis set of waves which oscillate less rapidly across a unit cell in the crystal, and therefore, have larger matrix elements with the lower states.

In the right-hand side of Fig. 9 one sees a long flat peak which is really a double peak. One might believe that the left peak of this pair of peaks is formed by a transition to an upper Bloch wave which passes out of the crystal with 99% probability, and the right peak is formed by a much stronger transition to a wave which forms only a 1% component of the final state, presumably with a much larger matrix element. Our calculations do not give any evidence for this second transition, possibly indicating that the composition of the final state for a better model of the surface region would be less strongly limited to one Bloch wave. Since successful calculations of low-energy-electron diffraction have been made by these same techniques at energies near to this upper-state energy,[35] we believe that this is not the true explanation. In recent work to be reported separately we find that fractional coverage of the surface by overlayers of the same atom, or a different kind of atom, is capable of increasing the number of Bloch waves important in the final state much as field emission is changed by such overlayers.[36] It is also possible that the second peak of the pair discussed here has some completely different origin.

In general this upper-state wave function, composed of only one Bloch wave, is a mixture of five to six beams with large coefficients inside the crystal. One of these beams inside the crystal has an amplitude three to four times larger than the amplitude of the other beams. This makes the intensity of this beam an order of magnitude larger than the others, but in the photoemission calculation, which involves coherent combinations of waves and matrix elements with cross terms, the ratio of amplitudes is a more valid comparison. Hence a representation of the upper state for photoemission by a single plane wave is of limited validity. The character of the upper state, both in its beam composition and its resolution into spherical waves, changes only slowly across the energy range of the present experiment, and perhaps could have been calculated only once at an intermediate energy for each figure, and used throughout the energy range.

In general a lower state can be a complicated wave function composed of several Bloch waves as well as the evanescent waves near the surface required by the matching. A band which overlaps the initial-state energy will always contain two bulk Bloch states at the k parallel and initial energy of the experiment, one moving toward the surface, and one coming back from it. If there is only one band at the initial energy, there is only one initial state for the photoemission process. It contains the Bloch wave in this band moving toward the surface matched at the surface to the wave coming back along with evanescent waves. If there is more than one band at this energy, there will be a Bloch wave moving toward the surface from each band, and each of these waves can couple with the waves from each of the bands moving back from the surface region to produce a properly matched initial state. Which waves moving back from the surface are coupled to which incoming waves to form an initial state is determined by the matching at the surface. It is interesting to ask whether this possible mixing of waves from different bands actually occurs, and whether its nature can be understood in simple terms. We find in our calculations that if there is a small bulge in a band across the $E=E_i$ line in the band plot (such as the bulges that occur across the top and bottom of the −4.0-V line in Fig. 4), the incoming and reflected Bloch waves corresponding to the points where this bulge crosses the $E=E_i$ line match well with each other. This means that the reflected wave of the pair at E_i carries nearly all of the flux back in the lower state corresponding to the incoming wave of this pair, and practically none for any other lower state. In other cases, the reflected flux in a typical lower state tends to be spread over the available reflected waves rather than localized in any particular wave. However, along symmetry directions, the reflected waves must have the same symmetry as the incident wave, which greatly reduces the possible mixing. It is not surprising that the representation of the lower-state wave functions in terms of beams changes radically over the energy range covered by the experiments, since this range includes all of the *d* bands as well as some bands of *sp* character.

A standard formula[37] for the intensity of photoemission expresses it as a sum of products of joint density of initial- and final-state factors times squared dipole matrix elements, with the sum taken over all transitions contributing to the measurement. The formulas we use, although equivalent to this expression, do not take quite this form, with the consequence that we do not evaluate the joint density of states. The density of final states is subsumed inside the expression for the LEED wave function and is not available, but the density of initial states for fixed *k* parallel is calculated explicitly. This is a one-dimensional density of states, because the calculation of the photoemission out of the crystal at a particular angle, and hence at a particular k_x, k_y, is a one-dimensional problem. This one-dimensional density of states is singular whenever the bands are flat as a function of k_z for fixed *k* parallel so that dE/dk_z is zero. This singularity is smoothed away when the photoemission and the corresponding density of states are averaged over a finite solid angle. Brillouin-zone boundaries, where bands tend to be flat, do not give peaks in our calculated photoemission, because the matrix element is large only near direct transitions, and these do not happen to occur near the edge of the zone in the data given. However, the sharpness of the right-most peak in a number of our curves is due to the flatness of the initial-state *d* band involved.

