

ANGULAR DEPENDENCE OF PHOTOEMISSION IN METALS*

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The angular dependence of the external photoemission is calculated for a free-electron-like metal. Numerical examples are given for sodium. Electrons which leave the solid without scattering have a very anisotropic spatial distribution: The intensity $dI/d\Omega$ has discontinuities caused by the sharpness of the Fermi surface. These distributions can be used to determine the band structure of the metal.

In this Letter we show that a measurement of the angular dependence of photoemitted electrons provides a new method of determining the band structure of metals.¹ Electrons which are excited by a band-to-band transition in the metal, and then leave the solid without any scattering, are emitted with a highly anisotropic angular dependence. A calculation is presented for metallic sodium. In this case the unscattered electrons come out with finite intensity in some directions and have no emission in other directions, and the intensity changes discontinuously as a function of angle in going between allowed and forbidden directions of emission. As experimentalists claim to see unscattered electrons,^{2,3} this angular anisotropy should be a spectacular and easily observable effect. It also will provide a means of distinguishing between the surface effect and the volume effect,⁴ since electrons emitted by the surface effect do not show sharp angular anisotropy.

Let us first see what happens to the volume photoemission in a free-electron metal like sodium. Inside the solid, in an extended zone scheme, the interband transition changes the electron wave vector from $\vec{K}-\vec{G}$ to \vec{K} , where \vec{G} is a reciprocal lattice vector. Energy conservation requires $K^2/2m = (2m)^{-1}(\vec{K}-\vec{G})^2 + \hbar\omega$. After solving for \vec{K} , the final energy of the electrons is

$$E = K^2/2m = \Lambda^2/4E_G \cos^2\theta_0,$$

$$E_G = G^2/2m, \quad \Lambda = \omega + E_G.$$

So electrons of a given energy have a conical distribution, where the cone is centered about the direction \vec{G} . The electron's energy increases as its angular direction θ_0 deviates from \vec{G} . Similarly, the angular intensity is $dI/d\Omega \sim E/\cos\theta_0 \sim \cos^{-3}\theta_0$, which also increases with angle. The internal intensity increases up to its maximum value, determined by $E < E_F + \omega$ or $\cos^2\theta_0 > \Lambda^2/4E_G(E_F + \omega)$, and then drops discontinuously to zero. This discontinuity is a consequence of the

sharp Fermi surface.

The external photoemission is obtained by determining how these cones (one for each \vec{G}) of electrons are projected outward through the surface. Let E and $\vec{P} = (p_z, \vec{p}_\parallel)$ be the energy and wave vector outside the crystal, where $p_z = (2mE)^{1/2} \times \cos\theta$, $p_\parallel = (2mE)^{1/2} \sin\theta$, and θ is the angle at which one is measuring. Let $\vec{K}-\vec{G}$ and $\vec{K} = (k_z, \vec{k}_\parallel)$ be the wave vectors inside the solid before and after the interband optical transition. If the bottom of the conduction band is V_0 below the vacuum, then $\vec{k}_\parallel = \vec{p}_\parallel$, $k_z^2 = p_z^2 + 2mV_0$, and energy conservation is

$$E = \omega - V_0 + (\vec{K}-\vec{G})^2/2m.$$

Solving this equation for E gives

$$E = \epsilon(\theta, \varphi) = \frac{1}{4}\Lambda^2[E_z^{1/2}(\cos^2\theta - 4V_0D/\Lambda^2)^{1/2} - E_\parallel^{1/2}\sin\theta\cos\varphi]^2/D^2,$$

$$D = E_z \cos^2\theta - E_\parallel \sin^2\theta \cos^2\varphi, \quad (1)$$

where φ is the angle between \vec{G}_\parallel and \vec{p}_\parallel , $E_z = G_z^2/2m$, and $E_\parallel = G_\parallel^2/2m$. This important result shows that for a given value of ω and G , then in any given direction (θ, φ) electrons come out at one energy. In sodium, at experimental frequencies, the lobes of electrons coming from different directions of \vec{G} do not seem to overlap. Furthermore, the maximum value of E is $E_{\max} = E_F + \omega - V_0$. Threshold conditions for ω have been given by Fan.⁵

In order to calculate the intensity of photoemitted electrons, we must learn how to evaluate the electron's Green's function

$$G_0(\vec{r}, \vec{r}') = \sum_\lambda \frac{\phi_\lambda^*(\vec{r})\phi_\lambda(\vec{r}')}{E_\lambda - E - i\delta},$$

where the wave functions $\phi_\lambda(\vec{r})$ are plane waves outside of the solid and Bloch functions inside. For the case that \vec{r}' is outside the crystal and going to minus infinity, while \vec{r} is in or about the crystal, then the Green's function for a fixed val-

ue of wave vector parallel to the surface \vec{p}_{\parallel} is⁶

$$G_0(\vec{r}, \vec{r}') = (im/p_z) e^{-i(p_z Z' + \vec{p}_{\parallel} \cdot \vec{r}')} \phi^>(p_z, \vec{p}_{\parallel}, r),$$

