Calculated Photoemission Spectra of Na

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We report a detailed calculation of the photoemission spectra of Na for electrons emitted normal to the (110) surface. The experimental results of Jensen and Plummer have been taken as an indication that the conduction band of Na is severely distorted and hence that a charge-density wave exists in the system. Our calculation confirms just the opposite, i.e., that the band is not strongly distorted from a free-electron band. The calculation is able to reproduce the experimental data closely; it also predicts an angle dependence of the spectra—a feature which needs to be examined experimentally.

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Photoemission is generally considered to be a simple process, in which one sends photons of a known frequency ($\hbar\omega$) towards a metal and measures the emitted electrons. By using energy conservation, one readily obtains the initial-state energy of the electron. Further analysis of the angle dependence of the spectrum can provide valuable information on the electronic band structure. However, in a recent study of the normal-emission spectrum from the Na (110) surface, Jensen and Plummer[1] (JP) found certain features which they were unable to explain. The band structure of Na is usually believed to be well represented by a nearly free-electron (NFE) band.[1] For such a band structure, one would expect that there is no photoemission from the Na (110) surface if $31.7 < \hbar\omega < 37.9$ eV. This gap is expected because vertical transitions at these photon energies would require initial states that lie above the Fermi level (see Fig. 1 of Ref. 1). JP actually found that, throughout this expected gap, there appears a stationary narrow peak that corresponds to initial states at the Fermi level. From this experimental result, they concluded that either the conduction band of Na is severely distorted from a NFE band, or there are important effects which have been neglected so far.

In this Letter, we report a calculation which follows closely a theory of angle-dependent photoemission by Mahan.[2] We find that, by properly including various surface and bulk effects as well as their interference terms, we can explain JP's result with a NFE band. Since this calculation is basically parameter free, its close agreement with the experiment therefore provides a strong argument that the band of Na is not strongly distorted from a NFE band. This assertion is in complete disagreement with that of Overhauser,[3] who regarded JP's findings as evidence that the band is severely distorted and hence that a charge-density wave exists in the system.

According to Mahan's theory,[2] we calculate the emitted current per solid angle per energy, $d^2I/d\Omega\, dE$. For normal emission, momentum that is parallel to the surface vanishes. As a result, Mahan's theory reduces to a simple one-dimensional integration ($k_{i\parallel}=0$ and $k_i = k_{i\perp}$):

$$\frac{d^2I}{d\Omega\, dE} = \frac{em}{2\pi^2}\int_{\text{occ.}} \frac{dk_i}{2\pi}\, p\,|M(p,k_i)|^2 \delta(E-\epsilon(k_i)-\hbar\omega+V_0), \tag{1}$$

where $\epsilon(k_i)$ is the initial-state energy and $E=p^2/2m$ is the energy of the emitted electron measured externally. The delta function spells out the energy conservation of the process, and V_0 is the surface barrier which the photoelectron must overcome to reach the outside. The excitation matrix element, $M(p,k_i)$, is discussed below.

As is well known, photon fields do not interact with a homogeneous electron system.[4] In other words, photoemission may take place only as a result of inhomogeneities in the system. We take into account those effects from the surface potential $V_s(z)$, and from the crystal potential $V_c(z)=\sum_G V_G \exp(-iGz)$, where the G's are reciprocal lattice vectors. These inhomogeneous factors are included by the expression[2]

$$M(p,k_i) = F(\omega)\int dz\, \phi^{>}(p,z)\{(-\partial/\partial z)[V_s(z)+V_c(z)]\}\phi(k_i,z), \tag{2}$$

where the z axis is normal to the surface and $|F(\omega)|^2 \propto \omega^{-3}$. $\phi(k_i,z)$ is the initial-state wave function and $\phi^{>}(p,z)$ is an ingoing wave which contains a factor describing the scattering by the surface.

