Surface Friedel oscillations and photoemission from simple metals

A. W. Overhauser

Department of Physics, Purdue University, West Lafayette, Indiana 47907

(Received 12 November 1985)

The question whether (or not) electronic potentials caused by surface Friedel oscillations can lead to a leveling off of $E(k)$ near the Fermi surface is investigated. Just the opposite behavior is found: $E(k)$ becomes *steeper* at k_F. It follows that narrow photoemission peaks recently observed in Na and K (from initial states near E_F) cannot be attributed to Friedel oscillations.

The recent discovery[1] of *sharp* photoemission peaks from (110) surfaces of Na and K leads naturally to a discussion of possible explanations. Surface states and resonances appear to have been ruled out,[1] whereas electronic excitations in the bulk, originating (in k space) near the energy gaps of a charge-density wave (CDW), do explain the data.[2] The crucial consequence of a CDW potential,

$$V(\mathbf{r}) = 2\alpha \cos(Qz) \quad , \tag{1}$$

having $\mathbf{Q}$ along $\hat{z}$ and normal to the metal surface, are strong wave-function mixing ($\mathbf{k} \rightleftharpoons \mathbf{k} \pm \mathbf{Q}$) and *severe* flattening of $E(k_z)$ near the Fermi energy E_F. It has been suggested that surface Friedel (SF) oscillations might lead to similar consequences.[1] Such a possibility is investigated here.

Consider an ideal metal slab of (small) thickness L, but macroscopic in the $\hat{x}$ and $\hat{y}$ directions. Let the boundary conditions be $\psi = 0$ at $z = 0$ and L. The conduction-electron wave functions are then

$$\psi_k = e^{i(k_x x + k_y y)} \sin(k_z z) \quad , \tag{2}$$

where the allowed values of k_z are

$$k_z = s\pi/L \quad , \tag{3}$$

with $s = 1, 2, 3$, etc. The wave functions (2) are normalized if we take the volume of the sample to be 2 cm^3. (ψ_k satisfies periodic boundary conditions along $\hat{x}$ and $\hat{y}$.) The total electron density $n(z)$ is then

$$n(z) = 2 \sum_k \sin^2(k_z z) \quad . \tag{4}$$

The occupied $\mathbf{k}$'s satisfy $\hbar^2 k^2/2m \leq E_F$ as well as Eq. (3). (The factor 2 is the spin degeneracy.) The sum is easily converted to an integral:

$$n(z) = \pi^{-2} \int_0^{k_F} (k_F^2 - k_z^2) \sin^2(k_z z) dk_z \quad . \tag{5}$$

With $q = 2k_z$, this expression becomes

$$n(z) = n_0 - (4\pi)^{-2} \int_0^{2k_F} [(2k_F)^2 - q^2] \cos(qz) dq \quad , \tag{6}$$

where n_0 $(= k_F^3/3\pi^2)$ is the mean electron density. Equation (6) is an important intermediate result because the coefficient of $\cos(qz)$,

$$P_{SF}(q) = (4\pi)^{-2}[(2k_F)^2 - q^2] \quad , \tag{7}$$

is the Fourier spectrum of the resulting oscillation $(0 < q < 2k_F)$. Equation (6) is easily evaluated.

$$n = n_0[1 - 3u^{-3}(\sin u - u \cos u)] \quad , \tag{8}$$

where $u = 2k_F z$. This result, which *is* the surface Friedel oscillation, is shown in Fig. 1. The wave vector of the oscillation is $2k_F$, but its amplitude versus z falls off asymptotically as $1/z^2$.

The Fourier spectrum $P_{SF}(q)$ of the surface Friedel oscillation is shown in Fig. 2. Also shown is the Fourier spectrum

$$P_{CDW}(\mathbf{q}) = a\delta(\mathbf{q} - \mathbf{Q}) \quad , \tag{9}$$

for a CDW state. (It is a Dirac δ function centered at $\mathbf{Q}$.) The magnitude of the CDW wave vector is[3]

$$Q \approx 2k_F(1 + \alpha/2E_F) \quad , \tag{10}$$

where 2α is the amplitude of the CDW potential, Eq. (1). It must be emphasized that the two spectra shown in Fig. 2 are qualitatively quite different. The surface Friedel oscillation has a continuous spectrum which goes to 0 at $q = 2k_F$. (There is no Fourier strength at all at the end point $2k_F$.) In contrast, all of the Fourier strength of the CDW oscillation is concentrated at $\mathbf{q} = \mathbf{Q}$. It would be surprising indeed if the two phenomena were to have similar consequences in photoemission.

