

Experimental Band Structure of Na

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Normal-emission angle-resolved photoemission data from Na(110) are presented. Two discrepancies between these data and the predictions of free-electron theory are observed. First, the occupied-band width is 2.5 eV, while theory predicts 3.2 eV. Second, the bands near the Fermi level appear to have been severely distorted, as could be produced by a charge-density wave oriented normal to the surface.

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The alkali metals Na and K are traditionally considered to be the simplest solids. Band calculations predict nearly free-electron (NFE) energy-band structure, with no occupied-band gaps. There are two important reasons to measure these bands experimentally. First, many-body effects distort this band structure. A narrowing of the occupied band by about 10% has been predicted.¹ These metals present unique opportunities to test the many-body theory, free from one-electron-band complications. Second, there are both theoretical arguments and experimental evidence that the bands near the Fermi level, E_F , are severely distorted because of the presence of a charge-density wave (CDW).²

In this Letter, we present the first angle-resolved photoemission study of an alkali-metal surface, Na(110). This technique allows a detailed measurement of energy versus momentum. We find an occupied-band width of 2.5 ± 0.1 eV. This is significantly smaller than the 3.2 eV predicted by NFE theory. It is also a much larger narrowing than that predicted by existing many-body theory, 0.7 eV rather than 0.2–0.3 eV.¹ We also find a sharp peak near E_F . This peak occurs at photon energies near those expected for NFE band transitions from E_F , but persists for a significant photon-energy range. It is too sharp to be identified as a bulk transition from undistorted NFE bands and occurs only very near to normal emission. It can be quantitatively explained as the band-distortion signature of a CDW.

The Na(110) samples were grown on top of a Ni(100) substrate held near 100 K, by a procedure similar to that described by Andersson, Pendry, and Echenique.³ Our Na sources were zeolite-getter sources.⁴ The films, typically 5000 Å thick,⁵ were then annealed to room temperature and allowed to recoil to 80 K before data acquisition. Low energy electron diffraction (LEED) and Auger electron spectroscopy were used to monitor surface order and contamination. Auger electron spectroscopy showed C and O signals of at most 1% of the Na 980-eV peak. LEED showed relatively sharp bcc(110) spots, but with two azimuthal orientations, as described in Ref. 4. The experiments

were performed at the Synchrotron Radiation Center of the University of Wisconsin, Madison. All data in this Letter were taken with p -polarized light incident at 45° from the sample normal. The electrons were collected along the normal, corresponding to the Γ - N , or Σ , direction in k space. The experimental apparatus is described elsewhere.^{6,7} Total energy resolution is typically 0.3 eV.

Figure 1 shows the relevant NFE band structure of Na along Σ . A typical transition is shown by the solid vertical arrow. In Fig. 2 we show some characteristic spectra. These spectra have been digitally smoothed and then hand traced. The dispersing bulk transition is

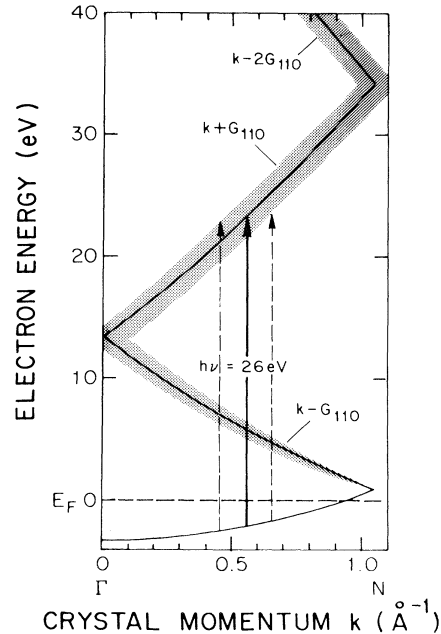


FIG. 1. Plot of the relevant free-electron bands along the Σ axis in Na. The solid arrow shows the center of the direct transition at 26-eV photon energy. The shaded region illustrates the energy uncertainty in the final band due to the finite mean free path of the photoelectron, and the dashed arrows show the effect that this has on the width of the observed peak.

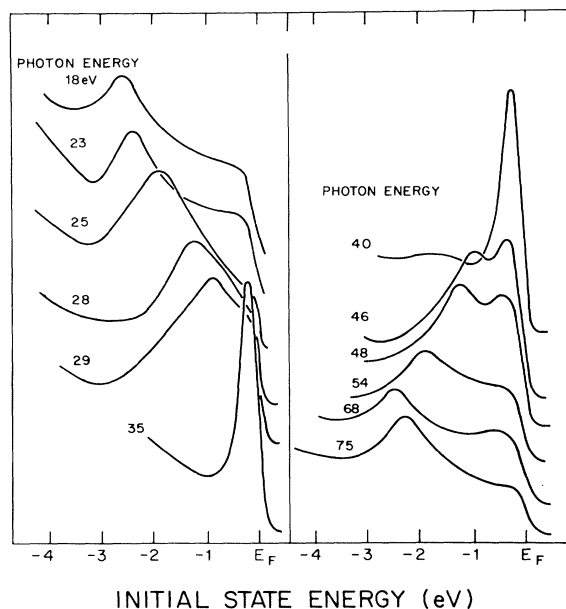


FIG. 2. Selected set of normal-emission photoemission spectra from Na(110).