It is clear that the calculation of the spectrum now hinges on the determination of ϕ and $\phi^{>}$. As was noted by Mahan,[2] once the surface potential is given, both ϕ and $\phi^{>}$ can be determined by solution of a one-dimensional Schrödinger's equation. If we approximate the metal surface by a step potential, we can express results in analytic forms.[2] Such results are illustrative, but not accurate for real metals. This is because the mean free path (MFP) of electrons is short (4–6 Å)[5] and hence details of the surface potential are very important. We find that it is necessary to use a realistic potential to describe the surface and, meanwhile, to include decay mechanisms of electrons appropriately.

For simple metals like Na, the best available surface potential is given by Lang and Kohn's[6] calculation, in which the potential is determined self-consistently via the density-functional theory. We use their results for inputs and calculate $\phi(k_i,z)$ and $\phi^>(p,z)$ numerically. In this calculation, the effects of the lattice potential on the electronic states are neglected. Such an approximation is valid for Na since the effects are small: E.g., E_F is merely shifted by −0.06 eV.[2]

The wave functions obtained above need to be modified so that the finite MFP can be accounted for. For this purpose, we have evaluated[7] the MFP of electrons following a method due to Quinn.[8] The calculation includes the damping effect due to Coulomb scattering, and is treated within the random-phase approximation. For electrons of ∼ 30 eV, we find that the half-width is ∼ 3 eV and the MFP is ∼ 5 Å.

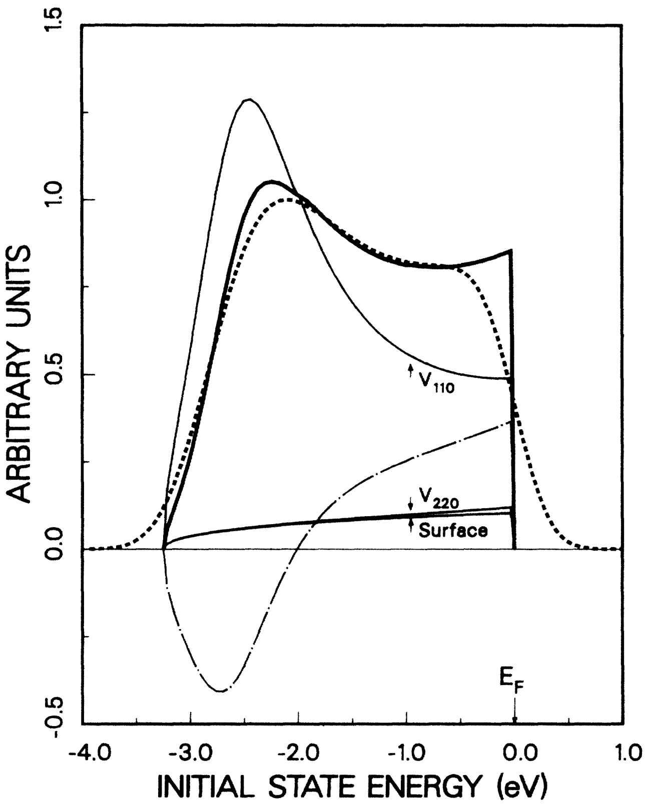

FIG. 1. The calculated spectrum at $\hbar\omega = 24$ eV is shown by the heavy solid curve. After the instrumental broadening effect is included, the result is shown by the dashed curve. The thin solid curves are diagonal terms from the effects as indicated. An interference term is plotted as the dash-dotted curve.

These values agree closely with measurements.[5] We include such Coulomb scattering effects by letting (if $z > 0$)

$$\phi^>(p,z) \to \phi^>(p,z)\exp[-z/2\lambda], \tag{3}$$

where we have assumed that the metal is in the $z > 0$ half-space, and λ is the calculated MFP. We neglect the broadening of initial states in our calculation. We do so because our primary concern here is the stationary peaks in the gap, and the corresponding initial states there are from the Fermi level and are therefore very sharp.

