

## Surface Effects in Photoemission Spectra of Na

Kenneth Wen-Kai Shung ( 熊文凱 ) and Shih-Kuei Ma ( 馬士貴 )

*Physics Department, National Tsing Hua University**Hsinchu, Taiwan, 30043 R.O.C.*

(Received Jan. 20.1990)

Recent angle-resolved photoemission studies of Na reveal an anomalous structure for photon energy ranging from **30 to 40 eV**. This anomaly corresponds to initial states close to the Fermi level. Also found in the spectra is that the bandwidth of Na appears to be  $2.65 \pm 0.05$  eV, instead of 3.24 eV from most band calculations. It is suggested in this work that these experimental findings are results of effects due to surfaces and to the broadening of the electronic states. With these effects properly included, we could explain the presence of the anomalous structure at the Fermi level; we also found the apparent bandwidth from the calculated spectra to be 2.6 eV — in close agreement with the measurement. We believe the above-mentioned effects to be sufficiently general to be applicable to other materials. Recently, we have extended our studies to alkali-metal ad-layers on Al substrate and found reasonable results.

## I. INTRODUCTION

There have been active studies in angle-resolved photoemission spectra of Na, both experimentally<sup>1,2</sup> and theoretically.<sup>3-10</sup> It turns out that the measured spectra can not be readily understood in terms of the calculated band structure of Na. Not only that the measured band width ( $2.65 \pm 0.05$  eV) is narrowed by -20% from calculated bandwidth (3.24 eV), but also there appear anomalous peaks in the spectra. Since Na is generally regarded as the best understood simple metal and, hence, held as a test ground for various theories, the revealed discrepancies surprised many and made us rethink: Do we really understand Na?

Our studies<sup>4,6,8,10</sup> show that our theoretical understanding of Na is generally accurate. The problem with the photoemission spectra lies on the fact that photoemission is a highly surface sensitive technique; thus, the measured results do not agree with band calculations for bulk Na — they shouldn't. We have calculated the Na spectrum in which we carefully treated the surface. From such calculated spectra we obtained a bandwidth of 2.60 eV for Na — in close agreement with the measurement. Similar spectral calculation has also been successfully applied to explain the anomalous peaks observed experimentally. The calcula-

tion also predicts a strong emission-angle dependence<sup>4</sup> for this peak structure, and this was later verified experimentally.<sup>6</sup>

Therefore, our calculations provide strong evidences that the surface effects, and related broadening effects (to be discussed later), are essential to the understanding of the Na spectra. This conclusion poses an open question: How general are these effects in the spectra of other materials? In order to answer this question one needs to know the electronic structure in the surface region. This is a difficult task for most materials, with the exception of simple metals; for which the jellium model and the density functional method are applicable. We have recently evaluated the electronic structure of alkali metal (e.g., Na and K) ad-layers on Al. We observed an ad-layer induced resonance close to the Fermi level. Such resonant levels could probably explain the K-covered dependent peak structure observed<sup>7</sup> in the spectra of the K/Al ad-layer system.

The rest of the paper is organized as follows. In Sec. II, the problem with Na spectra is discussed. In Sec. III, our calculation is given and the results will be discussed. Then, in Sec. IV, we present our calculations for the ad-layer systems (Na/Al and K/Al), which is followed by our concluding remarks in Sec. V.

## II. PROBLEMS WITH THE Na SPECTRA

Na is a metal of great theoretical interests since its Fermi surface is highly spherically symmetric in k-space and, hence, is generally regarded as a realization of the popular nearly-free-electron model (NFE). For the NFE systems, detailed theory is available, even if the Coulomb interaction among electrons is included. The band structure of a NFE system is particularly simple: It is parabolic (i.e.;  $E(k) \sim k^2$ ), and the Fermi energy,  $E_F$ , equals 3.24 eV for Na. Fig. 1. illustrates, in terms of the reduced-zone scheme, the band along the direction

