Parametrized scheme for calculating angle-resolved photoemission spectra from the fcc d-band metals

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(Received 21 December 1983; revised manuscript received 2 April 1984)

A parametrized scheme is developed for calculating angle-resolved photoemission spectra from the valence bands of the fcc d-band metals. We take as a starting point the result for the photocurrent in a one-step model when final-state damping and dielectric screening of the free-space electric field are neglected. With use of scattering theory, a model for the final-state wave function ψ^f near the surface is derived, in which ψ^f is written as a linear combination of orthogonalized plane waves with group velocities directed both into and out of the bulk. This result is then generalized to obtain a model for ψ^f in the presence of electron damping, and a parametrized, z-independent, model for the screened electric field within the solid is adopted. Initial-state energies and wave functions are obtained using a combined interpolation scheme. Optical transition matrix elements are evaluated by adopting parametrized expressions for integrals involving the radial wave functions for the various angular momentum components of the initial and final states within a muffin-tin sphere. The use of this scheme as an improved method for extracting initial-state band positions from experimental photoemission spectra is discussed.

I. INTRODUCTION

It has been demonstrated in recent years that angle-resolved photoemission (ARP) spectroscopy is capable of providing detailed information concerning the bulk band dispersions, $E(\vec{k})$, of solids. However, in order to extract band positions from the experimental spectra one must adopt a model for the photoemission process, and the accuracy of the "experimentally determined" $E(\vec{k})$ is limited by the accuracy of this model. Several workers[1-11] have performed calculations of ARP spectra from the fcc d-band metals as a means of testing various models of the photoemission process in these materials. Despite the fact that these calculations have varied greatly in complexity, they typically achieve a satisfactory level of agreement with many experimental spectra, yet contain significant disagreements with others. In the simpler schemes the final state ψ^f is assumed either to have a free-electron-like E versus $\vec{k}$ dispersion[1-5] or, within the context of the three-step model, to be describable in terms of bulk wave functions.[6,7] The optical excitation matrix elements are then either treated as being constant,[1,2] or are calculated with some form of parametrized procedure.[3-7] In schemes which are considerably more complex,[8-11] ψ^f is calculated using procedures similar to those developed for calculating low-energy electron diffraction (LEED) states, and the initial states and optical matrix elements are computed from first principles.

In this paper we present a parametrized scheme for performing relatively inexpensive calculations of ARP spectra from the fcc d-band metals. The major difference between this work and previous similar works[3-7] lies with the model we adopt for the final-state wave function. Rather than take a single orthogonalized plane wave (OPW) or the bulk final state of the three-step model, ψ^f is assumed to equal a linear combination of damped OPW's with wave vectors $\vec{K}$ which satisfy $\hbar^2K^2/2m = E^f + \Phi$, where Φ is the inner potential (and the energy zero is at the vacuum level). No attempt is made to present a method for calculating the relative amplitudes in ψ^f of the component OPW's. Instead, these are taken as disposable parameters. The need for a more accurate final-state model than has been used previously in parametrized schemes became apparent when we observed structures in experimental spectra from Cu which appeared to originate from initial states which could not couple with significant amplitudes to either a single OPW final state or the bulk final states of the three-step model, even if one were to allow for momentum broadening in the optical matrix elements. In the following paper (hereafter referred to as II) we discuss these results and show that the model for ψ^f adopted here can successfully account for such structures.

In Sec. II we describe the theoretical model which forms the starting point for developing the parametrized scheme. In Sec. III the model for ψ^f is derived. Our method for calculating the optical matrix elements is similar to that of Shevchik and Liebowitz;[12] however, several important refinements are introduced. In Sec. IV we derive an expression for these matrix elements which contains two kinds of unknowns: (a) the amplitudes of the various angular momentum components of the initial-state wave function within a muffin-tin sphere, and (b) quantities which depend on the amplitudes of the angular momentum components of the final state, and which are functionals of the initial- and final-state radial wave functions. In Sec. V we then describe a parametrized procedure for calculating these unknowns, which incorporates a combined interpolation scheme for evaluating the initial-state energies and wave functions of the fcc d-band metals.

II. ANGLE-RESOLVED PHOTOEMISSION IN THE PRESENCE OF ELECTRON DAMPING AND DIELECTRIC SCREENING

When setting out to develop a second-principles, or parametrized, scheme to calculate ARP, it is of course desirable to adopt at the start the most accurate possible model of the photoemission process so that inaccuracies are confined as much as possible to those resulting from the adoption of parametrized procedures for calculating the initial- and final-state wave functions, the electric field within the solid, etc. Feibelman and Eastman[13] have shown that when electron damping in the final state and dielectric screening of the incident electric field are neglected, the photocurrent $j(\hat{R},E)$ in the direction $\hat{R}$ with kinetic energy E is given by the following expression:

$$j(\hat{R},E)\propto v\sum_i \delta(E-\hbar\omega-E^i) \times\left|\int d^3r\,\psi'^{*}_{\hat{R},E}(\vec{r})\vec{A}^{0}(\vec{r})\cdot\vec{p}\psi^i(\vec{r})\right|^2, \quad (1)$$

where the sum is over the initial (i.e., occupied) states of the system, v is the photoelectron velocity in vacuum, and $\vec{A}^{0}(\vec{r})$ is the vector potential (in the Coulomb gauge) of the perturbing electromagnetic field in vacuum. The final-state wave function $\psi'_{\hat{R},E}$ is the complex conjugate of the LEED state $\psi_{-\hat{R},E}$, where $\psi_{-\hat{R},E}$ is defined as being the wave function corresponding to the boundary condition in which a plane wave $\langle\vec{r}\,|\,\vec{K}_I\rangle\equiv\exp(i\vec{K}_I\cdot\vec{r})$, where $\vec{K}_I\equiv-[(2mE)^{1/2}/\hbar]\hat{R}$ is incident on the solid (Fig. 1). Note that since $\psi'_{\hat{R},E}$ is here defined with respect to the zero damping limit, it is a solution to the Schrödinger equation for a crystal potential with a vanishing inelastic component. Unfortunately, Eq. (1) is not generally adequate, as it is necessary to make some provision in the theory for both final-state damping and dielectric screening of the free-space fields. One approach for including electron damping is to adopt the well-known three-step model of photoemission,[14] in which a photoexcited electron is assigned a certain probability (≤ 1) of reaching the surface without undergoing inelastic scattering. However, the three-step model suffers from the defect that the optical excitation step is assumed to proceed as if the mean free path were infinite, in that bulk final-state wave functions are used to calculate the optical excitation matrix elements. In addition, transitions to evanescent final states (corresponding to band-gap emission) are neglected. Accordingly, we will adopt the following as our starting expression for the photocurrent:

$$j(\hat{R},E)\propto v\sum_i \delta(E-\hbar\omega-E^i) \times\left|\int d^3r\,[\psi'^{d}_{\hat{R},E}(\vec{r})]^{*}\vec{A}_{sc}(\vec{r})\cdot\vec{p}\psi^i(\vec{r})\right|^2, \quad (2)$$

where the final-state wave function $\psi'^{d}_{\hat{R},E}$ is assumed to decay on the scale of a few atomic layers of the surface. Equation (2) can be considered to define $\psi'^{d}_{\hat{R},E}$, as being that wave function which produces, through this equation, the maximum agreement with the "one-electron" (i.e., excluding secondaries) component of the experimental $j(\hat{R},E)$. To take account of the dielectric response of the solid, we have simply replaced $\vec{A}^{0}(\vec{r})$ with $\vec{A}_{sc}(\vec{r})$, the screened vector potential within the solid.[13] The calculation of $\vec{A}_{sc}(\vec{r})$ is discussed in Sec. IV.

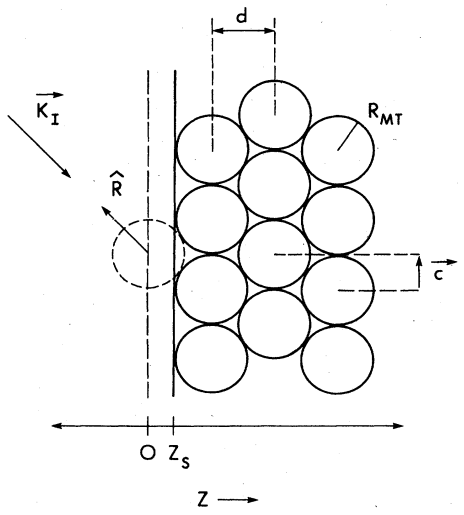

FIG. 1. Schematic diagram of the surface potential. For $z<z_s$, the potential is assumed to vanish. R_{MT} is the muffin-tin radius, d is the interlayer spacing, and $\vec{c}$ is the displacement in a plane parallel to the surface of one layer from the next. $\hat{R}$ is the electron emission direction and $\vec{K}_I$ is the incident wave vector characterizing the LEED state $\psi_{-\hat{R},E}$, where $E=\hbar^2K_I^2/2m$.