By now we have determined the wave functions ϕ and $\phi^>$. The remaining calculation of Eqs. (1) and (2) is numerically straightforward. In the calculation, we need to specify the crystal potential, and this is done by employment of Ashcroft's pseudopotential[9] for ions. The characteristic radius of Na is known ($r_c = 1.667$ a.u.),[9] and we thus get $V_{110} = 0.296$ eV and $V_{220} = 0.229$ eV. Our calculation only depends on two physical quantities: the electron density and r_c; the former ($r_s = 3.93$ a.u.) determines $V_s(z)$, ϕ and $\phi^>$, and the latter determines the crystal potential V_G.

Figures 1 and 2 demonstrate our calculated spectra at $\hbar\omega = 24$ and 33 eV, respectively; the latter energy lies in the "expected" gap. It should be emphasized that the interference term is very important in this cal-

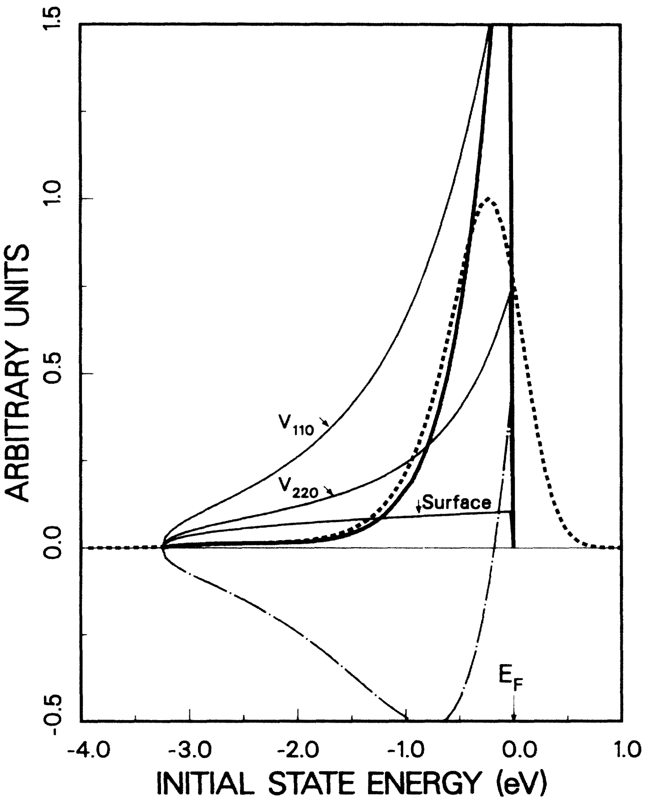

FIG. 2. Same as Fig. 1, but for $\hbar\omega = 33$ eV.

culation. The heavy solid curves are unbroadened spectra, which are then convoluted by a Gaussian of 0.3 eV in width to account for the reported instrumental broadening effect.[1] These results (dashed curves) show good overall agreement with JP's measurement, except on the low-energy side of the spectra, where the background contribution should be important but is not included in our calculation.

We shall examine the spectra in further detail, especially with regard to the peak width, the edge shape at E_F in Fig. 1, and the narrow peak in Fig. 2. A key feature is that the final states are very broad. As a result, both V_{110} and V_{220} can contribute.

First look at Fig. 1, where the major contribution is due to V_{110}. The observed peak width is determined by the final-state width times the ratio between the derivatives of the conduction band and of the final-state band—as has been discussed by JP[1] and Overhauser.[3] What has not been looked at is the fact that the sharp cutoff at E_F in the conduction band causes a similar structure in the spectrum, i.e., the edge at E_F in Fig. 1. The edge is thought[1] to be due to momentum-nonconserving processes, e.g., the surface effect. Such a view is consistent with our findings, since, with the electron states so broad, even transitions due to the bulk effects no longer strictly conserve the momentum. It should be noticed that the surface term alone would be too small to explain the observed edge structure.

