Photoemission from the Charge-Density Wave in Na and K

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(Received 20 May 1985)

Angle-resolved photoemission perpendicular to the surface of a Na or K film (for photon energies near 35 and 26 eV, respectively) can reveal the momentum mixing and band bending caused by the charge-density-wave potential.

PACS numbers: 79.60.Cn, 71.25.Pi

Recent photoemission studies of the simple metals[1] Al and[2] Be have demonstrated that fine details in the electronic spectrum $E(\mathbf{k})$ can be measured. It seems timely, therefore, to probe the charge-density-wave (CDW) structure of Na and K by this technique. Angle-resolved photoemission is especially suitable for the study of CDW's in these metals[3] because it is known from optical data that the CDW wave vector $\mathbf{Q}$ is oriented perpendicular to the surface of an evaporated film.[4] This feature, which prevents observation of the CDW optical anomaly in thin films,[5] allows one to excite photoelectrons near the CDW energy gap. Wave-function mixing and band bending caused by the CDW potential lead to verifiable predictions about the energy spectrum of photoelectrons emitted perpendicular to the surface. The theory presented here provides a basis for the interpretation of the experimental data on metallic Na given in the preceding paper.[6]

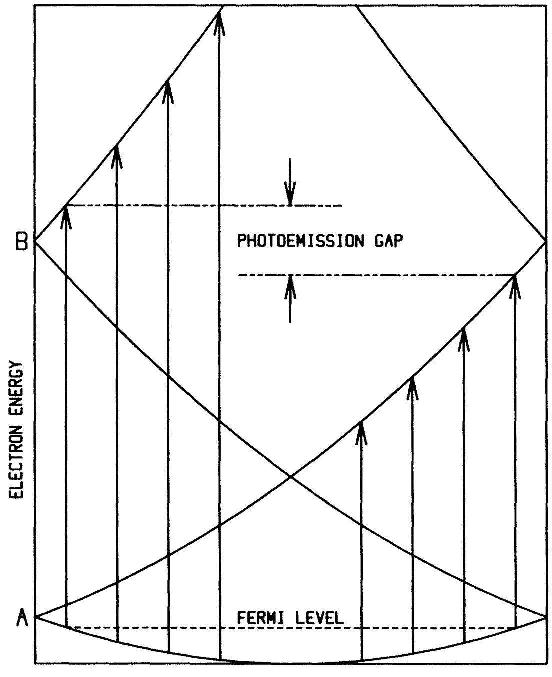

FIG. 1. Free-electron energy spectrum for a (bcc) alkali metal. The wave vector $\mathbf{k}$ is parallel to a [110] direction. The arrows denote photoelectric excitations. Small zone-boundary energy gaps at points A and B are not shown.

The free-electron energy spectrum $E(\mathbf{k})$ for $\mathbf{k}$ along a [110] direction is shown in Fig. 1 and is the same for all alkali metals. Thin films of Na and K having [110] normal to the surface can be grown on amorphous substrates[4] or on a clean Ni(100) surface.[6] The vertical arrows in Fig. 1 indicate photoelectric excitations (from occupied states, E_i, below the Fermi level to empty states above). The excited electron, of energy E_f, can escape from the metal perpendicular to the surface. Such photoelectrons cannot arise for all photon energies, $h\nu$, if the Fermi surface is spherical and if there is no CDW broken symmetry. The resulting excitation gap is shown in Fig. 1.

E_f and $h\nu$ are measured directly, and the initial energy is found from

$$E_i = E_f - h\nu. \tag{1}$$

A plot of E_i vs $h\nu$ is a valuable way to display photoemission data[1] since no assumptions about $E(\mathbf{k})$ need be made. Such a plot for the free-electron model of Na is shown in Fig. 2. Note particularly the gap, ~6 eV wide, near $h\nu = 35$ eV. It is clear from Fig. 1 that

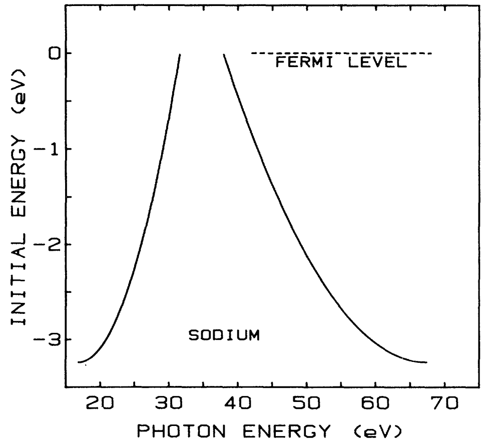

FIG. 2. Initial photoelectron energy vs photon energy for the free-electron model of Na (see Fig. 1).

