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Theoretical and experimental study of a surface state on Cr(110)

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A *d*-band surface state on the Cr(110) surface has been identified using angle-resolved photoemission experiments and theoretical calculations. The calculations predict that the surface state appears in an absolute gap of the bulk band structure for the paramagnetic phase of Cr. The surface-induced state observed in the experimental spectra is well modeled by the calculated results.

A theoretical and experimental study of a *d*-band surface state on Cr(110) is reported in this Rapid Communication. Angle-resolved photoemission spectra recorded along the ⟨001⟩ azimuthal direction using Ne I (16.8 eV) radiation show a strong contribution from a surface-induced state. Emission from this state is detected at emission angles corresponding to $k_{\parallel}$ between 0 and about $0.7(\pi/a)$. However, in the near normal emission spectra recorded using He I (21.2 eV) radiation no surface-related feature could be identified[1] unambiguously. Theoretical calculations were made of the band structure for the paramagnetic phase of chromium, and of photoemission spectra using two different methods. Both the band structure and the photocurrent calculations predict this new surface state on the Cr(110) surface. Surface states were recently identified[2–6] on Cr(100) and interpreted[5,6] as evidence that the Cr(100) surface is, in fact, ferromagnetic. The calculated[5] electronic structure of Cr in the antiferromagnetic phase predicts surface states both on the (100) and (110) surfaces and that the (100) surface will possess ferromagnetic order. The results of our theoretical calculations for the paramagnetic phase, and angle-resolved photoemission experiments, made on Cr(110) at temperatures above the Néel temperature ($T > 312$ K), are presented below.

The experiments were performed utilizing a Vacuum Generators ADES400 spectrometer equipped with a uv-resonance lamp. The electron analyzer has an acceptance angle of ±2° and was operated at an energy resolution of ≤ 0.2 eV. The Cr(110) crystal was cleaned by repeated cycles of Ar^+ sputtering and annealing. The surface orientation was checked using low-energy electron diffraction (LEED) and a sharp 1×1 diffraction pattern was observed after cleaning. Resonance radiation (Ne I and He I) was incident at an angle θ_i from the surface normal in the $(1\bar{1}0)$ mirror plane (i.e., along the ⟨001⟩ azimuth), and the electron momentum parallel to the surface was varied by rotating the analyzer in that plane. The electron emission angle θ_e is given a negative value when the emission is on the side of the surface normal on which the radiation is incident.

Figure 1 shows angle-resolved photoemission spectra of Cr(110) recorded for the clean and oxygen-exposed surface at $\theta_e = 12.5°$ using unpolarized Ne I radiation incidence at $\theta_i = 45°$. The structure located aroung -0.6 eV in the clean spectrum becomes strongly attenuated after an oxygen exposure of 0.5 L (1 L = 1 langmuir $= 10^{-6}$ torr sec) and is almost completely quenched after an exposure of 1.5 L. On the other hand, the structure located around -1.4 eV, originating from $\Sigma_1 - \Sigma_1$ bulk-band transitions,[7] is not much affected by these exposures. The sensitivity to surface contamination suggests that the -0.6-eV structure might arise from a surface state. Before assigning it as a surface state, however, it must be concluded that there is an absolute gap or a symmetry gap in the band structure corresponding to the experimental conditions used.

The results of a band-structure calculation for paramagnetic chromium along lines in **k** space in the $(1\bar{1}0)$ mirror plane (i.e., the *TNP* plane) is shown in Fig. 2. The linearized-augmented plane-wave (LAPW) method[8] was used to calculate a first-principles self-consistent potential. The calculation is based on the density functional theory, and a local approximation[9] for exchange and correlation was used. The potential was then used for calculating the bulk bands shown in Fig. 2 and for doing a relativistic band-structure calculation and two different calculations of photoemission spectra. The band-structure calculation was made for the $k_{\parallel}$ values given in the figure in the range $0 < k_{\perp} < \sqrt{2}$ ($k_{\perp}$ in units of π/a), thus giving all bulk