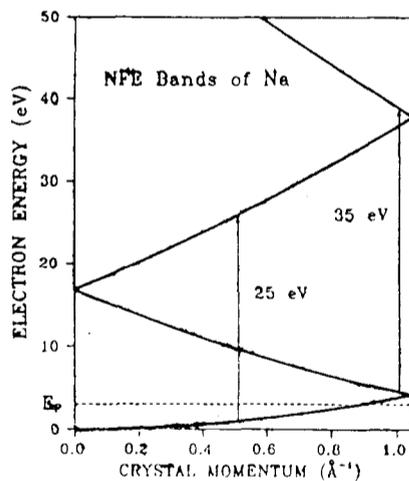


FIG. 1. The band structure of Na in the (110) direction. Vertical transitions at  $\hbar\omega = 25$  and 35 eV are shown by the upward arrows. The 35 eV excitation is forbidden since the initial state is located above  $E_F$ .

normal to the Na(110) surface. The angle-resolved spectra of our interest here, both the measured and the calculated ones, would be made about the norm of the Na(110) surface.

Photons at low energies (say, at 100 eV or less) carry negligible momentum compared with that of Bloch electrons in a metal. Therefore, in photo-excitations the laws of conservation of momentum and of energy are expressed as

$$\mathbf{k}_f = \mathbf{k}_i + \mathbf{G}, \quad \text{and}$$

$$E(\mathbf{k}_f) = E(\mathbf{k}_i) + \hbar\omega. \quad (1)$$

The subscripts  $i$  and  $f$ , respectively, denote the initial and the final electronic states, and  $\mathbf{G}$  is a reciprocal lattice wave-vector. Photo-excitations that satisfy the conservation laws of Eq. (1) are usually referred to as vertical transitions; they are indicated by the upward arrows in Fig. 1. It should be clear that, at a given photon energy, only one such vertical transition corresponding to a specific  $E(\mathbf{k}_i)$  is allowed, and would appear as a pronounced peak in the spectrum. Therefore, we could apply photoemission with different photon energies to probe and, after some analysis of the spectra using Eq. (1), to trace out the conduction band structure of Na. For normal emission from the Na(110) surface, we need to apply  $\hbar\omega = 15 - 32$  eV if  $\mathbf{G} = \mathbf{G}_{110}$  in Eq. (1), and  $\hbar\omega = 38 - 75$  eV if  $\mathbf{G} = -\mathbf{G}_{220}$ .

One focal point here is at  $\hbar\omega = 32 - 38$  eV; within this energy range the allowed vertical transitions would correspond to unoccupied initial states! (see Fig. 1.) This necessarily means, if our previous analysis is to hold true, vanishing photoemission signal at such energies. Experimentally the contrary was found by Jesen and Plummer (JP)<sup>1</sup>: A rather sharp peak with the initial state at  $E_F$  was observed! One might wonder if this peak could be explained by a surface state at  $E_F$ . However, a well-defined surface state should lie within a band gap. For the very reason that this anomalous peak sits right on the Fermi level of a conduction band and not inside a band gap, one could conclude immediately that it is not caused by a surface state.

JP's finding forces us to conclude either of the following two possibilities: One is that the band of Na may actually be severely distorted from the NFE band; then, for example, a flat band structure near  $E_F$  could possibly explain the observed anomalous peak. The other possibility is that the excitation in photoemission may not be strictly vertical as is suggested by Eq. (1); then, a NFE band could still result in peaks in the gap region. One should be aware of that, if the former is true, most of our existing electron gas theory would be severely challenged; whereas if the latter turns out to be responsible for the anomaly, the basics of our conventional spectra analysis [i.e., Eq. (1)], would have to be modified. So, JP's results pose a real threat to our conventional wisdom concerning the metal, photoemission as well.

Despite the unexpected presence of the narrow peaks in the forbidden gap, structures from vertical transitions, which are expected for  $\hbar\omega = 15 - 32$  and  $38 - 75$  eV, are easily identified. However, the conduction band traced out from these data yields a bandwidth of  $2.5 \pm 0.1$  eV — more than 20% reduction from the NFE band! Later, a more detailed study by the same group<sup>2</sup> confirms the result and put the bandwidth at  $2.65 \pm 0.05$  eV.