III. A MODEL FOR THE FINAL-STATE WAVE FUNCTION

In attempting to construct a model for $\psi'^{d}_{\hat{R},E}$, it is helpful to consider first the behavior of the undamped LEED state $\psi_{-\hat{R},E}$ in the outermost atomic layers, the region in which $\psi'^{d}_{\hat{R},E}$ has a significant amplitude. It is easier to arrive at a straightforward characterization of $\psi_{-\hat{R},E}$ in the surface region because the form of the wave function is known both in vacuum, where it equals $|\vec{K}_I\rangle$ plus a linear combination of outgoing plane waves, and for $z\rightarrow+\infty$ (Fig. 1), where it equals a linear combination of bulk Bloch states propagating toward positive z. $\psi_{-\hat{R},E}$ can thus be modeled by forcing the wave function to undergo a smooth transformation from its behavior in vacuum to its behavior for $z\rightarrow+\infty$. This forms a useful starting point for constructing a model for $\psi'^{d}_{\hat{R},E}$, since one can expect that some of the salient properties of $\psi'_{\hat{R},E}(=\psi^{*}_{-\hat{R},E})$ in the surface region will be shared by $\psi'^{d}_{\hat{R},E}$.

The behavior of $\psi_{-\hat{R},E}$ will be analyzed by deriving an expansion for it using simple scattering theory techniques, and then considering in turn the behavior of successive terms in the expansion. We assume that the semi-infinite solid is characterized by a potential $V(\vec{r})$ which vanishes for $z<z_s$, has a step of magnitude Φ (the inner potential)

at the surface plane $z=z_s$, and is described for $z>z_s$ within the muffin-tin approximation (Fig. 1). We assume further that the first layer of atoms is at $z=z_s+R_{\rm MT}$, where $R_{\rm MT}$ is the muffin-tin radius, that the potential within each muffin-tin sphere is identical, and that there is no surface relaxation or reconstruction. This rather restrictive model for the potential is adopted here mainly for convenience, the only essential feature being the decomposition into the nonoverlapping scattering centers represented by the muffin-tin spheres. The muffin-tin approximation has been exclusively used in the LEED-type calculations of ARP spectra based upon the one-step model.[8-11]

To develop an expansion for $\psi_{-\hat{R},E}$ we begin by defining a state $|K_s\rangle$ corresponding to the situation in which the incident LEED beam $\exp(i\vec{K}_I\cdot\vec{r})$ strikes a plane boundary at $z=z_s$ between a region of zero potential ($z<z_s$) and a region of potential $-\Phi$ ($z>z_s$). We have

$$\langle\vec{r}\,|K_s\rangle=\begin{cases}e^{i\vec{K}_I\cdot\vec{r}}+Re^{i\vec{K}_R\cdot\vec{r}}, & z\le z_s\\ \tau e^{i\vec{K}_\tau\cdot\vec{r}}, & z>z_s\end{cases}\tag{3}$$

where $\vec{K}_R$ and $\vec{K}_\tau$ are the wave vectors, and R and τ are the corresponding amplitudes, of the reflected and transmitted waves, respectively. When the potential for $z>z_s$ is taken to equal $V(\vec{r})$, the plane wave $\langle\vec{r}\,|\vec{K}_\tau\rangle\equiv\tau\exp(i\vec{K}_\tau\cdot\vec{r})$ can be thought of as the "new" incident wave formed by the refraction of $|\vec{K}_I\rangle$ at the potential step at the surface. We next redefine the energy zero to be at the muffin-tin zero, so that the energy E of $\psi_{-\hat{R},E}$ is equal to $\hbar^2K_\tau^2/2m$, the kinetic energy corresponding to $|\vec{K}_\tau\rangle$, rather than to $\hbar^2K_I^2/2m$, and decompose the potential $V(\vec{r})$ into components $V_1(\vec{r})$ and $V_2(\vec{r})$, where

$$V_1(\vec{r})=V_1(z)=\begin{cases}+\Phi, & z\le z_s\\ 0, & z>z_s\end{cases}\tag{4}$$

and

$$V_2(\vec{r})=\sum_{\vec{R}_n}V_{\rm MTS}(|\vec{r}-\vec{R}_n|)\,.\tag{5}$$

$V_{\rm MTS}$ in Eq. (5) represents the potential of a single muffin-tin sphere:

$$V_{\rm MTS}(|\vec{r}-\vec{R}_n|)=\begin{cases}V(\vec{r}), & |\vec{r}-\vec{R}_n|\le R_{\rm MT}\\ 0, & |\vec{r}-\vec{R}_n|>R_{\rm MT}\end{cases}\tag{6}$$

and the sum is over the atomic positions $\vec{R}_n$. Note that $V_2(\vec{r})$ vanishes outside of the muffin-tin spheres. We can now expand $\psi_{-\hat{R},E}$ as follows:

$$\begin{aligned}|\psi_{-\hat{R},E}\rangle=&\,|K_s\rangle+G_0(E)T_2(E)\,|\vec{K}_\tau\rangle\\&+G_0(E)T_1(E)G_0(E)T_2(E)\,|\vec{K}_\tau\rangle+G_0(E)T_2(E)G_0(E)T_1(E)G_0(E)T_2(E)\,|\vec{K}_\tau\rangle+\cdots\\&+[G_0(E)T_1(E)G_0(E)T_2(E)]^n\,|\vec{K}_\tau\rangle+G_0(E)T_2(E)[G_0(E)T_1(E)G_0(E)T_2(E)]^n\,|\vec{K}_\tau\rangle+\cdots\,,\end{aligned}\tag{7}$$

where G_0 is the free-particle Green function and T_1 and T_2 are the T matrices for the potentials V_1 and V_2, respectively. Each term in Eq. (7) has a straightforward physical interpretation. $G_0T_2\,|\vec{K}_\tau\rangle$ is the scattered wave which is produced when the plane wave $|\vec{K}_\tau\rangle$ is incident on the array of muffin-tin spheres. For $z\le z_s$, $\langle\vec{r}\,|G_0T_2\,|\vec{K}_\tau\rangle$ equals a linear combination of propagating and evanescent beams (plane waves) with wave vectors $\vec{K}^{-}(E,\vec{k}_s+\vec{G}_s)$, where the $\vec{G}_s$ are the surface reciprocal-lattice vectors corresponding to the two-dimensional real-space Bravais lattice characterizing the surface, $\vec{k}_s$ is the wave vector which characterizes $\psi_{-\hat{R},E}$ in the surface Brillouin zone (so that $\vec{k}_s+\vec{G}_s=\vec{K}_{\tau\|}=\vec{K}_{I\|}$ for some $\vec{G}_s$), and

$$\vec{K}^{\pm}(E,\vec{k}_s+\vec{G}_s)=\vec{k}_s+\vec{G}_s\pm\begin{cases}\left[\dfrac{2mE}{\hbar^2}-|\vec{k}_s+\vec{G}_s|^2\right]^{1/2}\hat{z}, & E\ge\dfrac{\hbar^2}{2m}|\vec{k}_s+\vec{G}_s|^2\\ i\left[|\vec{k}_s+\vec{G}_s|^2-\dfrac{2mE}{\hbar^2}\right]^{1/2}\hat{z}, & E<\dfrac{\hbar^2}{2m}|\vec{k}_s+\vec{G}_s|^2\,.\end{cases}\tag{8}$$

Each of the diffracted beams which comprise $\langle\vec{r}\,|G_0T_2\,|\vec{K}_\tau\rangle$ for $z\le z_s$ is incident on the potential step at $z=z_s$ and generates a scattered wave. The sum, over all the diffracted beams, of these scattered waves is given by the next term in the expansion, $G_0T_1G_0T_2\,|\vec{K}_\tau\rangle$. For $z>z_s$, $\langle\vec{r}\,|G_0T_1G_0T_2\,|\vec{K}_\tau\rangle$ equals a linear combination of reflected beams with wave vectors $\vec{K}^{+}(E,\vec{k}_s+\vec{G}_s)$ which are in turn incident on the set of muffin-tin spheres, generating more diffracted beams, and so on. Equation (7) can be proven by noting that each line on the right-hand side (RHS) of the equation is a solution to the Schrödinger equation for $z>z_s$, and that the sum of the second term in each line and the first term in the following line is a solution to the Schrödinger equation for $z\le z_s$

and is properly matched at the potential step at $z=z_s$. The RHS is therefore a good solution for all z to the Schrödinger equation for the potential $V(\vec{r})$. Since it furthermore satisfies the boundary condition of a plane wave $|\vec{K}_I\rangle$ incoming from vacuum, it must equal $|\psi_{-\hat{R},E}\rangle$.

Neglecting $G_0T_2|\vec{K}_\tau\rangle$ and succeeding terms in Eq. (7) yields the single plane-wave approximation for $\psi_{-\hat{R},E}$:

$$\psi_{-\hat{R},E}(\vec{r})=\psi^{(0)}_{-\hat{R},E}(\vec{r})\equiv\tau e^{i\vec{K}_\tau\cdot\vec{r}},\quad z>z_s\ . \tag{9}$$

Of course, a single plane wave may fail to be a good approximation for $\psi_{-\hat{R},E}$ within the muffin-tin spheres, where the atomiclike crystal potential is rapidly varying. When used, in fact, to compute photoexcitation matrix elements from the valence bands of Cu for relatively low photon energies, it has been shown to result in large inaccuracies in the predicted photoemission peak intensities.[1,4] It is therefore necessary to include at least one more term in the expansion for $\psi_{-\hat{R},E}$, which yields the approximation

$$\begin{aligned}\psi_{-\hat{R},E}(\vec{r})&=\psi^{(1)}_{-\hat{R},E}(\vec{r})\\&\equiv\langle\vec{r}|\vec{K}_\tau\rangle+\langle\vec{r}|G_0T_2|\vec{K}_\tau\rangle,\quad z>z_s\ .\end{aligned} \tag{10}$$

As mentioned above, $\psi^{(1)}_{-\hat{R},E}$ is a solution to the Schrödinger equation for $z>z_s$.

