RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 23 15 DECEMBER 1991-I

Rapid Communications

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Photoemission measurements of the quasiparticle band of Na

Kenneth W.-K. Shung
Physics Department, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China
(Received 2 April 1990; revised manuscript received 6 August 1990)

In this work, we calculate for Na the photoemission spectra at photon energy ~18 eV and, then, compare them with the "absolute" measurement made by Lyo and Plummer. We find that, quite contrary to the conventional belief, only about half of the observed bandwidth reduction (~0.6 eV) is caused by the self-energy correction. The remaining reduction is due to the surface-induced, momentum-nonconserving excitations and the broadening of quasiparticle states—these effects are intrinsic to photoemission. It is suggested that better band measurements should be done at higher photon energies, e.g., at about 70 eV for Na.

Recent angle-resolved photoemission measurements by Jensen and Plummer[1] (JP) and by Lyo and Plummer[2] (LP) revealed important discrepancies between the measured and calculated band structure of Na. The conduction band of this simple metal is generally regarded as a model system for the electron-gas theory. Therefore, the reported discrepancies are alarming. On the other hand, the relatively simple nature of Na provides us with an appropriate testing ground for studying photoemission itself. It is for these two main reasons that the results of Plummer and co-workers have prompted active theoretical investigations.[3–9]

One focal point has been on the bandwidth of Na. JP found it to be 2.5 ± 0.1 eV. Later, in what they called an absolute measurement, LP concluded that the band is 2.65 ± 0.05 eV in width. Both values are substantially smaller than 3.24 eV, a bandwidth from typical band-structure calculations, or from the nearly-free-electron (NFE) model. The discrepancy is usually attributed[2] to the self-energy correction; i.e., it is normally assumed that, in photoemission, one measures the well-defined quasiparticle states as

$$E(k)=\hbar^2k^2/2m+\Sigma_1(k)\,. \tag{1}$$

$\Sigma_1(k)$ is the real part of the self-energy $\Sigma(k)=\Sigma_1(k)+i\Sigma_2(k)$. There are many self-energy calculations;[2,5,6,9–11] each, suggesting a different mechanism, predicts a different bandwidth reduction for Na. The calculated width ranges widely from 2.4 (Ref. 3) to 2.95 eV.[11]

It is thus important to determine the correct self-energy of Na—the simplest metal available. LP's measurement represents such an attempt, and they claimed that Σ_1, which they calculated with a generalized plasmon-pole method, could explain the measured band of Na. Our present work, however, shows that the self-energy correction can only account for about half of the observed bandwidth reduction, while the remaining reduction is caused by effects due to surfaces and to the broadening of states. Since these are intrinsic properties of the system, they pose an intrinsic limitation on the accuracy of band measurements using photoemission. We also find that if higher energy photon probes are employed, one could do a better band-structure measurement.

The main purpose of this work is to compare our calculated spectra with the absolute measurement by LP. However, unlike LP's emphasis on the peak positions, we shall stress the overall line shape of the Na spectra. Our reason for this is that effects that shape the spectral profile could also shift the peak positions. The close agreement between our calculation and the measurement—on *both the line shape and the peak positions*—strongly indicates that the surface effect and the broadening effects are indeed important in photoemission.

It is conventionally assumed that photoexcitations are between two well-defined quasiparticle states. They are "vertical" transitions that satisfy the conservation laws:

$$\begin{aligned}E(k_f)&=\hbar\omega+E(k_i)\,,\\ \mathbf{k}_f&=\mathbf{k}_i+\mathbf{G}\,.\end{aligned} \tag{2}$$

$\mathbf{k}_i$ ($\mathbf{k}_f$) is the initial (final) momentum of the electron, $\hbar\omega$ is the photon energy, and $\mathbf{G}$ a reciprocal-lattice wave vector. In LP's measurement they choose not to analyze photoelectrons at a fixed emission angle, which is the procedure normally employed.[1] Instead, they[2] analyzed spectra at a fixed $k_\parallel$, the parallel (to the surface) component of the electron momentum. For a chosen $k_\parallel$, they measured at different photon energies and looked for the photoexcitation with the highest binding energy, which obviously corresponds to an initial state at $k_i=k_\parallel$. Accordingly, the peak position (relative to E_F) was assigned[2]