The experiment collects all electrons emitted in a 2° cone about the nominal angle. Calculations made by summing the contributions from five points within this angular resolution of the detector are shown as narrow lines for the bottom two curves in Fig. 3. In these results, narrow peaks are somewhat wider, because the narrow *d* band is moved up and down in energy with the change in k_x and k_y produced by the variation of the angles. Unfortunately, other features of the calculated curves are not brought into closer agreement with experiment by this angular average. The changes in other curves exhibited in this paper have been found to be similar to the changes exhibited here. Since our curves agree reasonably well with experiment, and since the averaging has very little effect except for very flat bands, it appears that calculations which use an average over the experimental aperture can usually be replaced by calculations at the nominal angle without serious loss of accuracy for such narrow aperture experiments. The nominal-angle calculation can fail to represent the data when the wave functions at this angle have a symmetry which is broken in the cone around the angle. In this case, a calculation at one angle slightly off the nominal angle where the symmetry is reduced is more appropriate. Including hole-lifetime effects would also smooth the curves and reduce the dependence on angle.

Based on the adequacy of our calculations, and in particular this one-dimensional form for the relevant density of states, we can develop some idea about the importance of the density of lower states in determining the intensity of emission. This can be accomplished very simply by comparing the calculated peak heights with the slopes of the lower-state k_z vs E lines at the crossings with the upper-state lines in the band-structure plots beneath the intensity curves[38] in Figs. 4–9. As we have seen, flat lower-state bands in the normal band-structure plot, shown in Figs.4–11, do indeed give sharp strong peaks in the calculated spectra. We note also that the density of upper states as measured by the slope of the upper-state band line is nearly constant over the energies concerned, and that there is no evidence of nesting, i.e., the upper-state line is never nearly parallel to a lower-state line, thus giving a shallow crossing which extends over a significant region of the Brillouin zone.

The other important factor governing the intensity of emission is the matrix element. Here the symmetry of the wave functions inside the muffin tins is of predominant importance. We find that the upper-state wave function has strong *s*, *p*, and *d* character, and little contribution from the *f*

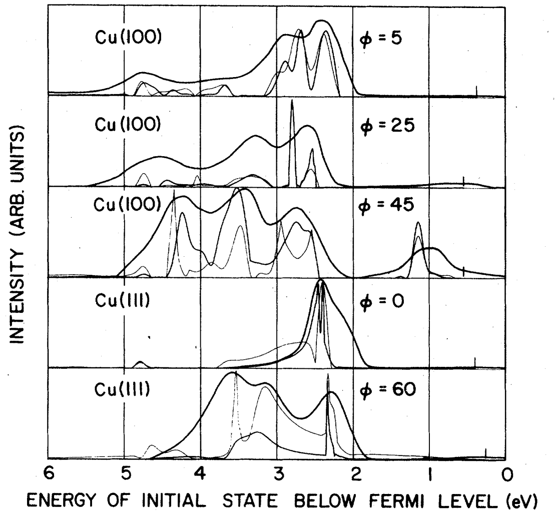

FIG. 10. Modified photoemission obtained by changing the sign of the matrix element of the photoemission from the lower-state Bloch wave moving toward the surface. This is equivalent to a change in the matching of the lower-state wave function at the surface by some change of the surface. The thinnest curves give the results of calculations with this modification. The other curves repeat the results shown in previous figures for the same conditions.

and higher components. Within 3 eV of the Fermi level most of the lower states seen in these experiments have *d*-wave coefficients an order of magnitude larger than those of any other symmetry. In general they lack *f* and higher *l* waves almost completely. However, the matrix element is larger for the higher *l* components so that the matrix element for transition is generally dominated by *d* to *f* coupling, even for some lower bands which are nominally of *sp* character. This means that the use of a simple *d* to *p* matrix element to describe the intensity of peaks[9] in copper is not generally adequate.

