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Photoemission spectra and charge-density waves of K

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We investigate the anomalous Fermi-level resonance observed in the K(110) spectra. A careful calculation of the spectra is performed in which surface effects, band-structure effects, and self-energy effects are included. The result indicates that a charge-density wave in the system is essential for the formation of the resonance. The close agreement between the calculation and the measurement strongly suggests that further investigation on charge-density waves in K is necessary. It also provides evidence for the need of careful matrix-element calculations to understand photoemission spectra, even for simple metals.

The photoemission spectra from the K(110) surface exhibit very interesting structures which cannot be understood readily.[1] The most unexpected feature in the spectra is a resonant peak near the Fermi level (E_F). This resonance appears in the normal emission spectra when the photon energy ($\hbar\omega$) is $\sim$23–25 eV where no vertical transition is allowed in accordance with the nearly-free-electron (NFE) band structure. The purpose of this work is to provide a theoretical understanding of such structures. A detailed calculation is performed in which the effects due to the band-structure corrections, the surface corrections, and the self-energy corrections have been properly taken into account. One surprising finding is that a charge-density wave[2] (CDW) in the system may be essential for the formation of the Fermi-level resonance. The existence of CDW's in the alkali metals has been a controversial issue for over thirty years.[2–6] The results of the present calculation strongly indicate that a closer study, both theoretical and experimental, of CDW's in K is necessary. This study of the potassium spectra, together with the early analysis of the spectra of Na (Refs. 4 and 7) and Al,[8] provide strong evidence that, even for simple metals, careful photoexcitation matrix-element evaluation is essential to the understanding of the spectra.

A comparison of the spectra of K and Na is useful here, since they both have the monatomic bcc structure and, hence, their bands are similar. There also exists in the Na(110) normal-emission spectra a gap (at $\hbar\omega$=31–37 eV) where vertical transitions are forbidden. But in fact a rather narrow peak at E_F was observed[7] in the gap region. This result was later explained by Shung and Mahan[4] (SM) who showed that the Fermi-level structure was the result of nonvertical transitions, which become possible due to the presence of a surface and also to the short photoelectron mean free path (MFP). The short MFP [$\sim$5 Å (Ref. 9)] makes the surface important in this problem. SM's theory not only explains the presence of the anomalous peak, but also successfully describes the peak structure in Na. One prediction from the theory which is relevant to the present work is that the peak intensity should decrease in the gap region because of the Fermi-level cutoff.[9] One would expect to observe similar behavior in the K(110) spectra because of the analogous band structures of Na and K.[4] Recently Itchkawitz, Lyo, and Plummer found that,[1] while the Fermi-level structure does exist in the spectra as expected, its intensity exhibits a strong resonant enhancement. This is a serious contradiction to SM's prediction and needs to be closely examined. In correspondence with the Na spectra, Overhauser has suggested that[3] the Fermi-level structure is due to a CDW in the system, but he did not calculate the matrix element to substantiate his claim. Quite interestingly, according to our detailed calculations, it is in K, not Na, where CDW's may have an important role to play. Details of our calculation are discussed below.

The normal emission spectra can be described by the formula[9] ($\hbar=1$)

$$\frac{d^2I}{dE\,d\Omega}=\frac{em}{2\pi^2}\int d\epsilon\, p\langle\phi^{>}(p)|H'A(\epsilon)H'|\phi^{>}(p)\rangle \times\delta(E-\epsilon-\omega+V_0), \tag{1}$$

where $E=p^2/2m$ is the photoelectron energy measured externally and V_0 the surface barrier. $H'\sim(i\omega)^{-1}[A_z\partial V(z)/\partial z]$ represents the electromagnetic interaction with the electrons in the so-called acceleration formalism.[10] Here z is the surface direction and $V(z)$ the effective one-body potential. $A(\epsilon)$ is the spectral function of finding an electron at ϵ. The quantity $\phi^{>}$ denotes the scattering final states of photoelectrons. The δ function describes the energy conservation in photoemission.

The many-body effect due to the Coulomb interaction among electrons is included in the complex self-energy, $\Sigma(k)=\Sigma_1(k)+i\Sigma_2(k)$. The self-energy has been evaluated within the Rayleigh-Schrödinger approximation.[9] When only $\Sigma_1(k)$ is included in Eq. (1), the state energy is normalized to $E(k)=k^2/2m+\Sigma_1(k)$ and $A(\epsilon)=\Sigma_k|k\rangle\langle k|\,\delta(\epsilon-E(k))$. In this case Eq. (1) would yield vertical transitions only, since the surface effect would become negligible when compared with the bulk transitions. This means photoexcitations would not be allowed inside the forbidden gap, in contradiction with the measurements. The state energy normalization, on the other hand, leads to a 0.2-eV conduction-band width reduction for K (i.e., $[\Sigma_1(k_F)-\Sigma_1(0)]=-0.2$ eV), which is about one-half the reduction observed in photoemission. According to our calculation the remaining part of the observed bandwidth reduction is caused by the photoexcitation process itself, as has been explained in detail in Ref. 9. We shall concentrate on the anomalous structure at E_F in this work.