$E(k_i=k_\parallel)$. Repeating the procedure for different $k_\parallel$, LP could, thus, determine the band structure, $E(k_i)$, of Na. The advantage of this scheme is that the band is determined without any assumption regarding $E(k_f)$; hence, LP called it an absolute measurement. However, the accuracy of such band measurements clearly hinges on how closely the conservation laws of Eq. (2) are followed—a condition that we found to be not strictly satisfied.

Our calculations parallel the procedure that LP applied; i.e., we calculate the spectra at a fixed $k_\parallel$ and look for $E(k_i=k_\parallel)$. The results are shown in Figs. 1 and 2. The calculation is based on a photoemission theory due to Mahan.[12] At a given emission angle [$\theta=\sin^{-1}(k_\parallel/p)$, with p the electron momentum outside of the metal], the spectrum is expressed as

$$\frac{d^2I}{dE\,d\Omega}=\frac{em}{2\pi^2}\int d\varepsilon\,\hbar p\langle\phi_\perp^>(p)|H'A(\varepsilon_\perp)H'|\phi_\perp^>(p)\rangle \times(E\cos^2\theta-\varepsilon_\perp-\hbar\omega+V_0)\,. \quad (3)$$

A similar relation has been used[6] for calculating the spectra at normal emission (i.e., $\theta=0$). In Eq. (3), $E=\hbar^2p^2/2m$ is the photoelectron energy measured externally, V_0 the surface barrier, and $H'\sim\mathbf{A}\cdot\mathbf{P}$ the interaction that induces the excitation. In this expression $k_\parallel$ appears only implicitly: $\phi_\perp^>(k_f)$ is the normal component of the scattered wave, and $A(\varepsilon_\perp)$ is the initial-state spectral function at ε, such that $\varepsilon_\perp=\varepsilon-\hbar^2k_\parallel^2/2m$. If we could neglect the broadening of state, we would have $A(\varepsilon_\perp)=\sum_{k_i}|\phi_\perp(k_i)\rangle\langle\phi_\perp(k_i)|\delta(\varepsilon_\perp-E_\perp(k_i))$, where $\phi_\perp(k_i)$ is the normal component of the initial-state wave function and the energy

$$E_\perp(k_i)=\hbar^2(k_i^2-k_\parallel^2)/2m+\Sigma_1(k_i)-\Sigma_1(k_F)\,.$$

The subtraction of $\Sigma_1(k_F)$ is to avoid double counting of this part.[6] To account for the state broadening, the δ function in $A(\varepsilon_\perp)$ is replaced by a Lorentzian of width $\Sigma_2(k_i)$.

Both $\phi_\perp^>(p)$ and $\phi_\perp(k_i)$ are determined in accordance with the surface potential of Lang and Kohn.[13] While $\phi_\perp(k_i)$ can be self-consistently evaluated in this scheme, the calculation of $\phi_\perp^>(p)$ is more subtle because the surface barrier is k_f dependent.[6] The treatment for this factor has been discussed in detail in Ref. 6 and can be applied here with minor modifications.

At a given $k_\parallel$, the decay factor of $\phi^>$ is approximated by $\exp[-z/2\lambda(k_f)\cos\theta']$ for $z>0$ (the metal occupies the $z>0$ half space), where the mean-free path (MFP) $\lambda(k_f)=\hbar^2k_f/2m\Sigma_2(k_f)$ and $\cos\theta'=k_\parallel/k_f$. $\phi^>$ is a scattered wave[12] and the decay factor represents the probability of the electron getting to the surface without scattering.[4] This decay factor is crucial since a short MFP means an enhancement of the surface effect, and transitions between broadened states need not be strictly vertical (see Fig. 1 of Ref. 8). For Na,[6] $\lambda(k_f)$ is only ~5 Å in the energy range of our interest; thus, the nonvertical transitions are expected to be important.