To construct a model for the term $G_0T_2|\vec{K}_\tau\rangle$ in Eq. (10), consider first that for large z, $\psi^{(1)}_{-\hat{R},E}$ must equal a linear combination of bulk wave functions $\phi^E_{\vec{k}n}$ with group velocities that are directed into the bulk. At energies $E\gtrsim\Phi$ the bulk bands of the fcc d-band metals are nearly-free-electron-like and have been successfully described using a combined interpolation scheme,[15] in which nearly-free-electron-like states are assumed to equal a linear combination of a small number of OPW's. Often, a single OPW totally dominates the wave function and in this case we arrive at the approximation that $\phi^E_{\vec{k}n}$ can be described by

$$\begin{aligned}|\phi^E_{\vec{k}n}\rangle&=|\mathrm{OPW}(\vec{k}+\vec{G})\rangle\\&\equiv|\vec{k}+\vec{G}\rangle-\sum_c|c(\vec{k})\rangle\langle c(\vec{k})|\vec{k}+\vec{G}\rangle\end{aligned} \tag{11a}$$

(where here $\langle\vec{r}|\vec{k}+\vec{G}\rangle\equiv\exp[i(\vec{k}+\vec{G})\cdot\vec{r}]$) and

$$E=\frac{\hbar^2}{2m}|\vec{k}+\vec{G}|^2 \tag{11b}$$

for some bulk reciprocal-lattice vector $\vec{G}$, where the $|c(\vec{k})\rangle$ are Bloch sums formed from the core orbitals $\phi_c(\vec{r})$:

$$\langle\vec{r}|c(\vec{k})\rangle=\sum_{\vec{R}_n}e^{i\vec{k}\cdot\vec{R}_n}\phi_c(\vec{r}-\vec{R}_n)\ . \tag{12}$$

[Note that since E is being measured with respect to the muffin-tin zero, the accuracy of Eq. (11b) will depend on the choice of inner potential Φ.] When Eqs. (11) apply, the necessary conditions for $\phi^E_{\vec{k}n}(\vec{r})$ to have a nonzero amplitude in $\psi^{(1)}_{-\hat{R},E}(\vec{r})$ for large z are that $\vec{k}_\parallel$ equal $\vec{k}_s+\vec{G}_s$ for some $\vec{G}_s$, and that $k_z+G_z>0$; i.e., the OPW wave vector $\vec{k}+\vec{G}$ must be one of the $\vec{K}^+(E,\vec{k}_s+\vec{G}_s)$ corresponding to a propagating beam [Eq. (8)]. There is always at least one such $\phi^E_{\vec{k}n}$, viz., $|\mathrm{OPW}(\vec{K}_\tau)\rangle$. If this is the only one, and you want to arrive at the approximation to $\psi^{(1)}_{-\hat{R},E}(\vec{r})$ for large z implied by Eqs. (11) by modeling the contribution of $G_0T_2|\vec{K}_\tau\rangle$ to $|\psi^{(1)}_{-\hat{R},E}\rangle$ [Eq. (10)], then it is clear that this term can be taken to do two things. First, it modifies the total amplitude in $\psi^{(1)}_{-\hat{R},E}$ of the plane wave $\langle\vec{r}|\vec{K}_\tau\rangle=\tau\exp(i\vec{K}_\tau\cdot\vec{r})$ so that its intensity in the interstitial region between the muffin-tin spheres is reduced from $|\tau|^2$ (assuming that some of the incident flux is diffracted toward negative z). Second, it orthogonalizes this modified plane wave to the core in the manner prescribed by Eq. (11a). If there are additional OPW's eligible to mix with $|\mathrm{OPW}(\vec{K}_\tau)\rangle$ for large z, then for each such OPW, G_0T_2 acting on $|\vec{K}_\tau\rangle$ must generate within both the interstitial and core regions the appropriate plane wave with the correct amplitude and within the core regions the appropriate orthogonalization terms as well.

For large negative z, $\langle\vec{r}|G_0T_2|\vec{K}_\tau\rangle$ equals a linear combination of diffracted beams with wave vectors $\vec{K}^-(E,\vec{k}_s+\vec{G}_s)$ which correspond to propagating beams. $\psi^{(1)}_{-\hat{R},E}$ must by continuity contain some evidence of these outgoing plane waves in the outermost atomic layers. It is evident in fact that these last few layers serve as a transition region in which $\psi^{(1)}_{-\hat{R},E}$ evolves between two quite different kinds of behavior: plane waves propagating toward $-\infty$ for $z\lesssim z_s$, and Bloch states propagating toward $+\infty$ for large z. We wish to formulate a model for $\langle\vec{r}|G_0T_2|\vec{K}_\tau\rangle$ for all $z>z_s$ which is consistent with this observation and which is consistent with and analogous to the behavior of $\langle\vec{r}|G_0T_2|\vec{K}_\tau\rangle$ for large z discussed above. Accordingly, we will assume that for $z>z_s$ G_0T_2 acting on $|\vec{K}_\tau\rangle$ generates a set of plane waves with wave vectors $\vec{K}^+(E,\vec{k}_s+\vec{G}_s)$ and $\vec{K}^-(E,\vec{k}_s+\vec{G}_s)$, but with amplitudes that are functions of z. Evanescent plane waves, with imaginary $K_z^\pm(E,\vec{k}_s+\vec{G}_s)$, will be neglected. In the core regions G_0T_2 is also assumed to generate appropriate orthogonalization terms. Specifically, and following Eq. (10), we adopt the following as a model for $\psi^{(1)}_{-\hat{R},E}$:

$$\psi^{(1)}_{-\hat{R},E}(\vec{r})=\sum_{\vec{G}_s}{}'\{f^+_{-\hat{R},E}(\vec{G}_s,z)\langle\vec{r}|\mathrm{OPW}[\vec{K}^+(E,\vec{k}_s+\vec{G}_s)]\rangle+f^-_{-\hat{R},E}(\vec{G}_s,z)\langle\vec{r}|\mathrm{OPW}[\vec{K}^-(E,\vec{k}_s+\vec{G}_s)]\rangle\},\quad z>z_s\ , \tag{13}$$

where the prime on the sum indicates that it is to be restricted to those $\vec{G}_s$ corresponding to propagating beams. The detailed behavior of the $f^{\pm}_{-\hat{R},E}(\vec{G}_s,z)$ is not known. However, it is evident that the following relationships are satisfied:

$$|f^{+}_{-\hat{R},E}(\vec{G}_s,z_s)| \geq \lim_{z\to\infty} |f^{+}_{-\hat{R},E}(\vec{G}_s,z)| \ , \tag{14a}$$

$$\vec{K}^{+}(E,\vec{k}_s+\vec{G}_s)=\vec{K}_\tau \ ,$$

$$\lim_{z\to\infty} |f^{+}_{-\hat{R},E}(\vec{G}_s,z)| \geq |f^{+}_{-\hat{R},E}(\vec{G}_s,z_s)| = 0 \ , \tag{14b}$$

$$\vec{K}^{+}(E,\vec{k}_s+\vec{G}_s)\neq\vec{K}_\tau \ ,$$

$$|f^{-}_{-\hat{R},E}(\vec{G}_s,z_s)| \geq \lim_{z\to\infty} |f^{-}_{-\hat{R},E}(\vec{G}_s,z)| = 0 \ . \tag{14c}$$

OPW's corresponding to evanescent plane waves are neglected in Eq. (13) because structures which would correspond to transitions which couple to such components of the final state do not appear to be observed in experimental ARP spectra (see II).

The question now arises as to whether $\psi^{(1)}_{-\hat{R},E}$ is a good approximation to $\psi_{-\hat{R},E}$. If the intensities of the diffracted beams generated when the plane wave $\tau\exp(i\vec{K}_\tau\cdot\vec{r})$ is incident on the set of muffin-tin spheres are sufficiently small, i.e., if $\langle\vec{r}\,|\,G_0T_2\,|\,\vec{K}_\tau\rangle$ is sufficiently close to zero for $z\leq z_s$, then $G_0T_1G_0T_2\,|\,\vec{K}_\tau\rangle$ and succeeding terms in Eq. (7) can be neglected. However, since we know of no reason for assuming that this is the case, we conclude that $G_0T_1G_0T_2\,|\,\vec{K}_\tau\rangle$ and succeeding terms should be retained if possible. The second line and each succeeding line of Eq. (7) differs from the first line in that the first term will generally contain incoming beams corresponding to all $\vec{K}^{+}(E,\vec{k}_s+\vec{G}_s)$. As above, we will neglect the evanescent beams. Following the same arguments as used above, we can model the sum of each propagating incoming beam and its corresponding scattered wave as in the RHS of Eq. (13), with the $f^{\pm}_{-\hat{R},E}(\vec{G}_s,z)$ again satisfying Eq. (14), except with $\vec{K}_\tau$ replaced with the wave vector of the incoming beam. When all the incoming and scattered waves in each line of Eq. (7) are summed to obtain $\psi_{-\hat{R},E}$, one finally arrives at an expression which is again in the form of the RHS of Eq. (13).