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The main effect due to $\Sigma_2(k)$ is a short MFP (~ 5 Å) for the photoelectrons. This effect is represented by a factor $\exp[z/\lambda(k)]$ for $z<0$ in $\phi^>(k)$; where $\lambda(k)=-k/2m\Sigma_2(k)$. Because of the short MFP, only those electrons photoexcited from the top few layers can reach the detector unscattered. It is those unscattered photoelectrons which carry the band information. In the surface region, however, states behave very differently from their bulk properties. A careful evaluation of the wave functions and the potential profiles near the surface is thus crucial to the understanding of photoemission spectra.

Early spectra calculations[4,9] for Na and K were carried out within the jellium model in which the band-structure effects are neglected. Such a NFE model is generally expected to be valid for simple metals like Na and K. But the result, despite its success with the Na spectra, fails to explain the Fermi-level enhancement in K, as discussed earlier. To our best knowledge, no theory has explained this resonance so far.

A CDW instability in K was predicted by Overhauser[2] to explain the anomalous optical absorption threshold. Recent neutron diffraction measurements[5,6] to determine the CDW in K have not been conclusive. Here, we explore the possible signature of CDW's in the photoemission spectra of K. An inviting feature about CDW's is that they cause a band gap just about the Fermi level. The gap flattens the band near E_F and thus enhances the density of states there. Since one is essentially measuring a one-dimensional band in angle-resolved photoemission (normal emission here), the density-of-states enhancement at E_F could be enormous; i.e., an enhancement of $A(\epsilon)$ of Eq. (1) at $\epsilon\sim E_F$. A detailed calculation is clearly needed to tell if this is relevant to the observed Fermi-level resonance in K.

A slab model is employed for the calculation. The slab is composed of n K layers located in the $z<0$ region. The top K layer is put at $Z=-d/2$; where $d=a/\sqrt{2}$ is the layer separation and a the lattice constant. The unscreened lattice potential has two components: the first one due to the K layers and the second one due to a CDW. The former is described by the Ashcroft-type pseudopotential with a soft core of radius $r_c=2.14$ in units of the Bohr radius. Since only the z-direction normal emission is considered here, the average of this potential in the xy plane is taken and denoted by $V_A(z)$. A one-component potential $V_{\rm CDW}\cos(Qz+\theta)$ is assumed to describe the CDW. So the unscreened potential is given by

$$\tilde{V}(z)=V_A(z)+V_{\rm CDW}\cos(Qz+\theta). \qquad (2)$$

The screened one-body potential, $V(z)$ of Eq. (1), is self-consistently determined from $\tilde{V}(z)$ by employing the density-functional theory within the local-density approximation. The spectra are then calculated with the employment of Eq. (1). Details of the calculation have been discussed in Refs. 8 and 9. The results indicate that the presence of a CDW is essential to the understanding of the K spectra.

It is well known that the CDW derives from electron interaction. The assumption made above that the CDW is a static potential and is screened by the self-consistent procedure may thus be an oversimplification; e.g., it may lead to double counting of the screening effect. However, the scheme is believed to have properly included the essential

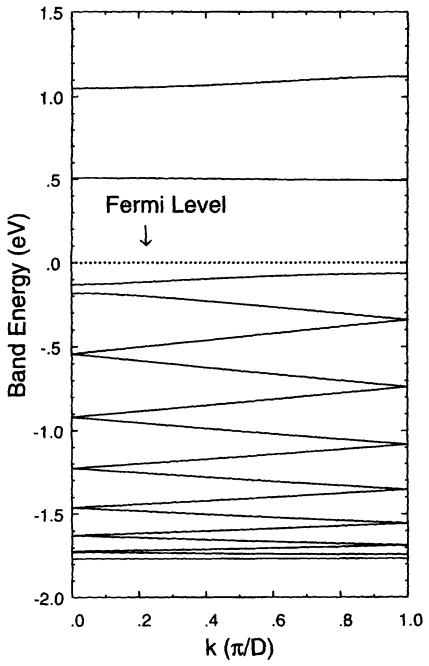

FIG. 1. Calculated band structure of K in the [110] direction; a CDW in the system is presumed. The energy gap, where the Fermi level lies, is mainly caused by the CDW potential.