One might argue that the band narrowing could be explained by the so-called self-energy correction: that is to take  $E(k)$  in Eq. (1) to be the quasi-particle energy:  $C(k) = \Sigma_1(k) + i\Sigma_2(k)$

$$E(k) = \hbar^2 k^2 / 2m + \Sigma_1(k) \quad (2)$$

However, the classic many-body calculation of Hedin<sup>13</sup> finds the quasi-particle bandwidth to be 2.95 eV, which is narrower than the NFE band but is still insufficient to explain the photoemission data. After JP's report, new mechanisms have been suggested for the self-energy calculation and even narrower bandwidth (to as low as 2.4 eV) was obtained.<sup>5,14</sup> The validity of these calculations remains to be checked. Our own calculation,<sup>6</sup> where the Rayleigh-Schrödinger method has been employed, puts the width at 2.87 eV; this value only slightly modifies Hedin's result.

It is thus appropriate to conclude that the two main discrepancies revealed by JP's measurement are: the anomalous peaks found at  $h\nu \sim 35$  eV and the band narrowing effect. We performed detailed calculation<sup>4,6,8,10</sup> and found that there exists one common cause for the two seemingly unrelated discrepancies; and that common cause is the surface and the broadening of the electronic states. Surfaces break the translational symmetry of a solid and hence relax the strict momentum conservation [i.e., Eq. (1)] requirement. Broadening of states (due to  $\Sigma_2$ ) means finite mean-free-path (MFP) for photo-electrons, and a short MFP would enhance the surface effect, or the non-vertical excitations. Our calculations, where the surface and the broadening of states were properly treated, quantitatively explain the JP results; they also come up with predictions which were only later verified experimentally.

### III. THE CALCULATIONS AND THE RESULTS

Two essential physical quantities must be evaluated with accuracy: the Na surface and the self-energy, both the real and the imaginary parts of it. For the former, we adopt the density functional method after Lang and Kohn.<sup>15</sup> This method is generally believed to be most suitable for simple metals like Na. As described earlier, we employed the Rayleigh-Schrödinger method to calculate the self-energies. The real part,  $\Sigma_1$ , only slightly differs from Hedin's result; the imaginary part,  $\Sigma_2$ , gives a rather short MFP of 4-5 Å for electrons of 20 – 70 eV in energy. Such a short MFP is in close agreement with measurements,<sup>16</sup> and is essential in the following discussion. We would like to stress here that the calculations above, and the rest of our calculations that follow, are essentially parameter-free. That is to say: All relevant quantities are fixed once the electronic density is given.

After the surface and the self-energy have been evaluated, we may proceed to calculate the spectra. We employ Mahan's theory of photoemission which is especially suitable for treating surface scattering of photo-electrons. In the case of normal emission, relevant electrons have vanishing momentum component along the surface direction and, hence, the

problem reduces to a one dimensional one. The spectral intensity at  $E = \hbar^2 p^2/2m$  (the electron energy measured outside of the metal) is expressed by:

$$\frac{d^2 I}{dE d\Omega} = \frac{em}{2\pi^2} \int d\epsilon \hbar p \langle \phi^{\rangle}(\mathbf{p}) | H' A(\epsilon) H' | \phi^{\rangle}(\mathbf{p}) \rangle \delta(E - \epsilon - \hbar\omega + V_0) , \quad (3)$$

where  $V_0$  is the surface barrier and  $H' \sim \mathbf{A} \cdot \mathbf{p}$  the interaction that induces the excitations.  $\phi^{\rangle}(\mathbf{p})$  is the scattered wave in the final state and  $A(\epsilon)$  the spectral function for finding a conduction electron at  $\epsilon$ . If the broadening of states is neglected we can put  $A(E) = \sum_{\mathbf{k}_i} |k_i\rangle \langle k_i| \delta(\epsilon - E(k_i))$  and Eq. (3) reduces to the familiar golden-rule form. To account for the initial state broadening, we replace the delta-function in  $A(E)$  with a Lorentzian of width  $\Sigma_2(k_i)$ . The initial wave functions,  $|k_i\rangle$ , were determined concurrently with the surface potential,  $V_s(z)$ , in the Lang and Kohn's scheme. Employing  $V_s(z)$  (the metal occupies the  $z > 0$  half-space by assumption) we may also evaluate  $\phi^{\rangle}(\mathbf{p})$  for the final state. Since the photo-electrons can be scattered by other electrons via the Coulomb interaction, we add a decaying part  $\exp[-z/2\lambda(k_f)]$  to  $\phi^{\rangle}(\mathbf{p})$  to cope with this fact.  $\lambda(k_f)$  is the MFP of the photo-electrons and equals  $\hbar^2 k_f / 2m\Sigma_2(k_f)$ . As is obviously seen, the surface effect has been built into the wave function  $\phi^{\rangle}(\mathbf{p})$ , and the short MFP ( $\sim 5 \text{ \AA}$ ) ensures that photo-emission is surface sensitive.