It should be appreciated that the surface Friedel oscillation is a kinematic effect of the boundary condition on the electronic wave functions. Perturbation of the electronic energy, $E(k) = \hbar^2 k^2/2m$, has still to be considered. The Coulomb interactions (between electrons) will try to suppress the oscillation because of their repulsive character.
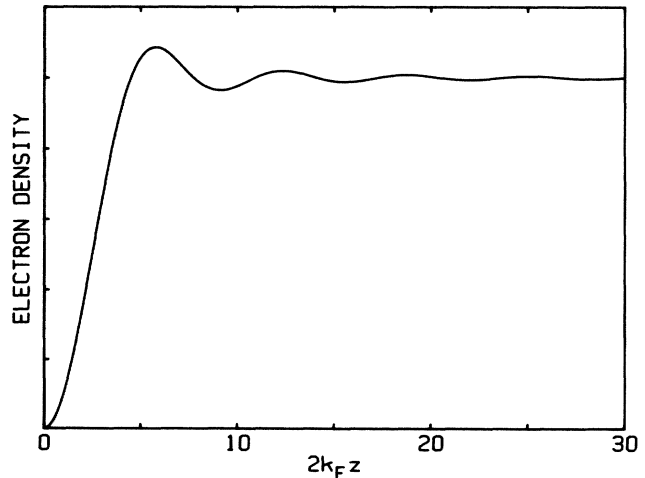

FIG. 1. Electron density vs distance z from a metal surface.
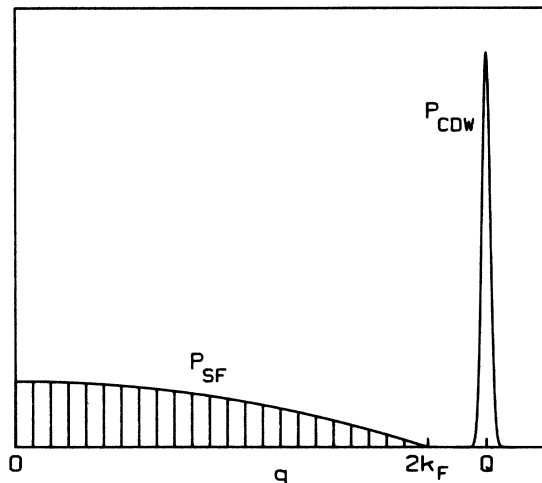
FIG. 2. Fourier spectrum of the electron-density modulation for a surface Friedel oscillation and for a CDW.

However, readjustment of the positive-ion positions will tend to cancel any electrostatic field. For simplicity the positive-ion background will be taken to be perfectly deformable, so the electrostatic field can be identically zero. What remains as a source of dynamic response is the exchange (and correlation) potential which, in the local-density approximation, is[4]

$$V_x(z) = - \frac{3e^2 k_F}{2\pi} \left[1 + \frac{\Delta n(z)}{n_0} \right]^{1/3} . \tag{11}$$

(The correlation contribution has been dropped since it is typically only a 10% correction.)

Since $V_x(z)$ is negative, it will enhance the oscillation of $\Delta n(z)$. Consideration of this enhancement will be postponed until after the influence of $V_x(z)$ on the electronic energy $E(\mathbf{k})$ is calculated. There are two contributions. The first-order correction is the expectation value of the oscillatory part, H', of Eq. (11),

$$H' \approx - \frac{e^2 k_F \Delta n(z)}{2\pi n_0} , \tag{12}$$

with the wave functions given by Eq. (2), which are normalized in 2 cm^3.

$$\Delta E_1(k_z) = - \frac{e^2 k_F}{\pi n_0 L} \int_0^L \sin^2(k_z z) \Delta n(z) dz . \tag{13}$$

(The integrals over dx and dy yield $2/L$.) Only the (discrete) Fourier component of $\Delta N(z)$ having $q = 2k_z$ contributes to (13).

$$(\Delta n)_q = - \frac{(k_F^2 - k_z^2)}{2\pi L} \cos(qz) . \tag{14}$$

The integration of (13) then leads to

$$\Delta E_1(k_z) = - \frac{3e^2}{8L} \left[1 - \left[\frac{k_z}{k_F} \right]^2 \right] . \tag{15}$$