effects due to the CDW. In a truly realistic calculation, one may like to treat the CDW more carefully, and to calculate the photocurrent with the employment of a three-dimensional potential in a one-step process—by employing the method pioneered by Pendry.[11]

Some details about the CDW potential need to be discussed. $V_{\rm CDW}=0.7$ eV is employed here, which produces a 0.6-eV gap just about E_F (Fig. 1)—as Overhauser has suggested.[2] The CDW has a wave vector $Q=\frac{15}{16}G$ (where $G=2\pi/d$), which is very close to the value proposed by Fragachán and Overhauser,[12] and remains commensurable with G. In accordance with the new period of the system, which is $16d$, the band structure $E(k)$ can be numerically determined[9] and the result is given in Fig. 1. Slightly above the 0.6-eV CDW gap there is a 0.55-eV gap due to the K lattice potential. There are also minigaps at the zone edge, which correspond to lattice scatterings of $(G-Q)$, $(2Q-G)$, etc. The band near E_F is fairly flat, which helps explaining the resonant E_F structure because of the enhanced density of states around E_F. However, the complicated band structure makes simple analysis based on vertical transitions obsolete—too many such excitations are possible at a given photon energy. A detailed matrix element evaluation is necessary to tell which of the transitions dominate and with what spectral profiles.

The relative phase [θ in Eq. (2)] between the lattice potential and the CDW would not affect the band structure. But, due to the short MFP of the photoelectrons, different θ could modify the spectra in an essential way. Near E_F, where our main concerns lie, the states near the zone edge may, in general, be described by $\cos[(G'-k)z+\theta']$ where $G'=15\pi/16d$ and θ' is a function of θ. The long period of the wave functions here, coupled with the short MFP, ensures

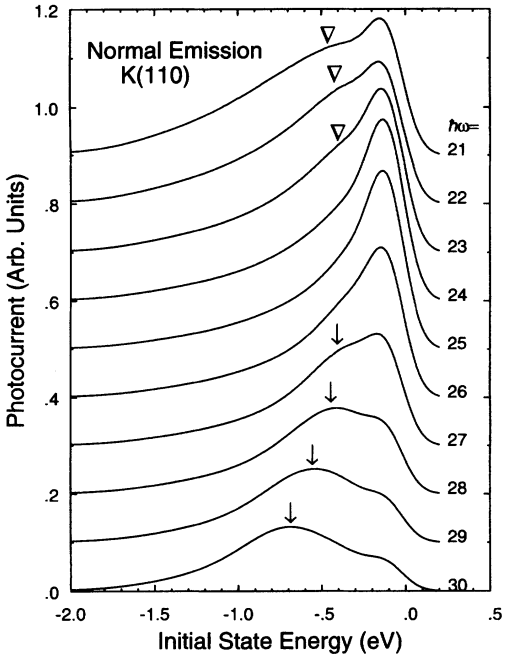

FIG. 2. Evaluated normal emission spectra at various photon energies around the forbidden gap, which is expected in accordance with the NFE band. Instead, pronounced structure at E_F is observed in the gap region.

an enhanced Fermi-level emission if $\theta' = 0$ and a depressed one if $\theta' = \pm \pi/2$. The relative phase θ could also change the sign of the interference between the bulk and the surface-induced terms and thus modifies the spectral profiles. The nature of this interference was discussed in Ref. 4. The value of θ, however, is not known *a priori*. Calculations with θ ranging from $-\pi$ to π have been performed and results compared with the measurements[1] to determine the best value for θ. In doing this, we choose the number of layers n such that the two surfaces of the slab remain symmetric in profile—only to reduce the calculation time. The best result is found at $\theta = -3\pi/8$ with $n = 22$, which are the values used in the following calculations.

Figure 2 shows a series of calculated spectra at various photon energies. This result compares favorably with the measurement shown by Fig. 2(a) of Ref. 1. A pronounced Fermi-level structure exists in the expected gap region at $\hbar\omega \sim 22$–26 eV, and actually extends well beyond the gap region. Besides the structure at E_F, also visible are enhanced spectral weights at -0.5 eV below E_F for $\hbar\omega < 23$ eV (triangles). Peaks also appear in this region for $\hbar\omega > 27$ eV (arrows), but they are of a different origin. The ~ -0.5-eV shoulders in the spectra below the gap would disappear if the CDW potential is turned off in the calculation, while those above the gap would still be there. It is thus clear that the ~ -0.5-eV structure at $\hbar\omega > 27$ eV is associated with the vertical transitions from a CDW-free K crystal, and the shoulders that appear at lower photon energies are induced by the CDW. Similar CDW structures also appear in the measurements[1] at $\hbar\omega \doteq 21$–25 eV, but at a somewhat lower state energy (~ -1 eV). Itchkawitz and co-workers argued that these structures are caused by a surface distortion.[13] Our