$\psi'_{\hat{R},E}$, the final state in photoemission in the absence of damping, can be obtained from $\psi_{-\hat{R},E}$ by simply taking the complex conjugate. However, except for the fact that $\lim_{z\to\infty}\psi'^{d}_{\hat{R},E}(\vec{r})$ must vanish, it is not known *a priori* how $\psi'^{d}_{\hat{R},E}$ might differ from $\psi'_{\hat{R},E}$. To obtain $\psi'^{d}_{\hat{R},E}$, we will therefore take the simplest possible approach and adopt the following model:

$$\psi'^{d}_{\hat{R},E}(\vec{r})=e^{-\Gamma(\hat{R},E)z}\sum_{\vec{G}_s}{}' \{f^{+}_{\hat{R},E}(\vec{G}_s,z)\langle\vec{r}\,|\,\mathrm{OPW}[\vec{K}^{+}(E,\vec{k}_s+\vec{G}_s)]\rangle+f^{-}_{\hat{R},E}(\vec{G}_s,z)\langle\vec{r}\,|\,\mathrm{OPW}[\vec{K}^{-}(E,\vec{k}_s+\vec{G}_s)]\rangle\} \ ,$$

$$z>z_s \ . \tag{15}$$

This form explicitly includes the decay of the wave function. The remaining effects of the electron-electron interaction are assumed to be absorbed into the $f^{\pm}_{\hat{R},E}$.

Equation (15) was arrived at under the assumption that the bulk final-state bands can be described by a single OPW, with a free-electron-like energy—versus—OPW wave-vector relationship. For energies E and emission directions $\hat{R}$ for which this is not the case, Eq. (13) for $\psi^{(1)}_{-\hat{R},E}(\vec{r})$ must become inaccurate for large z. However, both the incident beam $\tau\exp(i\vec{K}_\tau\cdot\vec{r})$ and the scattered wave $\langle\vec{r}\,|\,G_0T_2\,|\,\vec{K}_\tau\rangle$ for $z\leq z_s$ obey a free-electron-like dispersion relation. The distance over which $\psi^{(1)}_{-\hat{R},E}$ (and $\psi_{-\hat{R},E}$) heals to its bulk form is not known. If this distance is large compared to the mean free path, then Eq. (15) for $\psi'^{d}_{\hat{R},E}$ becomes plausible as a general result. If this distance is small compared to a mean free path then we might expect Eq. (15) to break down when Eqs. (11) are not a good approximation. In any case, however, it must be emphasized that the effect of electron damping on $\psi'_{\hat{R},E}$ is unpredictable. Our approach here will be to assume that Eq. (15) is always valid and so depart from the three-step model of photoemission, in which the final state is assumed to be always bulklike. Experimental support for this procedure in the case of photoemission from Cu for photon energies between 11.8 and 21.2 eV is presented in II where its relationship with previous ARP results from Cu is also discussed.

Even when Eqs. (11) are valid, Eq. (15) still represents a serious departure from the three-step model because of the presence of the OPW's with wave vectors $\vec{K}^{+}(E,\vec{k}_s+\vec{G}_s)$. These components of the final state would correspond to the wave functions of those bulk states which have group velocities that are directed into the bulk, and thus electrons photoexcited from initial states which couple to these OPW's would not be photoemitted in the three-step model. In II, however, we find that for Cu the amplitudes $f^{+}_{\hat{R},E}$ are sometimes quite large.

Equation (15) is intended to fully describe effects which, within the context of a three-step model, are assigned to propagation in secondary Mahan cones[16] or surface umklapp processes. Such effects can be associated with nonzero values for the functions $f^{-}_{\hat{R},E}(\vec{G}_s,z)$ for $\vec{K}^{-}(E,\vec{k}_s+\vec{G}_s)\neq-\vec{K}_\tau$.

Finally, the optical transition matrix element between a Bloch state $\phi_{\vec{k}n}$ and $\psi'^{d}_{\hat{R},E}$ tends to have its maximum magnitude when $\vec{k}$ is equal to some $\vec{K}^{\pm}(E,\vec{k}_s+\vec{G}_s)$,

modulo a bulk reciprocal-lattice vector (Sec. IV). Redefining the energy zero to be at the vacuum level, we have

$$K_z^{\pm}(E,\vec{k}_s+\vec{G}_s)=\pm\left[\frac{2m}{\hbar^2}(E+\Phi)-|\vec{k}_s+\vec{G}_s|^2\right]^{1/2}. \tag{16}$$

With this choice of $K_z^{\pm}$ the OPW "bands" have a free-electron-like dispersion with respect to the muffin-tin zero. However, it may occur that a more accurate final state is obtained with a value for $K_z^{\pm}$ that is slightly different from that given by Eq. (16). To make the final-state model sufficiently flexible to handle this possibility, the inner potential Φ can be regarded as adjustable and dependent on $\hat{R}$ and E, so that $\Phi=\Phi(\hat{R},E)$.

IV. CALCULATION OF THE PHOTOEXCITATION MATRIX ELEMENTS

To evaluate the matrix elements appearing in Eq. (2) one needs the perturbing vector potential $\vec{A}_{sc}(\vec{r})$ induced within the solid by the incident electric field. Ideally, $\vec{A}_{sc}(\vec{r})$ should be obtained by solving in a self-consistent manner the Schrödinger equation and the microscopic Maxwell equations. A much simpler procedure is to calculate $\vec{A}_{sc}(\vec{r})$ using the Fresnel equations. There is some experimental evidence, however, that this may not be adequate. Smith *et al.*[6] found that in order to reproduce in their calculated spectra the peak intensities observed experimentally in spectra from a Cu(111) surface, it was necessary to assign the ratio $|A_{sc\perp}/A_{sc||}|$ (where $\perp$ and $||$ denote the components of $\vec{A}_{sc}$ perpendicular and parallel to the surface, respectively) values which were much smaller than those predicted by the Fresnel equations. They concluded that nonlocal effects were important near the surface. Here, we will adopt the following expression to describe radiation that is polarized either in the plane of incidence, or perpendicular to it (corresponding to *p*- and *s*-polarized light, respectively):

$$\vec{A}_{sc}(\vec{r})\propto\vec{E}_{||}+\alpha_E(\psi)E_{\perp}\hat{z},\quad z>z_s\ . \tag{17}$$

$E_{||}$ and $E_{\perp}$ are the parallel and perpendicular components, respectively, of the electric field in vacuum and ψ is the angle of incidence of the light. Since $\alpha_E(\psi)$ might not be given accurately by the Fresnel equations, it can be chosen so as to maximize agreement with experiment. Note that we do not account in Eq. (17) for the possibility that $\vec{A}_{sc}(\vec{r})$ has a significant z dependence. Any such z dependence would lead to momentum broadening in $k_{\perp}$ in the photoexcitation matrix element, i.e., to an increase in transitions that are nondirect in $k_{\perp}$. Several theoretical studies have predicted a large contribution to the photocurrent from free-electron metals from the spatial variation of $A_{sc\perp}$.[17–19] These predictions have recently been confirmed experimentally in the case of a nearly-free-electron-like metal, Al.[20,21] It is clear, however, that the corresponding contribution to the photocurrent from the *d*-band metals must be relatively weak, as $k_{\perp}$ conservation effects are known to be very strong.

Rather than work directly with Eq. (2), it is convenient to return to Eq. (1) and make the replacement $\vec{A}^0(\vec{r})\rightarrow\vec{A}_{sc}$ via Eq. (17), transform the matrix element to its potential gradient form by using the relation $[H,\vec{p}]=i\hbar\nabla V(\vec{r})$, and then make the replacement $\psi'_{\hat{R},E}\rightarrow\psi'^{d}_{\hat{R},E}$. The optical matrix element then becomes (suppressing a factor $i\hbar$):

$$M(\psi'^{d}_{\hat{R},E},\psi^i)=\frac{1}{E-E^i}\sum_{\vec{R}_n}\int_{|\vec{r}-\vec{R}_n|<R_{MT}}d^3r[\psi'^{d}_{\hat{R},E}(\vec{r})]^*[\vec{E}_{||}+\alpha_E(\psi)E_{\perp}\hat{z}]\cdot\vec{\nabla}V(\vec{r})\psi^i(\vec{r})\ . \tag{18}$$

The contributions to the integral from the potential step at the surface and from any step at the surfaces of the muffin-tin spheres have been neglected. As discussed by Feibelman,[22] Eq. (18) is not equivalent to the result obtained by making the replacements $\vec{A}^0(\vec{r})\rightarrow\vec{A}_{sc}$ and $\psi'_{\hat{R},E}\rightarrow\psi'^{d}_{\hat{R},E}$ directly in Eq. (1), as ψ^i and $\psi'^{d}_{\hat{R},E}$ are not solutions to the Schrödinger equation for the same Hamiltonian. However, there is no reason *a priori* to suppose that the current procedure gives an inferior description of the matrix elements, especially since the parameters in $\psi'^{d}_{\hat{R},E}$ are to be chosen so as to maximize agreement with experiment. Substituting Eq. (15) into Eq. (18), we can write $M(\psi'^{d}_{\hat{R},E},\psi^i)$ as

$$M(\psi'^{d}_{\hat{R},E},\psi^i)=\sum_{\vec{G}_s}{}'[M^{+}_{\vec{G}_s}(\psi'^{d}_{\hat{R},E},\psi^i)+M^{-}_{\vec{G}_s}(\psi'^{d}_{\hat{R},E},\psi^i)]\ , \tag{19}$$

where the definition of $M^{\pm}_{\vec{G}_s}$ is obvious.