There is one another surface-related term in Eq. (3), coming directly from the interaction  $H'$ . Using the expression after Almladh,<sup>18</sup> we may put  $H'$  into the form  $(i\omega)^{-1} [A_z \partial V(z) / \partial z]$ , where  $V(z)$  is the effective one-body potential that electrons see.  $V(z)$  contains two parts:  $V_s(z)$ , which has been evaluated by means of Lang and Kohn's method, and the lattice potential which may be expressed as  $\sum_{\mathbf{G}} V_{\mathbf{G}} \exp(-i\mathbf{G}z)$ . The bulk term, i.e., the excitations due to the lattice potential, is what account for the vertical transitions that satisfy Eq. (1). At the photon energies of our concern here only the  $\mathbf{G}_{110}$  and  $\mathbf{G}_{220}$  terms are relevant. The surface term due to  $V_s$  is most interesting since it could induce non-vertical transitions. We found that at photon energies below  $\sim 40 \text{ eV}$  this surface term is very important and is strong enough to explain JP's spectra.

Figures 2. and 3. demonstrate the calculated spectra at  $\hbar\omega = 25$  and  $35 \text{ eV}$ , respectively. These calculated spectra differ from our earlier results<sup>4,8</sup> by having included both the broadening and the self-energy correction.

Let us examine the  $\hbar\omega = 25 \text{ eV}$  spectrum first. The thin, solid curves represent diagonal terms from various effects (e.g., vertical and surface-induced transitions), as indicated. Interference between these effects (the dashed curves) is obviously strong and important. The heavy solid curve is our spectrum by calculation. There are several important features worthy of mention. Firstly, there is a pronounced peak associated with the vertical transition:  $\mathbf{k}_i + \mathbf{G}_{110} \rightarrow \mathbf{k}_f$ . However, the peak position of this  $V_{110}$  curve, which follow Eq. (1) closely, is located at  $\sim 0.4 \text{ eV}$  below the peak in the spectrum (the heavy curve). The shift of the peak position is obviously due to the surface term and the large interference. If we took the peak position in the spectrum and use Eq. (1) to do analysis, we would indeed obtain a band width of  $2.6 \text{ eV}$  and not  $2.87 \text{ eV}$ , the quasistate bandwidth. State differently, we can not precisely measure the bulk bands with photoemission at such

low photon energies. However, since the surface effect would reduce<sup>4</sup> at higher photon energies, we could expect better band measurement at these energies. Secondly, because of the surface and the interference terms, there appears an edge structure at  $E(k_i) = E_F$ . The edge

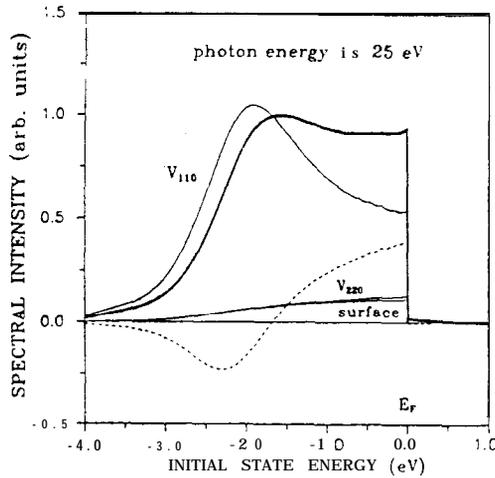


FIG. 2. The spectrum (the heavy solid curve) at  $\hbar\omega = 25$  eV. The thin curves are the spectral contributions from the surface,  $V_{110}$  and  $V_{220}$ , as indicated. The dashed curve is the interference between the surface and the bulk terms. An edge structure is formed at  $E_F$ , which would appear broader experimentally due to the instrumental broadening.