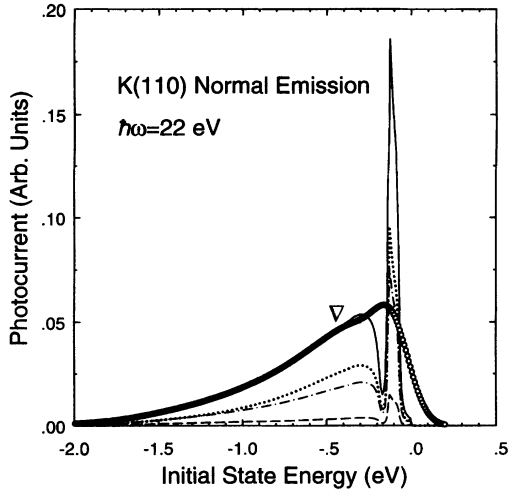

FIG. 3. The spectrum at $\hbar\omega = 22$ eV is shown, where various contributing components are also given (see text). The solid curve (circles) is the spectrum before (after) the instrumental broadening is included. The dip at -0.2 eV is due to the presence of a CDW.

study, on the other hand, strongly indicates that they are the results of a CDW in K.

A closer look at the 22-eV spectrum (solid curve) is given in Fig. 3, which also shows the various contributing components. In doing this, $V(z)$ of Eq. (1) has been decomposed into the bulk part $[V_B(z)]$ and the surface part $[V_S(z)]$, as was discussed in Ref. 8; the purpose of doing this is to distinguish their respective contributions. The dotted curve is the part caused by $V_B(z)$ and the dashed curve by $V_S(z)$. The interference between the bulk and the surface (dash-dotted curve) is strong and important. The spectrum clearly shows that, while the CDW flattens the band and makes the vertical transitions possible at this photon energy, the bulk-surface interference greatly enhances its intensity.

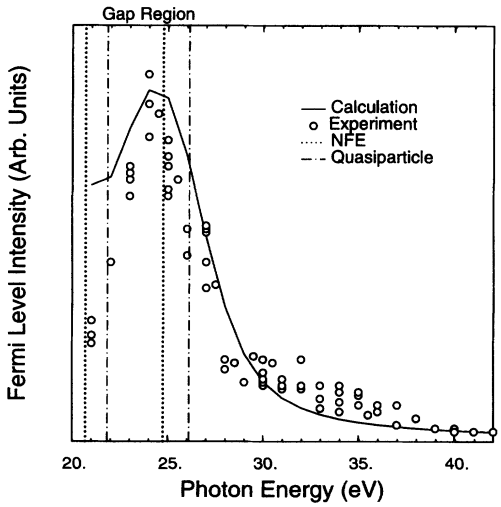

FIG. 4. The Fermi-level intensity has a resonant enhancement in the gap region. The quasiparticle bands (dash-dotted line), which include the self-energy correction, have a modified gap position from that of the NFE bands (dots).

There is a dip in the spectrum at -0.2 eV due to a minigap there caused by the CDW (Fig. 1). After an instrumental broadening of 0.2 eV in full width[1] is taken (the circles) the dip helps the formation of the -0.5-eV shoulder in the spectrum. The dip, which can be taken as an evidence of a CDW in the system, should become obvious if the resolution is reduced by half or more. An improved measurement could, hopefully, also reveal the details of the -0.5-eV (or -1-eV) shoulder so that its nature can be identified.

The strength of the Fermi-level structure as a function of $\hbar\omega$ is given in Fig. 4. Obviously, a good agreement exists between the measurement (circles) and the calculation (solid curve). The resonance, according to this calculation, is a combined effect of a short MFP, which makes the surface important, and the presence of a CDW. In the absence of a CDW the surface effect alone could induce a peak structure at E_F in the gap region, but the Fermi-level intensity decreases inside the gap, as was shown in Ref. 4. It is the CDW that strongly modifies the band and, consequently, leads to the resonance. But the surface effect is nonetheless important here, as illustrated by the size of the interference term in Fig. 3. A similar calculation but with a very long MFP, which artificially reduces the surface effect, would give a totally different spectral profile.

Strong evidence has been provided that the Fermi-level resonance in K is a consequence of a CDW in the system. The study also suggests that, at an improved resolution, photoemission could reveal important details of the spectra; e.g., the -0.2-eV dip due to a minigap and the -0.5-eV shoulders. Equally important to note is that the short MFP makes essential a careful analysis of surface effects. On the theoretical side, a detailed matrix-element calculation seems always necessary, as has been shown here for K and, elsewhere, for the Na (Ref. 4) and Al (Ref. 8) spectra.

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