seen for the photon-energy range 18–29 eV, and from 46–75 eV. The stationary peak near E_F is clearly seen at 35 and 40 eV. In Fig. 3, we plot the peak positions from data like those in Fig. 2 versus photon energy, and compare them to the predictions of NFE theory. The range 29–35 eV is obscured by the LVV Auger transition and by emission from the $2p$ core level with second-order light. When necessary, the second-order

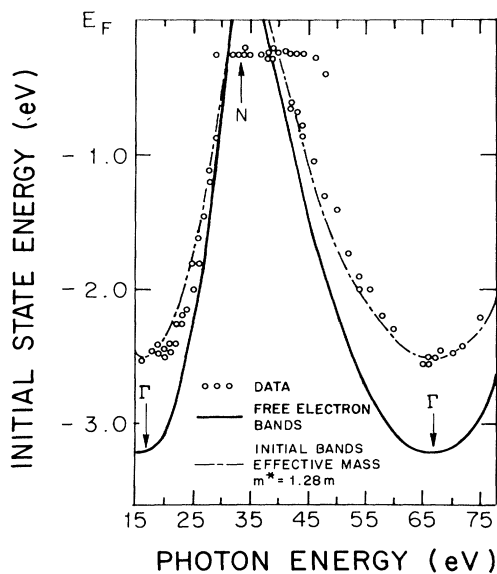


FIG. 3. Peak position measured as a function of photon energy for Na(110), at normal emission. The effects of instrumental resolution have not been subtracted.

structures have been digitally subtracted from the spectra, both for display in Fig. 2, and for reduction in Figs. 3 and 4. A computer fit was required to determine the position of the dispersing peak in spectra that contained both the dispersing and nondispersing peaks. Although the stationary peak near E_F appears at 0.25 eV, the effect of the instrumental resolution has not been deconvoluted from the spectra; if it were, the peak would appear much nearer E_F .

In Fig. 4, we present the measured dispersion of the occupied bands of Na along the normal Σ axis. It is well known that angle-resolved photoemission, as practiced here, does not uniquely determine both the energy and the perpendicular component of the crystal momentum of the electron⁸; one must make some assumptions about the unoccupied bands in order to determine the occupied band. We emphasize, however, that the results presented in Fig. 4 are relatively insensitive to reasonable changes in these assumptions, and that all of our important conclusions can be drawn directly from Fig. 3. The exact shape of the occupied band is directly dependent on these assumptions, and remains somewhat uncertain. To produce Fig. 4, we assumed that the final bands were NFE bands with a small, smoothly varying energy-dependent inner potential adjusted to agree with the experimental extrema. It is further assumed that all of the observed transitions are characterized by $k \rightarrow k - G_{110}$ or by $k \rightarrow k + 2G_{110}$, with G_{110} the [110] reciprocal-lattice vector. We also show in Fig. 4 the NFE occupied

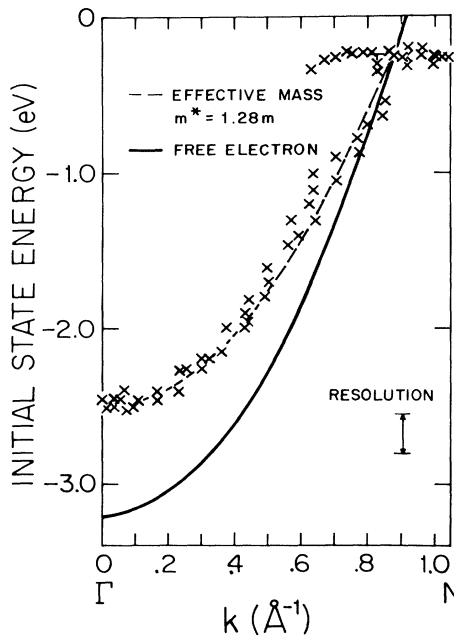


FIG. 4. Measured dispersion of the Na band along the normal Σ axis. The final bands are assumed to be nearly free electron (see text).

band, and a NFE band with an effective mass of $1.28m$, chosen to fit the observed bandwidth.

One prominent discrepancy between the NFE curve and the data points in Fig. 4 is the bandwidth, 2.5 eV for the data, while the NFE curve exhibits a width of 3.2 eV. Band calculations predict that the crystal lattice has a very small effect on the bandwidth.⁹ Many-body calculations predict a 0.2–0.3 eV narrowing of the width due to the energy dependence of the electron self-energy, or equivalently, the one-electron exchange-correlation potential.¹ This observed 0.7-eV narrowing is unexpectedly large. Similar results have been seen in other *sp*-band metals, where, however, the effects of the crystal lattice on the band structure were not negligible, and the blame could not be so clearly laid on the many-body theory.¹⁰ These data are important for two reasons. First, they show clear inaccuracies in the many-body theory. Second, they show that, even in the simplest possible cases, band calculations require significant correction for many-body effects before they can be compared to peak positions as observed in optical and photoemission spectra.