structure can also be seen clearly in  $JP'$  spectra and would be difficult to understand if only vertical excitations are allowed. Thirdly, there is a small contribution from the  $V_{220}$  term although it is forbidden from the strict viewpoint of vertical transitions. Its presence is due to the broadening of states, i.e., due to the fact that one-body states are merely approximations for interacting electrons. This  $V_{110}$  term is small here, but the very mechanism that explains its presence here also explains the anomalous peaks in the gap region where no

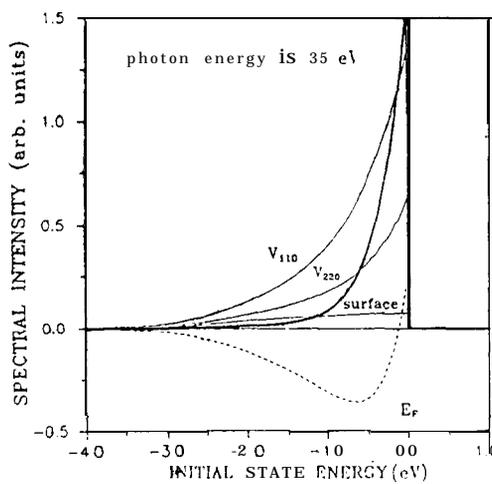


FIG. 3. Same plot as Fig. 2. but for  $\hbar\omega = 35$  eV. The excitation is forbidden if only vertical transitions are allowed (Fig. 1).

vertical transition is allowed.

Figure 3. shows the spectrum at  $h\nu = 35 \text{ eV}$ ; in which one finds a pronounced peak at  $E_F$  — the position the anomalous peak was observed experimentally. Here we notice that the  $V_{110}$  and  $V_{220}$  branches almost have equivalent contributions, although neither are allowed vertical transitions. As we have just explained, this is made possible because of the state broadening effect. One may interpret the spectrum as having a sharp cutoff at  $E_F$  which causes a large portion of the peak (that above  $E_F$ ) erased. This explains why such peaks appear much narrower than the peak found in, say, the  $h\nu = 25 \text{ eV}$  spectrum. The same reasoning led us to expect<sup>4</sup> these peaks to have reduced peak intensities — a feature later verified experimentally.<sup>19</sup> One another prediction that has also been verified is on the emission-angle-dependence of these peaks in the gap region. Their peak intensity strongly depends on the closeness between the Fermi level and the Brillouin zone boundary (see Fig. 1). A small deviation (say,  $3^\circ - 5^\circ$ ) from the normal direction ( $k_y = 0$  then) would put the Fermi level sufficiently away from the zone boundary to drastically reduce the peak intensity by  $\sim 50\%$ .<sup>4,6</sup> All of these results provide us a strong evidence that the surface effect and the broadening of states are key to the understanding of the photoemission spectra of Na, and maybe of other materials just as well.

#### IV. ALKALI-METAL AD-LAYERS ON Al

Evidences were provided in the previous section that the surface profile, i.e.,  $V_s(z)$ , plays a pivotal role in determining photoemission spectra. It stands to reason that  $V_s$  would be drastically altered if an ad-layer of foreign atoms were added to a simple metal surface. Recently, photoemission studies were carried out<sup>18</sup> for K on Al(111) surface. Many interesting features have been observed. For a comparison with this measurement, the following calculation would be performed for the K/Al system. We did also study the Na/Al system and obtained qualitatively similar results.<sup>20</sup>

It was observed<sup>11</sup> that, as the K coverage on the Al surface grows, so does the spectral intensity near  $E_F$  (25 eV photon probes is used in this study). When there is one monolayer of K on top of Al, a well-behaved peak (about 1.0 eV in full width) at about 0.3 eV below  $E_F$  was observed. The peak intensity also demonstrates high emission-angle-dependence. These features are similar in many ways to the Na spectra that we have just discussed, and we would like to extend our studies to these ad-layer systems.