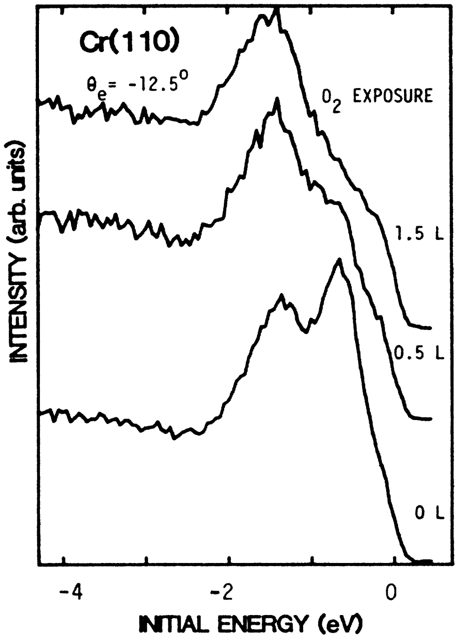

FIG. 1. Angle-resolved photoemission spectra of clean Cr(110) and after oxygen exposures of 0.5 and 1.5 L (1 L $= 10^{-6}$ torr sec). The spectra were recorded at an emission angle of $\theta_e = -12.5°$ using 16.8-eV radiation incident at $\theta_i = 45°$ in the $(1\bar{1}0)$ mirror plane.