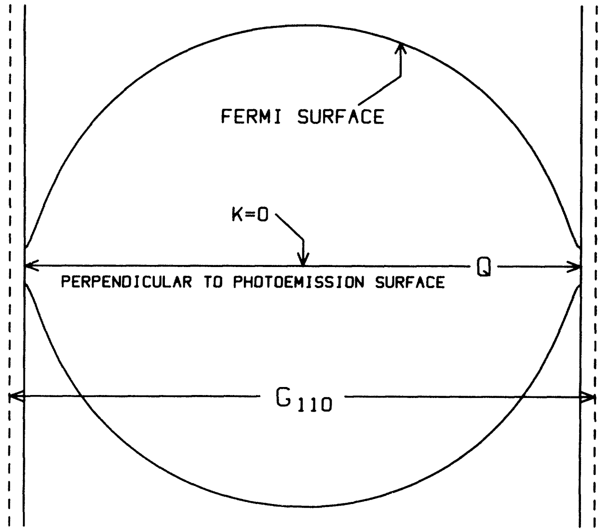

FIG. 3. Brillouin-zone energy gaps (dashed lines), CDW energy gaps (solid lines), and the distorted Fermi surface of an alkali metal having a CDW of wave vector **Q**. Several sets of higher-order gaps (minigaps and heterodyne gaps, see Ref. 9) are not shown.

this gap is caused by the failure of the Fermi sphere to reach the Brillouin-zone boundary. A CDW structure[7] leads to a drastic modification of Fig. 2.

Conduction electrons near the CDW energy gap are strongly influenced by two periodic potentials:

$$V(\mathbf{r}) = 2\alpha\cos(\mathbf{Q}\cdot\mathbf{r}) + 2\beta\cos(\mathbf{G}\cdot\mathbf{r}). \qquad (2)$$

G is the (110) reciprocal-lattice vector and is directed within a few degrees[8] of **Q**. For the present purpose, **Q** and **G** can be taken parallel, and both are perpendicular to the surface of the evaporated film. Two sets of energy gaps and the distorted Fermi surface are shown in Fig. 3. Electrons in a narrow tube surrounding the arrows of **Q** are the ones that (after excitation) leave the metal perpendicular to the surface. Electrons in states near the arrow heads are the ones which (as shown below) will bridge the gap in the spectrum of Fig. 2.

Solution of the Schrödinger equation having the potentials given in Eq. (2) is easily accomplished by a plane-wave expansion.[9] The basis functions are

$$|\mathbf{k}\rangle,\ |\mathbf{k}-\mathbf{Q}\rangle,\ |\mathbf{k}-\mathbf{G}\rangle,\ |\mathbf{k}-\mathbf{Q}+\mathbf{G}\rangle,$$
$$|\mathbf{k}-\mathbf{G}+\mathbf{Q}\rangle,\ |\mathbf{k}-2\mathbf{Q}+\mathbf{G}\rangle,\ |\mathbf{k}-2\mathbf{G}+\mathbf{Q}\rangle,$$
$$|\mathbf{k}-2\mathbf{Q}+2\mathbf{G}\rangle,\ \text{etc.} \qquad (3)$$

The off-diagonal matrix elements of the Hamiltonian matrix, from Eq. (2), have values α, β, or 0. The eigenvalue spectrum is periodic in a narrow strip in k space of thickness $G-Q$. The eigenvalues with the CDW potential $2\alpha=0$, and the crystal potential $2\beta=0.5$ eV, are shown in the left panel of Fig. 4. $Q=0.96G$ was used. The corresponding solution for $2\alpha=1.3$ eV, appropriate to the measured CDW optical anomaly in Na,[10] is shown in the right panel of Fig. 4. Observe that many of the (formerly) empty states have been pushed below the Fermi level. The strong mixing of the basis functions, (3), caused by the CDW, ensures that all "bare"-momentum states up to (and beyond) the zone boundary are included in the occupied eigenstates.