A surface term is explicitly included in Eq. (3). In the acceleration formalism (see Ref. 14), H' can be expressed by $(i\omega)^{-1}[A_z\partial V(z)/\partial z]$, where $V(z)$, the effective one-body potential, contains a surface part $V_s(z)$ and a bulk term $\sum_G V_G\exp(-iGz)$. We employ Lang and Kohn's surface potential[15] for $V_s(z)$. The self-energy (both Σ_1 and Σ_2) is calculated by means of the Rayleigh-Schrödinger method.[6] We remark that all of these quantities [i.e., Σ_1, Σ_2, $\phi^>$, ϕ, and $V_s(z)$] are uniquely determined once the electron density is given. As for V_G, we use the pseudopotential result:[4] $V_{110}=0.296$ eV and $V_{220}=0.229$ eV. Therefore, there is no adjustable parameter in this calculation.

It should be mentioned, however, that we have kept only G_{110} and G_{220} in this calculation. While these are the most relevant **G** vectors in the present case, other **G**'s might also be important, especially for the off-normal (i.e., finite $k_\parallel$) emissions. See, for example, Fig. 9 of Ref. 8 and the discussion given therein.

Before discussing our results, we emphasize that we could easily produce spectra that would satisfy the conservation relations, Eq. (2), if we choose to neglect the surface term and turn off the broadening (which we should not do). The point is that $\Sigma_2\neq0$ means more than just broadening of the spectra—it also leads to shifting of the peak position.

Figure 1 illustrates the calculated spectra at $k_\parallel=0.68$ Å^{-1}. At $\hbar\omega=14$–24 eV, the expected vertical transitions are for $k_f=k_i+G_{110}$. Following LP's analysis, we plot the peak position against $\hbar\omega$ in the inset, with which we can determine the band energy, as explained. $E(k_i=0.68$ Å$^{-1})$ is found to be -1.2 eV from the calculation (solid circles), and it is -1.16 eV from LP's measurement (squares). Both values are substantially reduced from -1.5 eV of a NFE band (dashed curve) or -1.35 eV after the self-energy correction (solid curve). The difference between the calculated result and the solid curve manifests the effects of surfaces and of the broadening which we have just discussed. We should not, therefore, neglect these momentum nonconserving effects when analyzing photoemission spectra of Na, or possibly of oth-