$$p_z = (2mE - p_{\parallel}^2)^{1/2}.$$

The ingoing wave function $\phi^>$ has the following form^{6,7}: Outside the solid it has a term representing a wave $\exp(ip_z Z + i\vec{p}_{\parallel} \cdot \vec{r})$ approaching the surface and other terms representing the reflected waves; inside the crystal it has the transmitted Bloch waves. The amplitudes of the reflected and transmitted waves may be calculated as Pendry has done for low-energy electron diffraction.⁷ Now imagine that the experiments measure the current at a distance R from the sample, where R is very large compared with the dimensions of the sample. The asymptotic form of the electron's wave function, for the unscattered electrons, is

$$\psi(R) = \frac{m}{2\pi R} e^{iPR} \int d^3r \phi^>(p_z, \vec{p}_{\parallel}, \vec{r}) \left(\frac{eA}{mc} \hat{\epsilon} \cdot \nabla \right) \phi_i(r),$$

$$\vec{P} = (p_z, \vec{p}_{\parallel}),$$

$$\vec{P}^2 = 2m(E_i + \omega), \quad (2)$$

where E_i and ϕ_i are the energy and wave function of the electron in the initial state. The current per unit solid angle is obtained by summing over the initial states:

$$\frac{dI}{d\Omega} = \frac{2e}{m} \int \frac{d^3k_i}{(2\pi)^3} \text{Im} \{ R \psi^*(R) \vec{R} \cdot \nabla_R \psi(R) \},$$

$$= \frac{2e}{m} \left(\frac{eA}{2\pi c} \right)^2 \int \frac{d^3k_i}{(2\pi)^3} P \left| \int d^3r \phi^>\hat{\epsilon} \cdot \nabla \phi_i \right|^2. \quad (3)$$

The properties of the scattered electrons may also be calculated using this formalism. In this case one replaces the $\vec{p} \cdot \vec{A}$ interaction in (2) by a T matrix. Only included in the T matrix are terms which have the $\vec{p} \cdot \vec{A}$ interaction acting once, but other interactions (electron-electron, etc.) may be included as many times as desired.

We follow Adawi⁶ and replace $\hat{\epsilon} \cdot \nabla$ by $i\hat{\epsilon} \cdot \nabla V(\vec{r})/\omega$. For a steplike boundary at the surface, this has the form

$$\hat{\epsilon} \cdot \nabla [-V_0 \theta(Z) + \sum_{R_j} v(\vec{r} - \vec{R}_j)]$$

$$= -\hat{\epsilon} \cdot \hat{Z} V_0 \delta(z) + \sum_j \hat{\epsilon} \cdot \nabla v(\vec{r} - \vec{R}_j). \quad (4)$$

The term $\hat{\epsilon} \cdot \hat{Z} V_0 \delta(z)$ provides the matrix element for the surface effect in the usual way, while the other terms contribute to the volume effect. The angular dependence $dI/d\Omega$ of the surface effect has been evaluated for the usual model of a free-electron-gas-like solid, and the results are a smooth distribution. This is to be expected when

all possible initial states are connected to all possible final states which have the same value of \vec{p}_{\parallel} .

In order to calculate approximately the intensity for the volume effect, take $\phi^> = T(p_z, k_z) \times \exp(ik_z Z + i\vec{k}_{\parallel} \cdot \vec{r})$ inside the solid. The matrix element is⁸

$$\int d^3r \phi^> i\hat{\epsilon} \cdot \nabla V(\vec{r}) \phi_i = \mathcal{V} \sum_{\vec{G}} \delta_{\vec{k} - \vec{G} - \vec{k}_i} \hat{\epsilon} \cdot \vec{G} V_G, \quad (5)$$

where \mathcal{V} is the volume of the solid and V_G is the ion potential. The external current is

$$\frac{dI}{d\Omega} = \frac{e\alpha F l}{\pi(\hbar\omega)^3} \sum_G \frac{(\hat{\epsilon} \cdot \vec{G})^2}{G} V_G^2 J_G^>(\theta, \varphi),$$

$$J_G^>(\theta, \varphi)$$

$$= (G/2m) \int d^3k_i \delta(\vec{k} - \vec{G} - \vec{k}_i) P |T(p_z, k_z)|^2, \quad (6)$$

where $\alpha = e^2/\hbar c$, F (photons/sec) is the photon flux density multiplied by the area of the sample, and l is the depth over which electrons can escape. The delta function eliminates the d^3k_i integral, although in doing this step keep in mind that K depends upon k_i since $E = \omega + k_i^2/2m - V_0$ at this stage in the calculation. We get

$$J_G(\theta, \varphi) = \epsilon(\theta, \varphi) |T(p_z, k_z)|^2 / \cos\theta',$$

$$\cos\theta' = (p_z G_z \cos\theta + k_z G_{\parallel} \sin\theta \cos\varphi) / G k_z,$$