The treatment of this paper is unlike the usual direct-transition model of photoemission in that the upper and lower states of the process in the bulk of the crystal are coherent combinations of Bloch waves obtained by surface matching. It has been shown that, for sufficiently small inelastic scattering, the direct transition between a particular Bloch wave in the lower state and a particular Bloch wave in the upper state dominate the transitions which arise from all of the other components of both these wave functions to such an extent that these other contributions can all be neglected.[4,5] Under these conditions, the direct-transition model is adequate, and coherent wave functions made up of more than one Bloch wave need not be constructed. The contributions from evanescent waves, which give the modification of the wave function near the surface, will also be negligible under these circumstances.

The single-step formulation of photoemission contains certain effects not found in a simple direct-transition model. In our comparison between theory and experiment, as seen in almost any of the figures of this paper, we notice that it is quite common for a single experimental peak to contain contributions from more than one direct transition. Since inelastic scattering spreads out direct transitions in energy, the matrix elements of more than one pair of lower and upper Bloch waves may be large at an energy near more than one crossing in the band structure. If two direct transitions occur from the same initial wave function, the theory tells us that the amplitudes rather than the intensities of these two direct transitions must be combined. Hence it is possible to have either constructive or destructive interference between them. In the first case the intensity should be filled in between the two crossings in the band structure, and the maximum in the intensity can even occur between the two crossings. In the case of destructive interference one can expect a strong dip in the intensity between the two points of crossing.

We have examined the theoretical and experimental curves shown in this paper, comparing peak positions with the positions of direct transitions in the calculations of the bands in an attempt to find evidence of this type of interference. Instances of destructive interference should be the most striking, but were not definitely detected. To check for interference between a transition from the incoming wave and a transition from a reflected wave, we have repeated some of our calculations with the sign of the contribution to the matrix element from the incoming wave reversed. This changes constructive interference into destructive interference and vice versa, but has no effect without such interference. This enables us to discern whether such effects have any importance. In Fig. 10 we show recalculations of several of our previous curves with this sign change. We note that interference *does* have a definite effect on the spectra, and in particular, that some peaks are broken up into separate components from different direct transitions. This shows that interference is involved in forming the original calculated curve.

The relative phases of the various Bloch waves in both the lower and upper states are determined by the matching in the surface region. This would appear to imply that constructive interference between direct transitions can be changed to destructive interference and vice versa by changing the nature of the surface. It is not yet clear that various surfaces can be sufficiently different from each other to achieve this. It is intriguing to note that at least one theoretical curve [Cu(111) at $\varphi = 60°$ in Fig. 10] is brought materially closer to the experimental data by this change of phase in the surface reflection. These interference effects should be reduced when the experiment is performed under conditions of high symmetry, because the mixing of some of the waves is eliminated by a selection rule. Interference should also be less important when direct transitions are well separated in energy.

IV. CONCLUSIONS

These calculations show that the positions of the peaks seen in these experiments are given by the direct transitions in the bulk band structure, but that an observed peak can contain contributions from more than one direct transition. When a peak does contain more than one direct transition, its shape can be strongly affected by interference between bulk Bloch waves. This interference is determined by the nature of the matching of these waves in the surface. We also see that the agreement between theory and experiment obtained in this paper would have been noticeably improved if narrow surface resonance structure obtained in the theory but not found in the experiment were suppressed in some way. This might be accomplished by introducing the broadening of the initial state that arises from hole-lifetime effects, or perhaps by a change in the shape of the potential at the surface. There is also evidence that the agreement in the shape of certain peaks which contain more than one direct transition might be improved by changing the potential in the surface region. Future work must determine which improvements of the calculation are most significant.

In this study the light was incident on the crystal along the normal. This may have improved the agreement between theory and experiment by reducing plasmon effects and photoemission in the surface dipole region.

In general, only one Bloch wave seems to be important in the composition of the upper state. Occasionally there is a small energy region where one Bloch wave is superceded by another so that, in this region, two Bloch waves are important. It is generally expected that upper-state Bloch waves which couple well with the waves outside the crystal do not have matrix elements with the initial state as large as the upper-state Bloch waves which are more confined to the crystal. In our calculations we find that only one Bloch wave is important in the upper state, because poor transmission to the detector eliminates the contributions from the others.

On the other hand, the single Bloch wave of the upper state is in turn usually made up of more than a single plane wave. Thus theories which represent the upper state by a single plane wave can give only limited agreement with experiment.

A lower state is a coherent combination of a wave moving toward the surface and waves coming back. The matching at the surface determines the relative phase of these waves, and sometimes in this way the matching affects the intensity and shape of peaks arising from direct transitions.

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