We noticed that edge structure similar to that of Na is also found in the spectra of Al[10] and Mg.[11] The argument we made in the discussion of Fig. 1 clearly applies to these cases too. But there is no structure at E_F in the spectra of Be(001).[12] This result is explained by the fact that the Fermi level passes through a band gap,[12] i.e., there is no state around E_F to form the edge. These experimental findings, therefore, all support our explanation regarding the edge at E_F.

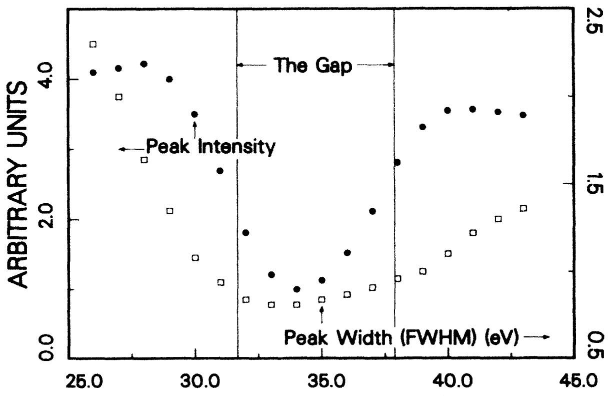

FIG. 3. The calculated peak intensities and the peak widths for photon energies in and around the gap. Both quantities decrease sharply inside the gap.

The composition of Fig. 2 is actually very similar to that of Fig. 1. The difference is that the two branches (V_{110} and V_{220}) almost have equivalent contributions now, and, more importantly, that the cutoff at the Fermi level causes a large portion of the peak to be erased in Fig. 2. One immediate consequence is that the "remaining" peak appears to have a width about one-half that of the $\hbar\omega = 24$ eV spectrum. This fact explains why the stationary peaks are very narrow.[1] Another effect is that the peak strength should decrease near $\hbar\omega \approx 33$ eV because much of the peak has been blocked. Figure 3 shows the calulated peak height and width. The two sets of data obviously vary in a correlated manner, as we have just explained. The calculated width matches with that from the measurement,[1] and the energy dependence of the peak strength has actually been observed.[13]

The reason that the peaks appear stationary across the gap is the fact that the Fermi level is very close to the band edge ($k = \frac{1}{2}G_{110}$). Such a band structure makes it possible that, as $\hbar\omega$ increases, the enhancement of the V_{220} term can compensate for the decrease of the V_{110} term. Accordingly, we can conclude that the band must satisfy

$$\tfrac{1}{2}G_{110} - k_F \lesssim \lambda^{-1}; \qquad (4)$$

otherwise, the peak will be diminishing in the gap region.

A study on the angle dependence of the peak intensity is shown in Fig. 4. This angle dependence varies a lot depending on whether the applied photon energy is

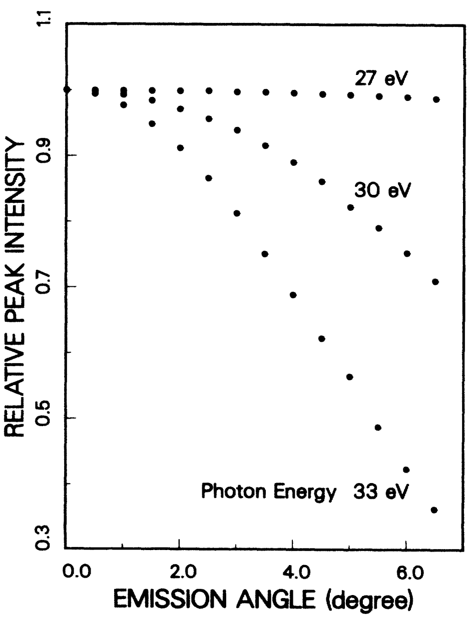

FIG. 4. The angle dependence of the spectrum intensity (the peak height) at three chosen energies. The angle is measured from the normal direction, and the instrumental broadening is included.