The remainder of this section is devoted to deriving an expression for $M^{\pm}_{\vec{G}_s}(\psi'^{d}_{\hat{R},E},\psi^i)$ which lends itself to a straightforward parametrization. It is convenient to expand the initial- and final-state wave functions within any given muffin-tin sphere in terms of functions containing the spherical harmonics defined with respect to that sphere. We have that an arbitrary function $H(\vec{r})$ can be expanded in the following form for $\vec{r}$ within the muffin-tin sphere at $\vec{R}_n$:

$$H(\vec{r})=\sum_{l,m}A_{l,m}(\vec{R}_n)i^lH_l(|\vec{r}-\vec{R}_n|)Y_{l,m}(\Omega_{\vec{r}-\vec{R}_n}),\quad |\vec{r}-\vec{R}_n|<R_{MT}\ . \tag{20}$$

If ψ^i is expanded as in Eq. (20) then, since ψ^i is a solution to the Schrödinger equation for energy E^i, the $H_l(|\vec{r}-\vec{R}_n|)$ must be solutions $R_l(|\vec{r}-\vec{R}_n|,E^i)$ of the radial Schrödinger equation for energy E^i. When

$|\,\mathrm{OPW}[\vec{\mathrm{K}}^{\pm}(E,\vec{k}_s+\vec{G}_s)]\rangle$ [Eq. (15)] is expanded as in Eq. (20), the corresponding $H_l(|\vec{r}-\vec{R}_n|)$ depend only on E and not on the direction of the OPW wave vector. We will denote these radial functions $S_l(|\vec{r}-\vec{R}_n|,E)$. The coefficients $A_{l,m}(\vec{R}_n)$ characterizing OPW $[\vec{K}^{\pm}(E,\vec{k}_s+\vec{G}_s)]$ will be denoted $A^{\pm}_{L,\vec{G}_s}(\vec{R}_n)$. We have $A^{\pm}_{L,\vec{G}_s}(\vec{R}_n)=\exp[i\vec{K}^{\pm}(E,\vec{k}_s+\vec{G}_s)\cdot\vec{R}_n]A^{\pm}_{L,\vec{G}_s}(0)$, which we will write more simply as $\exp[i\vec{K}^{\pm}(\vec{G}_s)\cdot\vec{R}_n]A^{\pm}_{L,\vec{G}_s}$. To evaluate a particular term in Eq. (19) we can take the z axis to point in the direction of the OPW wave vector $\vec{K}^{\pm}(\vec{G}_s)$.[3,12] We then have that $A^{\pm}_{l,m,\vec{G}_s}$ (which can now be written simply $A_{l,m}$) vanishes for $m\neq 0$. Finally, we shall assume that the functions $\exp[-\Gamma(\hat{R},E)z]$ and $f^{\pm}_{\hat{R},E}(\vec{G}_s,z)$ which appear in Eq. (15) vary sufficiently slowly over a muffin-tin sphere that for each term in the sum over $\vec{R}_n$ [Eq. (18)] it is acceptable to replace these quantities with their values at $\vec{R}_n$ and take them out of the integral. Collecting these results, we arrive at the following expression for $M^{\pm}_{\vec{G}_s}$:

$$M^{\pm}_{\vec{G}_s}(\psi'^{d}_{\hat{R},E},\psi^i)=\frac{1}{E-E^i}[\vec{E}_{||}+\alpha_E(\psi)E_{\perp}\hat{z}]\cdot\sum_{\vec{R}_n}e^{-\Gamma(\hat{R},E)R_{nz}}f^{\pm *}_{\hat{R},E}(\vec{G}_s,R_{nz})\times e^{-i\vec{K}^{\pm}(\vec{G}_s)\cdot\vec{R}_n}\vec{P}^{i\pm}_{\vec{G}_s}(E,E^i,\vec{R}_n)\,. \tag{21}$$

Equation (21) is written with respect to the usual coordinate system in which the z axis points along the surface normal. However, in a coordinate system in which the z axis points in the direction of $\vec{K}^{\pm}(\vec{G}_s)$, the "P vector" $\vec{P}^{i\pm}_{\vec{G}_s}(E,E^i,\vec{R}_n)$ takes on the relatively simple form

$$\vec{P}^{i\pm}_{\vec{G}_s}(E,E^i,\vec{R}_n)=\sum_{l,L'}(-1)^l i^{l+l'}A_{l,0}A^i_{L'}(\vec{R}_n)\times\vec{D}(l,0,L',E,E^i)\,, \tag{22}$$

where $\vec{D}$ is independent of $\vec{R}_n$ and is given by

$$\vec{D}(L,L',E,E^i)=\int_{r<R_{\mathrm{MT}}}d^3r\,S_l(r,E)Y^*_L(\Omega)[\nabla V_{\mathrm{MTS}}(r)]\times R_{l'}(r,E^i)Y_{L'}(\Omega)\,. \tag{23}$$

The matrix elements in an angular momentum basis set of a vector operator $\vec{T}$ which satisfies $[L_i,T_j]=i\hbar\epsilon_{ijk}T_k$ obey certain relationships which are given by Condon and Shortley.[23] Since $\vec{\nabla}V_{\mathrm{MTS}}(r)$ satisfies this commutation rule, and furthermore is odd under inversion, we find for instance that $\vec{D}(l,0,L',E,E^i)$ vanishes unless the dipole selection rules $l=l'\pm 1$ and $m'=0,\pm 1$ are satisfied, thus restricting the sum over l and m' in Eq. (22) [$A^i_{L'}(\vec{R}_n)\approx 0$ for $l'\geq 3$]. It is also convenient in simplifying Eq. (22) to write the initial-state orbital coefficients $A^i_{L'}(\vec{R}_n)$ for $l'=1,2$ in terms of the corresponding coefficients for the Kubic harmonics. We have (suppressing the $\vec{R}_n$ dependence)

$$\begin{aligned}A^i_x&=(3/8\pi)^{1/2}(A^i_{1,-1}-A^i_{1,1})\,,\\ A^i_y&=-(3/8\pi)^{1/2}i(A^i_{1,-1}+A^i_{1,1})\,,\\ A^i_z&=(3/4\pi)^{1/2}A^i_{1,0}\,,\end{aligned} \tag{24}$$

and, for the xz, yz, and $3z^2-r^2$ components of the initial state,

$$\begin{aligned}A^i_{xz}&=(15/8\pi)^{1/2}(A^i_{2,-1}-A^i_{2,1})\,,\\ A^i_{yz}&=-(15/8\pi)^{1/2}i(A^i_{2,1}+A^i_{2,-1})\,,\\ A^i_{3z^3}&=(15/4\pi)^{1/2}A^i_{2,0}\,.\end{aligned} \tag{25}$$

With Eqs. (24) and (25) and the results given in Ref. 23 we find that we can write $\vec{P}^{i\pm}_{\vec{G}_s}$ as

$$\vec{P}^{i\pm}_{\vec{G}_s}(E,E^i,\vec{R}_n)=\beta(E,E^i)\{[A^i_{xz}(\vec{R}_n)+\alpha_p(E,E^i)A^i_x(\vec{R}_n)]\hat{x}+[A^i_{yz}(\vec{R}_n)+\alpha_p(E,E^i)A^i_y(\vec{R}_n)]\hat{y}+[\xi_d(E,E^i)A^i_{3z^2}(\vec{R}_n)+\alpha_p(E,E^i)\xi_p(E,E^i)A^i_z(\vec{R}_n)+\alpha_s(E,E^i)A^i_{0,0}(\vec{R}_n)]\hat{z}\}\,. \tag{26}$$

Equation (26) is an exact restatement of Eqs. (22) and (23), once one neglects the contribution to the P vector from the components of the initial state with angular momentum $l\geq 3$. It is of the same general form as an expression obtained by Shevchik *et al.*[12] by considering photoemission from a free atom. The quantities β, α_p, ξ_p, ξ_d, and α_s are given by rather complicated expressions which are functionals of the initial- and final-state radial wave functions within the muffin-tin spheres and which depend on the final-state angular momentum amplitudes $A_{l,0}$. These expressions are given in the Appendix. Reiterating, the OPW dependence of the RHS of Eq. (26) lies in the orientation of the coordinate system: the unit vector $\hat{z}$ is assumed to point in the direction of the OPW wave vector $\vec{K}^{\pm}(\vec{G}_s)$.