The most interesting effect observed in this investigation is the sharp peak near E_F visible for $30 < \hbar\omega < 46$ eV. This peak is not a bulk transition from undistorted NFE bands. This is obvious from Fig. 3; there is no NFE band in this region. More significantly, there should be no bulk transition at all in much of this photon-energy range, as all NFE bands have dispersed above E_F . In off-normal-emission spectra, the bulk transition can be seen to disperse up to E_F and then disappear. Finally, this peak is too narrow to be a bulk transition. For peaks near E_F , widths are generated by momentum averaging due to the small mean free path of the photoelectron. The mechanism is illustrated in Fig. 1. One must average the occupied band over the indicated range. This leads to observed widths proportional to the slope of the occupied band. The measured 4-Å mean free path for Na in this kinetic energy range¹¹ requires half-widths of 0.7–0.8 eV. This is in good agreement with the widths observed for the dispersing peaks in Fig. 2, but it is more than twice as large as the width of the E_F peak.

In addition to bulk transitions, there are two more categories of peaks commonly seen in valence-band photoemission spectra, surface states and surface resonances. Both are due to additional one-electron states near the surface of the crystal. Surface states are by definition restricted to bulk band gaps. Surface resonances are not, and thus may hybridize with bulk levels. It is clear that this peak cannot be a surface state in undistorted NFE bands, because these bands contain no occupied-band gaps. We also believe it unlikely that this peak is a surface resonance. Because of hybridization with bulk states, surface resonances are

usually much broader than this peak is. Surface band calculations are now quite successful at describing surface states and resonances for prescribed surface geometries. A recent calculation exhibits no such resonance.¹²

We are left with two reasonable descriptions of this anomalous peak. It may be a bulk transition, directly indicating severely distorted bulk bands. The observed band is bent over near E_F , remains flat for a significant region, and is below E_F for most of the Brillouin zone. This is indicated in Fig. 4. This distortion also explains the observed peak width; the final-state momentum averaging does not have a large energy broadening effect on flat bands. Alternately, this peak could be a surface state, indirectly indicating that the bulk band has been distorted so as to produce a band gap below E_F . Once again, the small width is explained, because momentum averaging perpendicular to the surface does not affect surface states.

The important point is that both explanations require severely distorted bulk bands. Such a distortion has been predicted by Overhauser.¹³ He has claimed that the electronic structure of thick Na films is distorted by the presence of a CDW oriented normal to the surface. The one-electron potential associated with this distortion creates a band gap just above E_F , the main CDW band gap, and forces the bands below E_F to flatten out as they approach E_F . Our data can now be straightforwardly interpreted as bulk transitions, and details are provided in the following paper.¹⁴ The presence of two peaks in some of the spectra can be explained either as an effect of the momentum averaging or by the mixing of the two incommensurate potentials. In addition, the interaction of the lattice and CDW potentials creates smaller gaps below E_F . These are just what are needed to permit a surface state. Either explanation is sufficient; both require the existence of a CDW distortion normal to the surface. The surface-state explanation is an unnecessary complication, included only for completeness. If the bands are distorted because of a CDW, our data can be most easily explained as bulk transitions.¹⁵

It is important to emphasize the following: Conventional descriptions of the electronic structure of Na cannot easily explain the presence of a sharp peak near E_F in the normal-emission photoelectron spectra, while such a peak follows naturally and quantitatively from the CDW description using parameters derived 10 and 20 years ago. Nevertheless, other explanations are possible. The electronic structure of metals and the photoemission process are both complex subjects. As yet unspecified surface and/or many-body effects could be responsible for the existence of this peak. We note that the observed effects are not limited to Na(110). Very recent data from K(110) show similar behavior.¹⁶

We would like to speculate on one more possible explanation. Overhauser's CDW description of the alkali metals requires the occurrence of two phenomena. First, according to Overhauser, there is a natural tendency of the electron gas to distort to a structure with a wave vector near twice the Fermi wave vector, k_F , in order to reduce its exchange and correlation energy. Second, there is a screening response of the positive lattice to reduce the electrostatic energy associated with the electronic distortion. It is not generally accepted that these phenomena occur in the bulk. Near the surface, however, neither is considered surprising. The distortions to the electron density with wave vector near $2k_F$ are the so-called Friedel oscillations. Oscillatory relaxations of the first several lattice planes are also known to exist at some metal surfaces.¹⁷ However, each of these phenomena is typically considered independently and generally found to be too small to produce the observed effects. Perhaps if they were put together self-consistently, along the lines proposed by Overhauser for the bulk, enhancement of the Friedel oscillations could occur, generating a CDW-like distortion in the near surface region. If this distortion were to persist for a depth significantly larger than the probing depth of photoemission, say tens of hundreds of angstroms, then photoemission could not distinguish it from a true bulk CDW. We add that a total-energy calculation¹⁸ and LEED experiment³ do not predict significant motion of the outermost plane for Na(110).

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