$$p_z^2 = k_z^2 - 2mV_0 = 2mE \cos^2\theta.$$

Numerical calculations of the external angular distributions for a (100) face of sodium are given in Fig. 1 for $\omega = 5.0$ eV and $\omega = 10.0$ eV. At these energies, one need only consider the twelve reciprocal lattice vectors of the type $G = 2\pi/a$ (110). Of these, neither the four which point into the solid nor the four which point in the plane of the surface contribute to external photoemission. Photoemission is caused by the four which point out of the solid, e.g., $2\pi(0, \pm 1, -1)/a$ and $2\pi(\pm 1, 0, -1)/a$. Each of these four give a lobe of external electrons of the type shown in Fig. 1. In the figure, φ is measured from the direction of \vec{G}_{\parallel} , and θ from the normal to the plane. The solid lines are the contours of constant energy, given in units of eV; the dashed lines are contours of constant intensity, where we have plotted values of J_G which also have the units of eV. Note that the intensity is zero outside of the region of the contour lines, so that there is a discontinuous change of intensity in crossing the contour line of maximum energy E_{max} .

These are just the contours of the unscattered electrons. In an actual experiment, electrons will come out in all directions because of the sur-

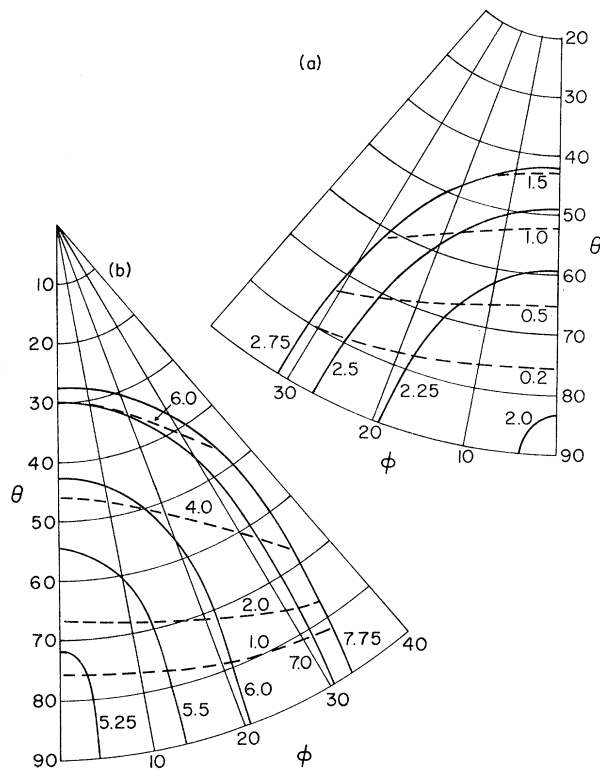


FIG. 1. The angular distribution of external electrons for a (100) face of a free-electronlike bcc metal. The parameters are appropriate to sodium: $E_F = 3.16$ eV, $E_G = 16.40$ eV, $V_0 = 5.41$ eV. Part (a) has $\omega = 5.0$ eV and $E_{\max} = 2.75$ eV; part (b) has $\omega = 10.0$ eV and $E_{\max} = 7.75$ eV. The solid lines are contours of constant energy, the dashed lines are contours of constant intensity. $\theta = 0$ is the normal to the surface, $\phi = 0$ is in the direction of \vec{G}_{11} , and the results are symmetric in ϕ so only half a distribution is shown in each case.

face effect, and also because of the scattering of electrons coming from the bulk. These contributions should be a smooth background, upon which should be superimposed this discontinuous distribution of the unscattered electrons.

Sodium is such a free-electron metal that the energy contours probably closely follow those shown in Fig. 1, or given by (1). But our calculation of the intensity factor J_G is probably too crude to be realistic. The step barrier $T^2 = 4p_z^2 \times (p_z + k_z)^{-2}$ we used can certainly be improved upon; the distance l is energy and perhaps wave-vector dependent, etc. Improvements in this re-

spect will change J_G , but do not alter our conclusions about the discontinuities in intensities, nor affect the shape of the energy contours. These calculations were presented as a simple example.

In most metals, one would expect the observed energy contours to deviate from the free-electron predictions of (1). These deviations are caused by the crystalline potential, and thereby serve as a means of determining this potential. One method of determining the pseudopotential parameters V_G from the energy contours is to assume a value of V_G , calculate the expected external energy contours, and then vary V_G until a best fit with the data is obtained. Other methods of fitting are possible, and one of these will be discussed in a longer article where more of the details of the present work are given.

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⁸Discerning readers will notice that Eq. (5) is wrong. Because the sum in (4) only extends over the half-space $Z_j > 0$, then the integral in (5) does not give wave vector conservation in the Z direction. If one does the calculation properly—standing waves for φ_j , evaluate the sum in the half space, and then square the matrix element—one gets (6). This differs by a factor of $\frac{1}{2}$ from what one would get using (5).