The CDW spectrum of Fig. 4 was computed by diagonalization of a 15×15 matrix. The eigenvalues were

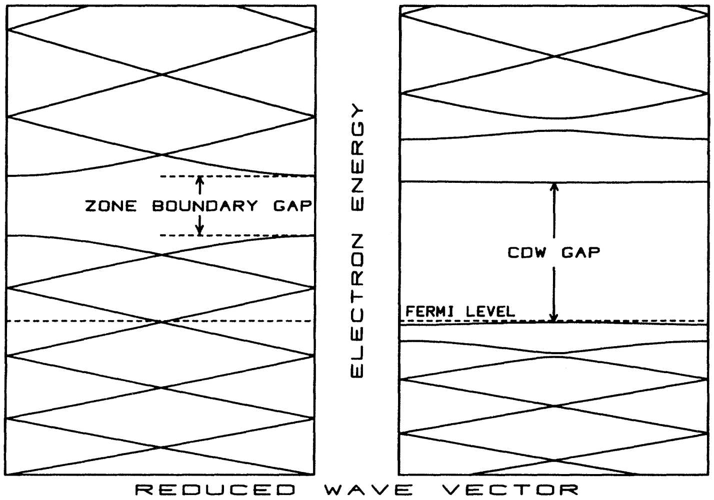

FIG. 4. Conduction-electron energy spectrum for Na in a reduced zone of width $G-Q=0.04G$. The left panel applies when the only periodic potential is that of the bcc lattice. The right panel applies when there is also a CDW potential, as given in Eq. (2) with α and β having values for Na.

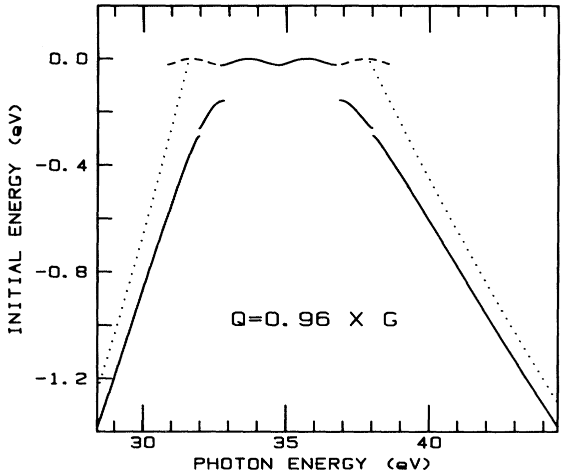

FIG. 5. Initial photoelectron energy vs photon energy for Na. The solid curve results when the CDW structure is recognized. The nearly flat "bridge" near 35 eV is the dominant consequence of the CDW. The dotted curve is the free-electron result from Fig. 2.

used to calculate a photoelectron plot, analogous to Fig. 2, and the result is shown in Fig. 5. Note the appearance of the first and second minigaps.[9] The most important feature is that the 6-eV opening of Fig. 2 is now bridged by an almost flat top just below the Fermi level. The "bare"-momentum mixing will permit weak extensions of the flat top to appear on either side of the central flat top. For clarity these have been shown as dashed.

An important characteristic of the CDW "bridge" in Fig. 5 is the energy width w of the external photoelectrons. If the initial-state width is neglected (as is permissible near the Fermi level), the formula[11] for w reduces to

$$w \cong RW/(1-R), \tag{4}$$

where W, ~ 5 eV,[1] is the width of the excited states, and R is the ratio of the initial-state slope, dE/dk, to the final-state slope. For the transitions of Fig. 5, excluding the bridge, $R\sim\frac{1}{3}$; so that w should be 2–3 eV. However, the initial states that cause the bridge have a very small dE/dk. (These states come from the band just below the Fermi level in the right half of Fig. 4.) Consequently, the width of the external photoelectron peak in the bridge region of Fig. 5 should be *much* smaller than elsewhere.

Confirmation of the foregoing features would be an important addition to the many[5,12] unusual properties of Na and K caused by their CDW broken symmetry.[7] All that has been described above for Na applies without change to K, except that the bridge is near $h\nu = 26$ eV. The Fermi surface shown in Fig. 3 is (in reality) fractured by several higher-order gaps,[9] which cause[13] numerous open-orbit peaks in the magnetoresistance.[14] Such minute details cannot be resolved in photoemission.

The writer is grateful to Eric Jensen for several illuminating discussions about photoemission and to the National Science Foundation for research support.

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