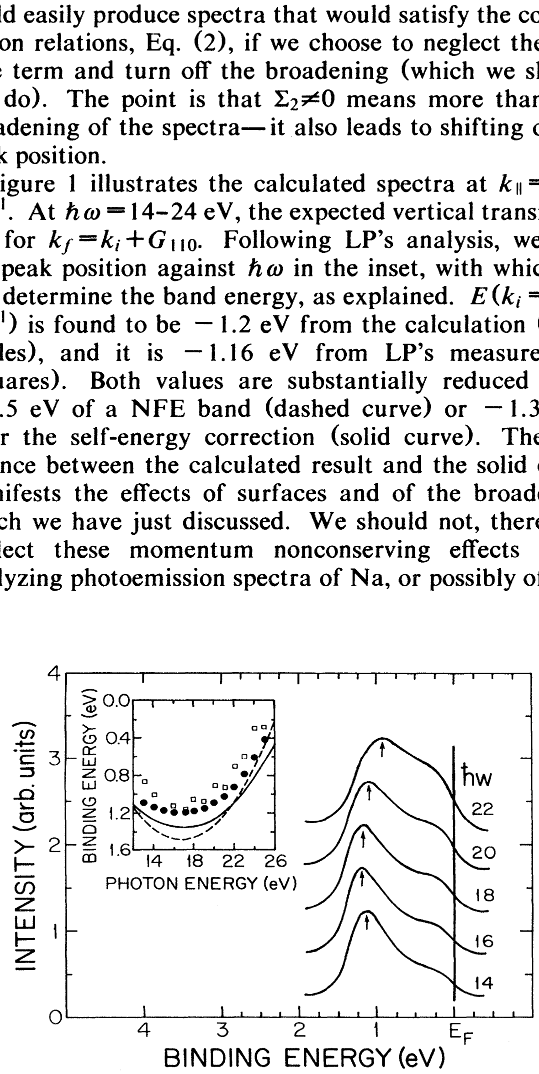

FIG. 1. The spectra at fixed $k_\parallel=0.68$ Å^{-1}. The peak positions (indicated by small arrows), as a function of the photon energy, are plotted in the inset. The solid circles are from this calculation and the squares from LP's measurements. The solid and the dashed curves show, respectively, the quasiparticle and the NFE bands of the expected peak positions if only vertical transitions are allowed.

er metals.

The surface effect is most obviously seen at the enhanced Fermi edge—observed both in Fig. 1 and in LP's measurement. The asymmetric (about the peak) spectral profile would be difficult to understand if there are only vertical transitions. We also found that the spectral density close to the Fermi edge increases with the photon energy, e.g., the edge intensity at $\hbar\omega = 24$ eV is almost twice that at 16 eV. In our theory, this effect is due to a $\hbar\omega$-dependent interference between the bulk and the surface-induced excitations.[4] Such photon-energy dependence also shows up clearly in LP's measurement (see Fig. 1), which, again, would be hard to understand by means of vertical transitions alone.

The same surface effect had been found[4] to be responsible for the anomalous peaks observed in the Na[110] normal-emission spectra.[1] These peaks appear at $\hbar\omega = 30$–40 eV. They are totally unexpected, since they would correspond to vertical transitions from unoccupied initial states. With the inclusion of the surface effect in the theory, we quite successfully explained[4] the anomalous peaks—including their strong emission-angle dependence.[6,8] Overhauser provided an alternative explanation for the anomalies based on a charge-density-wave theory.[3] However, he did not calculate the transition matrix elements to substantiate his claim. The core spectrum analysis by Bruhwiler and Schnatterly[15] does not support Overhauser's explanation either. Thus we believe that our theory has provided a consistent basis for understanding the two seemingly unrelated features in the Na photoemission spectra: the anomalous peaks in the forbidden region and the observed bandwidth reduction.

By repeating the same procedure summarized by Fig. 1 but for different $k_\parallel$'s, we could trace out the band structure of Na (Fig. 2). For example, from Fig. 1 we obtain one data point at $E(k = 0.68\ \text{Å}^{-1}) = -1.2$ eV. The calculations (solid circles) are clearly in close agreement with LP's measurement (squares). The measured width is 2.65 eV (2.55 eV from the earlier measurement of JP). We found the "apparent" bandwidth to be 2.6 eV, about 0.33 eV narrower than the quasiparticle band (solid curve) used for this calculation—i.e., the nonvertical excitations cause a reduction similar in magnitude to that from the self-energy correction. It is clear, then, that we should not take the measured band for a direct comparison with calculated quasiparticle bands. Unfortunately, that is the procedure people normally follow.[1,2,5,11]

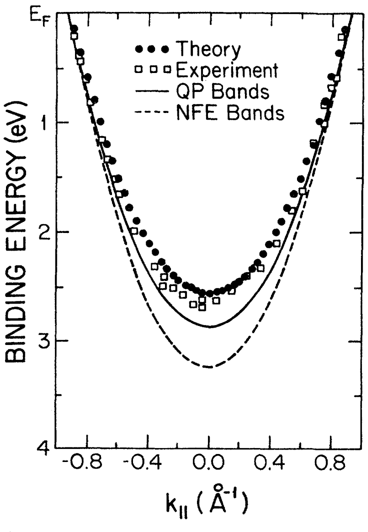

FIG. 2. The "observed" band structure from our calculated (circles) and the measured [squares (Ref. 2)] photoemission spectra of Na. The solid and the dashed curves are, respectively, the quasiparticle band and the NFE band.