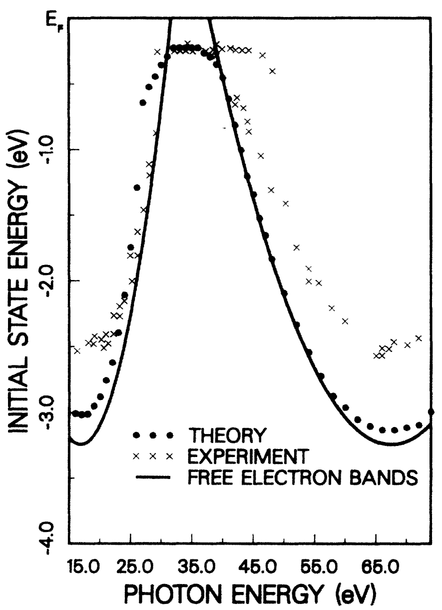

FIG. 5. Comparison of the calculated and the measured peak position as a function of the photon energy. Both sets of data contain the instrumental broadening effect.

in the gap or not. When $\hbar\omega = 33$ eV, the intensity decreases by 60% with a deviation of only 6° in the emission angle (θ). This result can be understood by our noticing that the electron in the initial state has a momentum of $(2mE)^{1/2}\sin(\theta)$ in the direction parallel to the surface. The consequence is that $k_{i\perp}$, the perpendicular part of the initial-state momentum, must be smaller than k_F as θ increases from zero; hence the initial state is kept away from the band edge. The argument that leads to Eq. (4), then, explains why peaks formed in the gap are so sensitive to θ. This angle dependence should be easy to check experimentally and would be a good test of our theory.

From the peak positions, we can determine the band structure of Na (Fig. 5). It is somewhat surprising that, with such strong broadening effects involved, the calculation could agree so closely with the NFE band. When compared with JP's result, it also agrees very well, especially in the gap. The peaks in the gap are not exactly at E_F, because of the effect of instrumental resolution. This is explained by JP, and is now confirmed by this calculation. The same effect also causes the bottom of the band to be shifted upwards by 0.1–0.2 eV according to our calculation (see also Fig. 1). We believe that this partially explains the reported bandwidth reduction of Na.[1] We expect that the effect would be further enhanced if the initial-state broadening effect is included.

We have also performed similar calculations for K, and obtained results which are analogous to that of Na. This similarity can actually be expected since the band structures of K and Na are similar. Further details, concerning both the theory and the calculation, will be given elsewhere. From our calculation, it seems reasonable for us to conclude the following: The band structure of Na (or simple metals) is indeed simple, although it does not always reveal itself in a simple way.

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

[2] G. D. Mahan, Phys. Rev. B **2**, 4334 (1970).

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

[4] See, for example, G. D. Mahan, *Many-Particle Physics*, (Plenum, New York, 1981).

[5] R. Kammerer, J. Barth, F. Gerken, C. Kunz, S. A. Flodstrom, and L. I. Johansson, Phys. Rev. B **26**, 3491 (1982).

[6] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970).

[7] B. Sernelius, private communication.

[8] J. J. Quinn, Phys. Rev. **126**, 1453 (1962).

[9] N. W. Ashcroft, Phys. Lett. **23**, 48 (1966).

[10] H. J. Levinson, F. Greuter, and E. W. Plummer, Phys. Rev. B **27**, 727 (1983).

[11] R. A. Bartynski, R. H. Gaylord, T. Gustafsson, and E. W. Plummer, Phys. Rev. B **33**, 3644 (1986).

[12] E. Jensen, R. A. Bartynski, T. Gustafsson, E. W. Plummer, M. Y. Chon, M. L. Cohen, and G. B. Hoflund, Phys. Rev. B **30**, 5500 (1984).

[13] E. Jensen, private communication.