To evaluate the lattice sum in Eq. (21) we will take the initial states ψ^i to be the bulk Bloch states $\phi_{\vec{k}n}$. No attempt will be made to calculate the photocurrent from surface-state bands. Indeed, it is uncertain whether one could adequately describe surface states within the muffin-tin approximation. We thus have $A^i_L(\vec{R}_n)=\exp(i\vec{k}^i\cdot\vec{R}_n)A^i_L(0)\equiv\exp(i\vec{k}^i\cdot\vec{R}_n)A^i_L$. Also, it is necessary to choose a specific form for the $f^{\pm}_{\hat{R},E}(\vec{G}_s,R_{nz})$, and we adopt the following:

$$f^{\pm}_{\hat{R},E}(\vec{G}_s,R_{nz})=f^{\pm}_{\hat{R},E}(\vec{G}_s)e^{-\Gamma^{\pm}_{\hat{R},E}(\vec{G}_s)R_{nz}}\,. \tag{27}$$

By allowing $\Gamma^{\pm}(\hat{R},E,\vec{G}_s)=\Gamma(\hat{R},E)+\Gamma^{\pm}_{\hat{R},E}(\vec{G}_s)$, Eq. (21) becomes

$$M^{\pm}_{\vec{G}_s}(\psi'^{d}_{\hat{R},E},\phi^{i}_{\vec{k}n})=\frac{1}{E-E^i}f^{\pm *}_{\hat{R},E}(\vec{G}_s)[\vec{E}_{||}+\alpha_E(\psi)E_{\perp}\hat{z}]\cdot\vec{P}^{i\pm}_{\vec{G}_s}(E,E^i)$$
$$\times\sum_{\vec{R}_n}e^{-\Gamma^{\pm}(\hat{R},E,\vec{G}_s)R_{nz}}e^{i[\vec{k}^i-\vec{K}^{\pm(r)}(\vec{G}_s)]\cdot\vec{R}_n}, \tag{28}$$

where the superscript (r) on $\vec{K}^{\pm}(\vec{G}_s)$ denotes the corresponding vector in the bulk reduced zone scheme, and $\vec{P}^{i\pm}_{\vec{G}_s}(E,E^i)\equiv\vec{P}^{i\pm}_{\vec{G}_s}(E,E^i,0)$. Evaluating the lattice sum, we have

$$M^{\pm}_{\vec{G}_s}(\psi'^{d}_{\hat{R},E},\phi^{i}_{\vec{k}n})\propto\frac{1}{E-E^i}f^{\pm *}_{\hat{R},E}(\vec{G}_s)e^{i[k^i_z-K^{\pm(r)}_z(\vec{G}_s)]d-\Gamma^{\pm}(\hat{R},E,G_s)d}\delta_{[\vec{k}^i_{||}-\vec{K}^{\pm(r)}_{||}(\vec{G}_s)],\vec{G}_s}$$
$$\times B_{\Gamma^{\pm}(\hat{R},E,\vec{G}_s)}[\vec{k}^i-\vec{K}^{\pm(r)}(\vec{G}_s)][\vec{E}_{||}+\alpha_E(\psi)E_{\perp}\hat{z}]\cdot\vec{P}^{i\pm}_{\vec{G}_s}(E,E^i), \tag{29}$$

where the momentum broadening function $B_{\Gamma}(\vec{k})$ is given by

$$B_{\Gamma}(\vec{k})=\frac{1}{1-e^{i\vec{k}_{||}\cdot\vec{c}}e^{-(\Gamma-ik_z)d}}, \tag{30}$$

d is the interlayer spacing, and $\vec{c}$ is a vector which lies in a plane parallel to the surface and which has the property that when the mth layer is translated by $\vec{c}$ the atoms lie directly on top of the atoms in the $(m+1)$th layer (Fig. 1). Note that $B_{\Gamma^{\pm}(\hat{R},E,\vec{G}_s)}[\vec{k}^i-\vec{K}^{\pm(r)}(\vec{G}_s)]$ has its maximum value when $k^i_{\perp}=K^{\pm(r)}_{\perp}(\vec{G}_s)$ and $[\vec{k}^i_{||}-\vec{K}^{\pm(r)}_{||}(\vec{G}_s)]\cdot\vec{c}=2\pi m$.

V. PARAMETRIZATION OF THE P VECTOR

In this section we describe a parametrized procedure for evaluating the P vector $\vec{P}^{i\pm}_{\vec{G}_s}(E,E^i)$:

$$\vec{P}^{i\pm}_{\vec{G}_s}(E,E^i)=\beta(E,E^i)\{[A^i_{xz}+\alpha_p(E,E^i)A^i_x]\hat{x}+[A^i_{yz}+\alpha_p(E,E^i)A^i_y]\hat{y}$$
$$+[\xi_d(E,E^i)A^i_{3z^2}+\alpha_p(E,E^i)\xi_p(E,E^i)A^i_z+\alpha_s(E,E^i)A^i_{0,0}]\hat{z}\}. \tag{31}$$

We shall assume that the initial-state energies E^i and orbital coefficients A^i are to be computed using a combined interpolation scheme.[15,24,25] In these schemes, Bloch states $\phi^i_{\vec{k}}$ are described with a basis set consisting of nine $\vec{k}$-dependent states $|\alpha_j(\vec{k})\rangle$. Five are Bloch sums of atomiclike orbitals $\chi^d_j(\vec{r})$ with d $(l=2)$ symmetry:

$$\langle\vec{r}\,|\,\alpha_j(\vec{k})\rangle=N^{-1/2}\sum_{\vec{R}_n}e^{i\vec{k}\cdot\vec{R}_n}\chi^d_j(\vec{r}-\vec{R}_n),\quad j=1\text{–}5, \tag{32}$$

where N is the number of atoms in the crystal. Here the χ_j are assumed to have the angular symmetry of the Kubic harmonics. The remaining four $|\alpha_j(\vec{k})\rangle$ are plane waves which can be explicitly orthogonalized to the d states:[15,25]

$$|\alpha_j(\vec{k})\rangle=a_{j-5}\left[|\vec{k}_{j-5}(\vec{k})\rangle-\sum_{s=1}^{5}|\alpha_s(\vec{k})\rangle\langle\alpha_s(\vec{k})\,|\,\vec{k}_{j-5}(\vec{k})\rangle\right],\quad j=6\text{–}9 \tag{33}$$

where

$$\langle\vec{r}\,|\,\vec{k}_j(\vec{k})\rangle=\frac{1}{\sqrt{V}}e^{i\vec{k}_j(\vec{k})\cdot\vec{r}},\quad j=1\text{–}4 \tag{34}$$

and a_j is a normalization constant. The $\vec{k}_j(\vec{k})$ are wave vectors of the form $\vec{k}+\vec{G}$, and V is the crystal volume. For $j=6$–9, $|\alpha_j(\vec{k})\rangle$ is a "pseudo wave function" corresponding to the OPW $|\beta_{j-5}(\vec{k})\rangle$, which is orthogonalized to the core states $|c(\vec{k})\rangle$ [Eq. (12)] as well as to the $|\alpha_j(\vec{k})\rangle$ for $j=1$–5, and given by

$$|\beta_j(\vec{k})\rangle=b_j\left[|\vec{k}_j(\vec{k})\rangle-\sum_{s=1}^{5}|\alpha_s(\vec{k})\rangle\langle\alpha_s(\vec{k})\,|\,\vec{k}_j(\vec{k})\rangle-N^{-1}\sum_{c}|c(\vec{k})\rangle\langle c(\vec{k})\,|\,\vec{k}_j(\vec{k})\rangle\right],\quad j=1\text{–}4, \tag{35}$$

where b_j is a normalization constant. When the combined interpolation scheme's model Hamiltonian for some $\vec{k}$ is diagonalized to obtain a set of coefficients C^i_j characterizing the wave function $\phi^i_{\vec{k}}(\vec{r})$, we will therefore assume that

$$\phi^i_{\vec{k}}(\vec{r})=\sum_{j=1}^{5}C^i_j\langle\vec{r}\,|\,\alpha_j(\vec{k})\rangle+\sum_{j=1}^{4}C^i_{j+5}\langle\vec{r}\,|\,\beta_j(\vec{k})\rangle. \tag{36}$$

We need to find the A^i of Eq. (31) in terms of the C^i_j. This can be accomplished by expanding both sides of Eq. (36) as in Eq. (20) for $\vec{R}_n=0$. Consider first the individual terms on the RHS. Since the $|\alpha_j\rangle$ for $j=1$–5 (for convenience, we will henceforth often suppress the $\vec{k}$ dependence of $|\alpha_j\rangle$, $|\beta_j\rangle$, $|c\rangle$, and $|\vec{k}_j\rangle$) are Bloch sums of the $|\chi^d_j\rangle$, $\langle\vec{r}|\alpha_j\rangle$ must have the same angular symmetry within a muffin-tin sphere as $\chi^d_j(\vec{r})$. We can therefore simply write

$$\langle\vec{r}|\alpha_j\rangle=-Q_2(r)Y_j(\Omega),\quad r<R_{\rm MT},\ j=1\text{–}5\ , \tag{37}$$

where the $Y_j(\Omega)$ are the $l=2$ Kubic harmonics and $Q_2(r)$ includes contributions from the radial wave function contained in $\chi^d_j(\vec{r})$, as well as from the overlap of the $\chi^d_j(\vec{r}-\vec{R}_n)$ for $\vec{R}_n\neq 0$. The $|\beta_j\rangle$ generally contain nonvanishing components for all values of l. The contribution of the $|\beta_j\rangle$ to the d component of $|\phi^i_{\vec{k}}\rangle$ is expected to be small, however, as these states are included in the basis set primarily to describe the s-p component of the band structure. When the d orthogonalization term appearing in Eq. (35) was in fact retained in the calculation it was found to provide a negligible contribution to the photocurrent. We will therefore neglect the d component of $|\beta_j\rangle$. Focusing, then, on the s and p components, it is straightforward to show that when $|\beta_j\rangle$ is expanded as in Eq. (20) with $\vec{R}_n=0$ we obtain

$$A_{l,m[\,|\beta_j\rangle]}=\frac{4\pi}{\sqrt{V}}b_j Y^*_{l,m}(\Omega_{\vec{k}_j})\ , \tag{38}$$

and

$$[H_l(r)]_{[\,|\beta_j\rangle]}=\begin{cases} j_0(k_jr)-\dfrac{N^{1/2}}{4\pi}\displaystyle\sum_{n=1}^{3}f_{n,0}(k_j)R_{n,0}(r), & l=0 \\ j_1(k_jr)-\dfrac{N^{1/2}}{4\pi i}\displaystyle\sum_{n=2}^{3}f_{n,1}(k_j)R_{n,1}(r), & l=1\ , \end{cases} \tag{39}$$

where the j_l are the spherical Bessel functions, the $R_{n,l}$ are the radial wave functions for the core orbitals with principle quantum number n and angular momentum l, and $f_{n,l}(k_j)$ is given by

$$f_{n,l}(k_j)=4\pi i^l\int dr\, r^2R_{n,l}(r)j_l(k_jr)\ . \tag{40}$$

Substituting Eq. (37) into Eq. (36) and expanding the left-hand side (LHS) as in Eq. (20) (reexpressed in terms of the Kubic harmonics), we immediately obtain $A^i_{xz(yz,3z^2-r^2)}=C^i_{xz(yz,3z^2-r^2)}$ and $R_2(r,E^i)=Q_2(r)$. For the s-p component of Eq. (36) we have

$$\sum_{l=0,1}\sum_m A^i_{l,m}i^lR_l(r,E^i)Y_{l,m}(\Omega)=\sum_{j=1}^{4}\sum_{l=0,1}\sum_m C^i_{j+5}A_{l,m[\,|\beta_j\rangle]}i^l[H_l(r)]_{[\,|\beta_j\rangle]}Y_{l,m}(\Omega),\quad r<R_{\rm MT}\ . \tag{41}$$