For the K/Al system the calculations parallel that of Na, but is considerably more complicated since the system itself is. As we did for the Na surface, we used the jellium model to treat the Al(111) surface and also the K/Al compound. Fig. 4. illustrates the surface potential for the bare Al and for one monolayer of K on top of the Al surface. The zero potential level is put at  $z = \alpha$  for the both cases. There are two notable features from this calculation. One is that the potential develops a shoulder in the region where the ad-layer is. Since the matrix element of photo-excitation corresponds to the derivative of  $V(z)$  (see Eq. (3) and discussions that follow), the ad-layer-induced structure in  $V_s(z)$  is expected to

affect the spectra in a profound way. Secondly, the potential inside the bulk has been elevated by  $\sim 1.5\text{eV}$  due to the K alayer. Experimentally, this effect has been verified that the work function of the K/Al system is indeed reduced from that of Al by  $\sim 1.9\text{eV}$ .<sup>11</sup> The work function reduction is caused by the redistribution of the 4s electrons of K: the density of which is shown by the heavy-dashed curve in Fig. 4. There is a certain portion of these s-electrons goes into the bulk of Al, leaving the K-covered surface slightly positively charged. As a result, conduction electrons would find it easier to come out of the solid, or the work function is reduced.

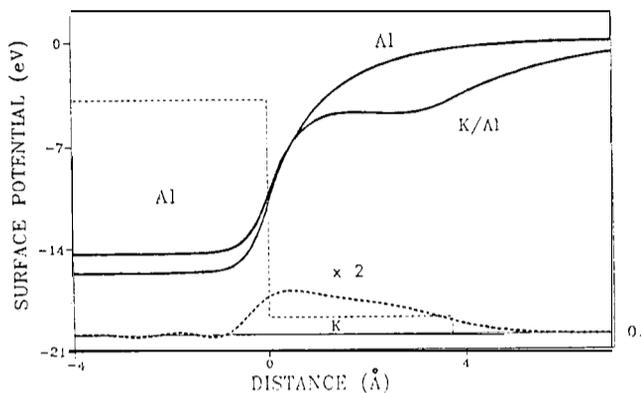


FIG. 4. The surface potentials of the naked Al(111) surface, and of one monolayer of K on the Al surface, are shown by the heavy curves as, respectively, indicated. The positively charged ion density (in the jellium model) of the K/Al system is shown by the thin-dashed curve. The density of the valence electrons from the K layer (times a factor of 2) is shown by the heavy-dashed curve. The zero-density level is marked on the right of the plot.

In energy-space, the distribution of the 4s electrons of K is plotted in Fig. 5. There clearly appears an ad-layer-induced resonance centered at  $0.75\text{eV}$  below  $E_F$ , and the full width of which is about  $1\text{eV}$ . By comparing this resonance with the photoemission spectra,<sup>11</sup> it seems quite obvious that the observed peak at  $0.3\text{eV}$  below  $E_F$  is due to this ad-layer-induced structure.

For a detailed comparison with the measured spectra (e.g., the K-coverage dependence and the emission-angle-dependence),<sup>11</sup> further calculation is required. Mainly, we need to include the lattice potential in our self-consistent calculation of  $V_s(z)$ ; since the surface resonance is expected to be sensitive about the lattice potential. Once  $V_s(z)$  is faithfully determined, the rest of the spectral calculation would resemble that for Na.

By properly treating the lattice potential in the calculation of  $V_s(z)$ , we anticipate that we could better explain the work function reduction in the K/Al system and the position of the ad-layer-induced resonance. But even before that is done, our experience with the Na spectra suggests strongly that the resonant structure would be prominent in the spectra of K/Al: It is located in the surface region (Fig. 4.) and the short MFP of photo-electrons would make its contribution important; also, it is close to  $E_1$  (Fig. 5.) where strong interference between the surface and the bulk terms could be expected (Figs. 2. and 3.).

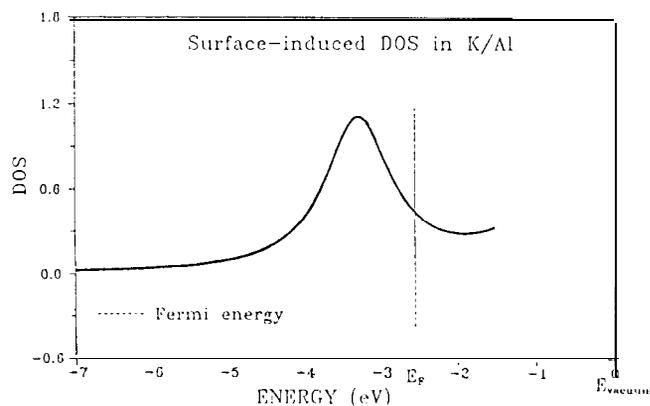


FIG. 5. The distribution, in energy-space, of the valence electrons from the K ad-layer.