We have also calculated the spectra with $\hbar\omega \sim 60$–80 eV for vertical transitions: $-k_i + G_{220} \rightarrow k_f$. Figure 3 illustrates the results for $k_\parallel = 0.68\ \text{Å}^{-1}$. The main interest here is that the nonvertical surface term is substantially reduced at the higher photon energies,[8] since, then, the outgoing wave must oscillate many times in the surface region, which leads to a strong cancellation of the surface term. This is evidenced from a much reduced Fermi-edge intensity in Fig. 3. As a consequence, the peaks due to the vertical transitions become much more well defined and their positions (solid circles) closer to the quasiparticle state (the solid curve in the inset). The apparent bandwidth is found to be 2.73 eV, in better agreement with the quasiparticle band. Even better agreement can be expected for measurements with still higher photon energy (e.g., a few hundred eV), since there would be a further reduction of the surface effect and an increase of the mean-free path of the photoelectrons. However, this would require a higher angular resolution when the photoexcitation cross section becomes much reduced at higher energies. In brief, higher-energy photoemission studies are more difficult to perform experimentally, but would be better for band analysis. We believe that a careful experimental study at different photon energies could reveal the details of the nonvertical transitions.

It is true that JP has measured Na at both $\hbar\omega \sim 18$ eV and 70 eV and observed no difference in its bandwidth. However, their resolution (~ 0.3 eV) is probably not good enough to differentiate the suggested difference of 0.13 eV in the measured bandwidth at these two photon energies. With an improved resolution (~ 0.15 eV) LP found that the bandwidth, measured at $\hbar\omega \sim 18$ eV, is 2.65 eV—not

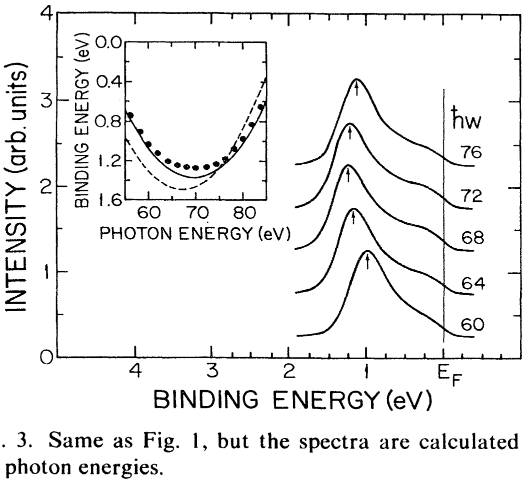

FIG. 3. Same as Fig. 1, but the spectra are calculated with higher photon energies.

2.5 eV as JP claimed. It should be very interesting to repeat the measurement, with the improved resolution, at the two photon energies again.

Lastly, the normal-emission spectra have been discussed extensively in Ref. 8. Important issues regarding the relative phase of the surface and the bulk terms (i.e., the sign of the pseudopotential and the surface position) have been addressed. Respective effects, on the apparent bandwidth, due to surfaces and to broadening were also examined (see Fig. 3 and Table II of Ref. 8). Interested readers are referred to that paper for details.

In summary, I have calculated the spectra of Na, and the results are in close agreement with Lyo and Plummer's absolute measurement. I, accordingly, conclude the following: (1) Nonvertical excitations due to surfaces and broadenings are important in photoemission; (2) these effects cause the band to appear narrower than the quasiparticle band; (3) they could cause an enhancement at the Fermi edge. If it is further suggested that photoemission studies at $\hbar\omega \sim 70$ eV, or at even higher energies, could reveal important details regarding these nonvertical excitations, which we expect to affect spectra of other metals, too. Photoemission from composite systems, e.g., K adlayers on Al,[16] is currently under investigation.

This work was supported in part by the National Science Council of the Republic of China, under Contract No. 78-0208-M007-104.

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