To set the RHS of Eq. (41) in the same form as the LHS, we will make use of an approximate procedure based on the following two observations. First, for states $\phi^i_{\vec{k}}$ below the Fermi level, it is usually the case that the only $|\beta_j\rangle$ for which C^i_{j+5} is not close to zero is the one corresponding to the wave vector $\vec{k}_j$ with the smallest magnitude (which we will denote $\vec{k}_1$), the remaining components being important for reproducing the bands near s-p band gaps and at energies above the Fermi level. Second, when it does happen that there is more than one $|\beta_j\rangle$ for which C^i_{j+5} is not small for occupied $\phi^i_{\vec{k}}$, the corresponding wave vectors $\vec{k}_j$ have similar magnitudes, so that the corresponding $[H_l(r)]_{[\,|\beta_j\rangle]}$ are approximately independent of j [Eq. (39)]. In light of these observations, we will simply assume that $[H_l(r)]_{[\,|\beta_j\rangle]}$ for $j=2$–4 equals $[H_l(r)]_{[\,|\beta_1\rangle]}$, take $R_l(r,E^i)$ to be given by $[H_l(r)]_{[\,|\beta_1\rangle]}$, and so obtain for $A^i_{0,0}$ and $A^i_{x(y,z)}$

$$A^i_{0,0}=(4\pi/V)^{1/2}\sum_{j=1}^{4}b_jC^i_{j+5}\ , \tag{42}$$

and

$$A^i_{x(yz)}=\frac{3}{\sqrt{V}}\sum_{j=1}^{4}C^i_{j+5}b_jY_{x(y,z)}(\vec{k}_j)\ . \tag{43}$$

We now turn to the derivation of parametrized expressions for the quantities $\beta(E,E^i)$, $\alpha_s(E,E^i)$, $\alpha_p(E,E^i)$, $\xi_p(E,E^i)$, and $\xi_d(E,E^i)$ (see the Appendix) contained in Eq. (31). In doing this, it proves convenient to parametrize certain integrals of the form

$$I_l(k)=\int_{r<R_{\rm MT}}dr\,G(r)j_l(kr) \tag{44}$$

for $l=0$ and 1, while retaining their k dependence. This can be accomplished by linearly interpolating the spherical Bessel functions $j_l(kr)$ between the origin and the muffin-tin radius $R_{\rm MT}$. We then obtain that $I_1(k)$ can be written in the form

$$I_1(k)=Aj_1(kR_{\rm MT})\ , \tag{45}$$

where

$$A=\int_{r<R_{\rm MT}}dr\,G(r)r/R_{\rm MT}\ , \tag{46}$$

and that $I_0(k)$ can be written as

$$I_0(k)=Bj_0(kR_{\rm MT})+D\ , \tag{47}$$

where

$$B=\int_{r<R_{\rm MT}} dr\, G(r) r/R_{\rm MT}\ ,$$
$$D=\int_{r<R_{\rm MT}} dr\, G(r)[1-r/R_{\rm MT}]\ . \tag{48}$$

Note that if $G(r)$ is energy dependent, then the parameters A, B, and D will be energy dependent.

For spectra obtained with a given photon energy $\hbar\omega$, E equals $E^i+\hbar\omega$, so that $\beta(E,E^i)$, $\alpha_s(E,E^i)$, $\alpha_p(E,E^i)$, $\xi_p(E,E^i)$, and $\xi_d(E,E^i)$ can be considered to be functions of E^i only. In computing the E^i dependence, one should account not only for the E^i dependence of the initial-state radial wave function $R_l(r,E^i)$, but also for the E^i dependence of the final-state radial wave function $S_l(r,E^i+\hbar\omega)$. Since we cannot simply model the latter, however, we will treat $S_l(r,E^i+\hbar\omega)$ as being energy independent (again, for a fixed photon energy).

The E^i dependence of $\xi_d(E^i)$ [Eq. (A8)] is through the radial wave function $R_2(r,E^i)$. Since the d bands are relatively narrow, the E^i dependence of $R_2(r,E^i)$, and therefore of $\xi_d(E^i)$, is probably small for energies within the d bands, and will be neglected. This assumption is also inherent in the approach toward describing the d bands taken within the combined interpolation scheme [Eq. (32)]. Thus, $\xi_d(E^i)$ becomes simply ξ_d. Since $\beta(E^i)$ [Eq. (A12)] also depends on E^i through $R_2(r,E^i)$, we replace the products $\beta(E^i)A^i_{xz(yz,3z^2)}$ which appear in Eq. (31) with $\beta A^i_{xz(yz,3z^2)}$. The products $\beta(E^i)\alpha_s(E^i)$ and $\beta(E^i)\alpha_p(E^i)$ [Eqs. (A10)—(A12)] are functionals of the radial wave functions $R_0(r,E^i)$ and $R_1(r,E^i)$, respectively. To parametrize $\beta(E^i)\alpha_s(E^i)$ and $\beta(E^i)\alpha_p(E^i)$ we will assume that $R_0(r,E^i)$ and $R_1(r,E^i)$ for any initial state $\phi^i_{\vec{k}}$ are equal to the radial functions $H_l(r)$ obtained by expanding OPW $(\vec{k}^{\,i})$ according to Eq. (20). We therefore have [Eq. (39)]

$$R_0(r,E^i)=j_0(k^i r)-\frac{N^{1/2}}{4\pi}\sum_{n=1}^{3} f_{n,0}(k^i)R_{n,0}(r)\ , \tag{49}$$

$$R_1(r,E^i)=j_1(k^i r)-\frac{N^{1/2}}{4\pi i}\sum_{n=2}^{3} f_{n,1}(r)R_{n,1}(r)\ . \tag{50}$$

Substituting these in the expressions for $\beta(E^i)\alpha_s(E^i)$ and $\beta(E^i)\alpha_p(E^i)$ obtained from Eqs. (A10)—(A12), and making use of Eqs. (46) and (48), we find that $\beta(E^i)\alpha_p(E^i)$ and $\beta(E^i)\alpha_s(E^i)$ can be parametrized as $\beta\alpha'_p j_1(k^i R_{\rm MT})$ and $\beta\alpha'_s[j_0(k^i R_{\rm MT})+\beta_s]$, respectively. Substituting Eq. (50) in Eq. (A9) for $\xi_p(E^i)$, we find that the $\vec{k}^{\,i}$ dependence drops out, and so $\xi_p(E^i)$ becomes simply ξ_p.

Finally, we shall neglect the $\vec{k}_j$ dependence of the b_j [Eqs. (42) and (43)], and define parameters $\alpha_s=b_j\alpha'_s(4\pi/V)^{1/2}$ and $\alpha_p=3b_j\alpha'_p/\sqrt{V}$. Collecting these results and dropping an overall constant β, we have for the P vector

$$\vec{P}^{i\,\pm}_{\vec{G}_s}=[A^i_{xz}+\alpha_p j_1(k^i R_{\rm MT})A^i_x]\hat{x}+[A^i_{yz}+\alpha_p j_1(k^i R_{\rm MT})A^i_y]\hat{y}$$
$$+\{\xi_d A^i_{3z^2-r^2}+\alpha_p j_1(k^i R_{\rm MT})\xi_p A^i_z+\alpha_s[j_0(k^i R_{\rm MT})+\beta_s]A^i_{0,0}\}\hat{z}\ , \tag{51}$$

where

$$A^i_{0,0}=\sum_{j=1}^{4} C^i_{j+5}\ , \tag{52a}$$

$$A^i_{x(y,z)}=\sum_{j=1}^{4} C^i_{j+5}Y_{x(y,z)}(\vec{k}_j)\ , \tag{52b}$$

$$A^i_{3z^2-r^2(xz,yz)}=C^i_{3z^2-r^2(xz,yz)}\ . \tag{52c}$$

Reiterating, the RHS of Eq. (51) is understood to be written with respect to a coordinate system in which the z axis points in the direction $\vec{K}^{\,\pm}(E,\vec{k}_s+\vec{G}_s)$.