## V. CONCLUDING REMARKS

We have performed a detailed spectra calculation for Na. It is based on a photoemission theory of Mahan,<sup>17</sup> with which we are able to include various surface and bulk effects in the calculation. The results show that the surface effect, coupled with the self-energy effects, could modify the photoemission spectra in a profound way. With these effects properly treated, we have essentially explained the major discrepancies reported by the Plummer's group:<sup>1,2</sup> (1) there appears an edge structure at  $E_F$  in the spectra (Fig. 2.); (2) there are prominent peaks in the gap region (Fig. 3.); (3) the band width of Na appears reduced by  $\sim 0.6$  eV.<sup>9,10</sup>

The close agreement between our calculations and the measurements is a strong indication that one should not naively apply the simple condition of vertical transitions (Eq. 1) when analysing photoemission data – especially when photon energy is low (e.g., less than 40 eV is considered low for Na). At higher energies the importance of surfaces decreases, and, only then, could we possibly measure band structures of metals with accuracy. We have suggested that, by varying photon energies in photoemission studies, one could test the present theory experimentally.

Lastly, we have performed a self-consistent calculation of  $V_s(z)$  for the ad-layer system, K/Al; in which the potential is drastically modified at the surface. We found an ad-layer-induced resonance near  $E_F$ , which we expect to account for the peak observed in the photoemission spectra." Detailed spectral calculation for this system is underway. We expect that the result could shed some light on the generality of our theory – that is. of the importance of the surface effect in photoemission.

## ACKNOWLEDGEMENTS

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

## REFERENCES

1. E. Jensen and E. W. Plummer, *Phys. Rev. Lett.* **55**, 1912 (1985).
2. In-Whan Lyo and E. W. Plummer, *Phys. Rev. Lett.* **60**, 1588 (1988).
3. A. W. Overhauser, *Phys. Rev. Lett.* **55**, 1916 (1985).
4. K. W.-K. Shung and G. D. Mahan, *Phys. Rev. Lett.* **57**, 1076 (1986).
5. J. E. Northrup, M. S. Hybertsen and S. G. Louie, *Phys. Rev. Lett.* **59**, 819 (1987).
6. K. W.-K. Shung, B. E. Semelius and G. D. Mahan, *Phys. Rev.* **B36**, 4499 (1987).
7. J. H. Kaiser, J. E. Ingelsfield and G. C. Aers, *Solid State Commun.* **63**, 689 (1987).
8. K. W.-K. Shung and G. D. Mahan, *Phys. Rev.* **B38**, 3856 (1988).
9. G. D. Mahan and B. E. Semelius, *Phys. Rev. Lett.* **62**, 2718 (1989).
10. K. W.-K. Shung, to be published.
11. K. Horn, A. Hohlfeld, J. Somers, Th. Lindner, P. Hollins, and A. M. Bradshaw, *Phys. Rev. Lett.* **61**, 2488 (1988).
12. P. A. Bruhwiler and S. E. Schnatterly, *Phys. Rev. Lett.* **61**, 357 (1988).
13. L. Hedin, *Phys. Rev.* **139**, A796 (1965).
14. X. Zhu and A. W. Overhauser, *Phys. Rev.* **B33**, 925 (1986).
15. N. Lang and W. Kohn, *Phys. Rev.* **B1**, 4555 (1970).
16. R. Kammerer, J. Barth, F. Gerken, C. Kunz, S. A. Flodstrom, and L. I. Johansson, *Phys. Rev.* **B26**, 3491 (1982).
17. G. D. Mahan, *Phys. Rev.* **B2**, 4334 (1970).
18. C.-O. Almbladh, *Phys. Rev.* **B34**, 3798 (1987).
19. See the references of Ref. 6.
20. S.-K. Ma and K. W.-K. Shung, unpublished.