Because the Fourier spectrum $P_{SF}(q)$ is (quasi)continuous, the second-order contribution to $E(\mathbf{k})$

can be calculated by perturbation theory.

$$\Delta E_2(k_z) = \sum_q \left[\frac{m_q^2}{E(k_z) - E(k_z + q)} + \frac{m_q^2}{E(k_z) - E(k_z - q)} \right] . \tag{16}$$

From Eq. (3) the allowed q's are $2\pi s/L$. The matrix elements are those of H', which from Eqs. (2), (12), and (14) are

$$m_q = \frac{3e^2}{8L} \left[1 - \left[\frac{q}{2k_F} \right]^2 \right] . \tag{17}$$

The (one-dimensional) sum in Eq. (16) can be converted to an integral $(0 < q < 2k_F)$ in the usual way and evaluated. Accordingly, with $v = k_z / k_F$,

$$\Delta E_2(k_z) = \left[\frac{me^2}{\pi \hbar^2 k_F} \right] \frac{3e^2}{8L} F(v) , \tag{18}$$

where

$$F(v) = \frac{5}{8} - \frac{3}{8} v^2 + \frac{3(1-v^2)^2}{16v} \ln \left| \frac{1+v}{1-v} \right| . \tag{19}$$

$F(0) = 1$, and F decreases monotonically to $\frac{1}{4}$ at $k_z = k_F$.

The sum of (15) and (18) is shown in Fig. 3 for the case of a Na film having thickness $L = 5000$ Å. Not only is the total change in $E(k_z)$ exceedingly small, ~ 0.5 meV, but the sign of the effect leads to an *increase* in the slope at E_F. It is clear from this result that any enhancement of the Friedel oscillations (as a consequence of many-body effects) should not be expected to result in flattening of $E(k_z)$, as needed to explain the photoemission anomalies observed in Na and K. The impotence of surface Friedel oscillations in influencing $E(k_z)$ stems from the feature (emphasized previously) that the Fourier spectrum of the oscillation is a continuum and, moreover, provides no component at or above $q = 2k_F$ on which to "build."

It seems appropriate to emphasize the remarkable sharpness of the observed anomaly (which arises from states near E_F). The energy width, from the published data, is ~ 0.35
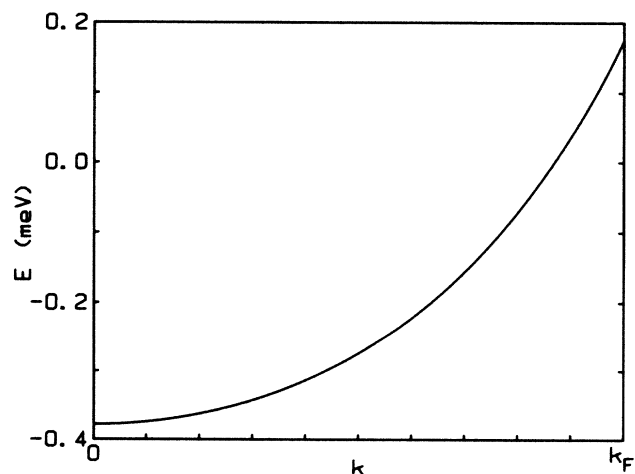

FIG. 3. Energy shift $E(k_z)$ vs k_z caused by a surface Friedel oscillation in a Na film of thickness 5000 Å. ($\hat{z}$ is the surface normal.)

eV. However, the experimental energy resolution was about 0.3 eV. Any reasonable deconvolution leads to an intrinsic width of ~ 0.15 eV (or less). This value is ~ 15 times smaller than the observed (and expected) widths for photoelectrons arising from the free-electron part of the spectrum. Such a characteristic (together with a large photoemission intensity at photon energies where no emission at all is expected) is consistent with the band bending and wave-function mixing of a CDW broken symmetry.[2] The sharpness is caused by the very small slope, dE/dk_z, of occupied states near the CDW energy gap.

[1]E. Jensen and E. W. Plummer, Phys. Rev. Lett. 55, 1912 (1985).

[2]A. W. Overhauser, Phys. Rev. Lett. 55, 1916 (1985).

[3]A. W. Overhauser, Phys. Rev. Lett. 13, 190 (1964).

[4]J. C. Slater, Phys. Rev. 81, 383 (1951).