VI. CONCLUDING REMARKS

In summary, we have developed a parametrized scheme for calculating ARP spectra from the fcc d-band metals, based on a one-step model of the photoemission process. Our starting point, Eq. (2), is similar to a result suggested by Feibelman and Eastman[13] for the photocurrent in a one-step model when electron damping in the final state and dielectric screening of the incident electric field are not neglected. However, we do not retain their assumption that the final state is equal to a LEED state (or the complex conjugate of a LEED state), as this result can be justified only in the limit of zero damping. Our final-state model implicitly accounts for the presence of a surface and consists of a linear combination of incoming and outgoing OPW's with amplitudes which decay exponentially into the bulk. For an electron in an initial state for which $\vec{k}$ conservation effects allow coupling to a single OPW, the total probability of excitation, transport to the surface, and escape into vacuum is determined by a single quantity, the OPW amplitude $f^{\pm}_{\hat{R},E}(\vec{G}_s,z)$ [Eq. (15)]. Equation (15) is compatible with a three-step model only when the emission direction $\hat{R}$ and energy E are such that (a) corresponding to each nonvanishing $f^{-}_{\hat{R},E}(\vec{G}_s,z)$ there is a bulk state given to a good approximation by $|\,\mathrm{OPW}[\vec{K}^{\,-}(E,\vec{k}_s+\vec{G}_s)]\rangle$, (b) the amplitudes $f^{+}_{\hat{R},E}(\vec{G}_s,z)$ of the incoming OPW's vanish, and (c) the momentum broadening caused by the decay of the final state is unimportant. The energy—versus—OPW-wave-vector relationship [Eq. (16)] is assumed to be free-electron-like with respect to an effective energy zero defined by an inner potential which is treated as a function of $\hat{R}$ and E. A z-independent expression for the screened electric field within the solid is adopted [Eq. (17)]. The initial states are taken to be the bulk Bloch states of the infinite crystal, and our resulting expression for the optical matrix elements is given in Eqs. (29) and (30) in terms of a P vector

which contains the dependence of the matrix element on the initial- and final-state wave functions within a muffin-tin sphere. A parametrized procedure for evaluating the P vector is derived, in part by assuming that the initial states are computed with a combined interpolation scheme, and the results are summarized in Eqs. (51) and (52).

In addition to the improved model for the final state, refinements of the present scheme over that of Shevchik and Liebowitz[12] are the inclusion of refraction effects for the incident electric field, a more accurate result for the momentum broadening in $k_\perp$ in the optical matrix element, and a more accurate procedure for computing cross sections from the s-p component of the initial states.

Finally, we emphasize that the adoption of a parametrized model for the final-state wave function is not merely a matter of computational convenience but deals with both the inadequacies of single OPW, single APW, or bulk final states, and the failure of the LEED-type calculations to achieve a level of agreement that is commensurate with their complexity, presumably because of the difficulty of accurately incorporating the effects of the electron-electron interaction. In practice, the final-state parameters can be chosen so as to optimize the agreement between calculated and experimental spectra. Any remaining discrepancies can then be taken to reflect the minimum possible errors in the assumed initial-state band structure. This procedure cannot provide an absolute determination of band positions, due to the inherent uncertainty in the values arrived at for the final-state parameters. However, it frequently happens (see II) that there are discrepancies between experimental and calculated spectra for a given set of final-state parameters which can only be reasonably attributed to inaccurate values for these parameters. Adjusting them so as to remove such discrepancies results in a more accurate final state and hence a more reliable interpretation of the experimental spectrum in terms of the initial-state band structure.

ACKNOWLEDGMENTS

I wish to gratefully acknowledge the support and guidance of Franco Jona while this work was carried out, and many invaluable discussions with P. B. Allen and J. W. Davenport. This work was supported in part by the National Science Foundation.

APPENDIX

To define the quantities $\xi_d(E,E^i)$, $\xi_p(E,E^i)$, $\alpha_p(E,E^i)$, $\alpha_s(E,E^i)$, and $\beta_s(E,E^i)$, we first define the energy-dependent integrals over a muffin-tin sphere, $\zeta^{l,l+1}(E,E^i)$ and $\zeta^{l,l-1}(E,E^i)$, as follows:

$$\zeta^{l,l+1}(E,E^i)=\frac{1}{l+1}\int_{r<R_{\mathrm{MT}}} d^3r\, S_l(r,E)Y_{l,0}(\Omega) \times\left[\frac{\partial}{\partial z}V_{\mathrm{MTS}}(r)\right] \times R_{l+1}(r,E^i)Y_{l+1,0}(\Omega)\ , \tag{A1}$$

$$\zeta^{l,l-1}(E,E^i)=\frac{1}{l}\int_{r<R_{\mathrm{MT}}} d^3r\, S_l(r,E)Y_{l,0}(\Omega) \times\left[\frac{\partial}{\partial z}V_{\mathrm{MTS}}(r)\right] \times R_{l-1}(r,E^i)Y_{l-1,0}(\Omega)\ . \tag{A2}$$

Next we define the quantities $F_{l,l\pm1}(E,E^i)$:

$$F_{p,d}(E,E^i)=2\sqrt{(\pi/5)}iA_{1,0}\zeta^{p,d}(E,E^i)\ , \tag{A3}$$

$$F_{f,d}(E,E^i)=2\sqrt{(\pi/5)}iA_{3,0}\zeta^{f,d}(E,E^i)\ , \tag{A4}$$

$$F_{s,p}(E,E^i)=2\sqrt{(\pi/3)}iA_{0,0}\zeta^{s,p}(E,E^i)\ , \tag{A5}$$

$$F_{d,p}(E,E^i)=2\sqrt{(\pi/3)}iA_{2,0}\zeta^{d,p}(E,E^i)\ , \tag{A6}$$

$$F_{p,s}(E,E^i)=-iA_{1,0}\zeta^{p,s}(E,E^i)\ . \tag{A7}$$

The quantities in question are then given by

$$\xi_d(E,E^i)=\frac{(2\sqrt{3}/3)F_{p,d}(E,E^i)-\sqrt{3}F_{f,d}(E,E^i)}{F_{p,d}(E,E^i)+F_{f,d}(E,E^i)}\ , \tag{A8}$$

$$\xi_p(E,E^i)=\frac{F_{s,p}(E,E^i)-2F_{d,p}(E,E^i)}{F_{s,p}(E,E^i)+F_{d,p}(E,E^i)}\ , \tag{A9}$$

$$\alpha_p(E,E^i)=\frac{F_{s,p}(E,E^i)+F_{d,p}(E,E^i)}{F_{p,d}(E,E^i)+F_{f,d}(E,E^i)}\ , \tag{A10}$$

$$\alpha_s(E,E^i)=\frac{F_{p,s}(E,E^i)}{F_{p,d}(E,E^i)+F_{f,d}(E,E^i)}\ , \tag{A11}$$

$$\beta(E,E^i)=F_{p,d}(E,E^i)+F_{f,d}(E,E^i)\ . \tag{A12}$$

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[1]L. F. Wagner, Z. Hussain, and C. S. Fadley, Solid State Commun. 21, 257 (1977).
[2]Z. Hussain, S. Kono, L.-G. Petersson, C. S. Fadley, and L F. Wagner, Phys. Rev. B 23, 724 (1981).
[3]D. Liebowitz, M. Sagurton, J. Colbert, and N. J. Shevchik, Phys. Rev. Lett. 39, 1625 (1977).
[4]M. Sagurton and N. J. Shevchik, Phys. Rev. B 17, 3859 (1978).
[5]D. Liebowitz and N. J. Shevchik, Phys. Rev. B 18, 1630 (1978).
[6]N. V. Smith, R. L. Benbow, and Z. Hurych, Phys. Rev. B 21, 4331 (1980).

[7]S. Holloway, D. E. Grider, and J. K. Sass, Solid State Commun. **39**, 953 (1981).
[8]J. B. Pendry and D. J. Titterington, Commun. Phys. **2**, 31 (1977).
[9]J. B. Pendry and J. F. L. Hopkinson, J. Phys. F **8**, 1009 (1978).
[10]D. W. Jepsen, Phys. Rev. B **20**, 402 (1979).
[11]P. O. Nilsson, J. Kanski, and C. G. Larsson, Solid State Commun. **36**, 111 (1980).
[12]N. J. Shevchik and D. Liebowitz, Phys. Rev. B **18**, 1618 (1978).
[13]P. J. Feibelman and D. E. Eastman, Phys. Rev. B **10**, 4932 (1974).
[14]C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1030 (1964); **136**, A1044 (1964).
[15]N. V. Smith and L. F. Mattheiss, Phys. Rev. B **9**, 1341 (1974).
[16]G. D. Mahan, Phys. Rev. B **2**, 4334 (1970).
[17]J. G. Endriz, Phys. Rev. B **7**, 3464 (1973).
[18]P. J. Feibelman, Phys. Rev. Lett. **34**, 1092 (1975); Phys. Rev. B **12**, 1319 (1975).
[19]K. L. Kliewer, Phys. Rev. Lett. **33**, 900 (1974); Phys. Rev. B **14**, 1412 (1976); **15**, 3759 (1977).
[20]H. J. Levinson, E. W. Plummer, and P. J. Feibelman, Phys. Rev. Lett. **43**, 952 (1979).
[21]H. J. Levinson and E. W. Plummer, Phys. Rev. B **24**, 628 (1981).
[22]P. J. Feibelman, Surf. Sci. **46**, 558 (1974).
[23]E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1970), p. 63.
[24]L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. **152**, 505 (1966).
[25]F. M. Mueller, Phys. Rev. **153**, 659 (1967).