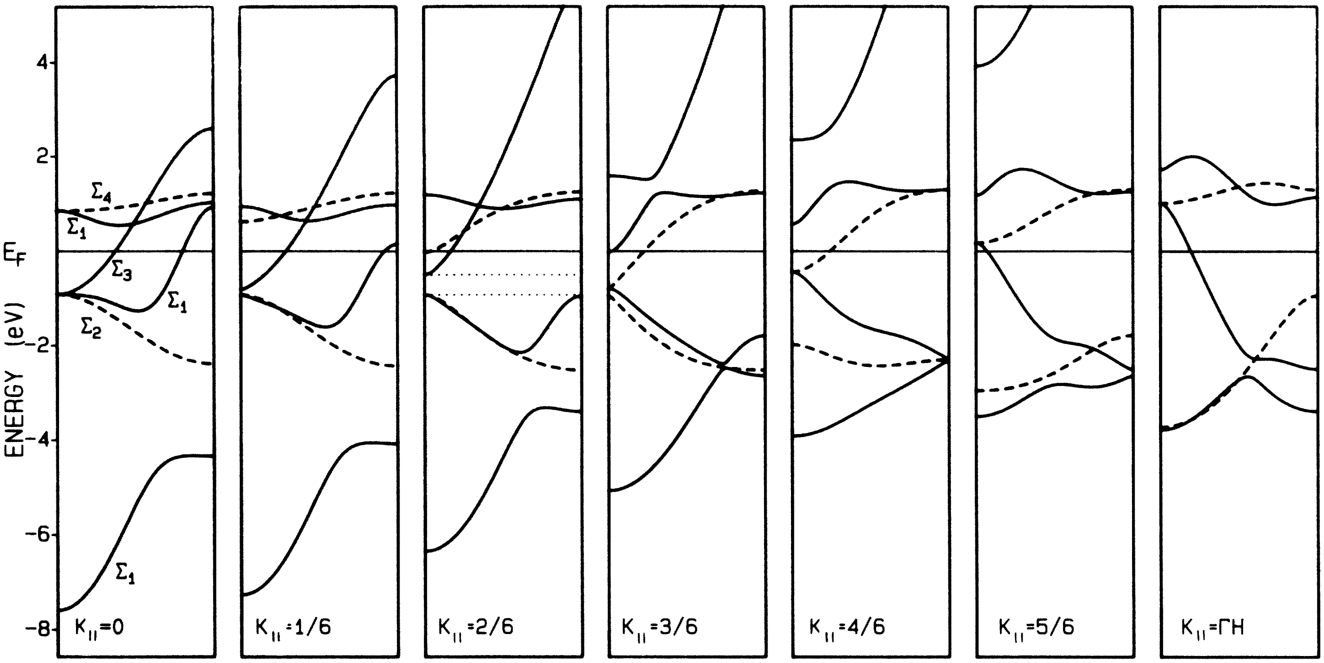

FIG. 2. Calculated band structure of paramagnetic Cr along lines perpendicular to the (110) surface in the *TNP* plane, i.e., in the $(1\bar{1}0)$ mirror plane. The $k_\perp$ region is $0<k_\perp<\sqrt{2}\pi/a$, and the $k_\|$ values are given as fractions of the ΓH value $(3\pi/2a)$ of the surface Brillouin zone. The single group-symmetry labels of the bands along the Σ line $(k_\| = 0)$ are also indicated. The solid (dashed) lines show the bands with even (odd) parity under reflection through the $(1\bar{1}0)$ mirror plane. The absolute gap, appearing at $k_\| = \frac{2}{6}\Gamma\,\mathrm{H}$ in the figure is indicated.

bands along these lines. The bands indicated by solid (dashed) lines have even (odd) parity under reflection through the $(1\bar{1}0)$ mirror plane. The nonrelativistic symmetry classification of the bands are shown in the figure. A fully relativistic band-structure calculation was also made using the relativistic-augmented plane-wave (RAPW) method,[10] but since those results were very similar to the nonrelativistic band structure, only the latter is shown here. In principle, the spin-orbit coupling is important since it mixes bands of different parity. For example, in the *TNP* plane, the even (Q_1) and odd (Q_2) states are mixed together giving only $Q_3\times Q_4$ states.[11] For Cr, however, this mixing is very small, and we found no evidence that it is necessary to include relativistic effects. The calculated band structure shows that an absolute gap exists along lines parallel to the Σ line in the *TNP* plane, indicated by the horizontally hatched region in Fig. 2. An occupied surface state in this band gap would appear about half an eV below the Fermi level in a photoemission spectrum recorded at $\theta_e = -12.5°$ using Ne I radiation. We therefore interpret the -0.6-eV structure in Fig. 1 as originating from a surface state. The band gap is found to exist for $k_\|$ values corresponding to emission angle of about $|\theta_e| > 10°$ for Ne I radiation. For smaller $k_\|$ values, no absolute gap exists, and thus no surface state, but surface resonances, may then appear. In order to estimate the possibility for and location of surface states and resonances, the band structure calculation was extended to complex **k** values. At $k_\| = 0$ a loop in complex k space was found to connect the two upper Σ_1 bands, giving an energy value of about -0.5 eV. This simple approximation thus indicates that a surface resonance can exist at small $k_\|$ values before the band gap opens up and a true surface state appears. Whether a structure originates from a surface state or a surface resonance in a photoemission spectrum would show up merely as differences in the emission intensity.

In the experimental spectra, the surface-induced structure is best resolved at emission angles between $-10°$ and $-20°$, as illustrated in Fig. 3(a) where spectra recorded at different emission angles between $-20°$ and $+20°$, using Ne I radiation incident at $\theta_i = 45°$, are shown. Emission from the surface-induced state is observed also at positive emission angles but much less pronounced than at the corresponding negative angles. No surface-induced structure was observed at normal incidence $(\theta_i = 0°)$ of the radiation, which is taken as evidence that the parity mixing is small in Cr. The surface-induced structure is seen to disperse in Fig. 3(a) towards the Fermi level when decreasing $|\theta_e|$ towards normal emission. The energy position changes smoothly from -0.8 eV at $|\theta_e| = 20°$ to about -0.3 eV at normal emission. For angles larger than $|\theta_e| > 25°$ the surface-induced structure could no longer be detected, possibly due to interference with strong bulk-band emission.

Theoretical photoemission spectra were calculated using two different methods. Spectra calculated using the time-reversed LEED-theory scheme[12] are presented in Fig. 3(b). The bulk LAPW potential was utilized and the surface barrier was located in the conventional way, so that it touches the muffin tins of the surface layer. The results presented in Fig. 3(c) were obtained by computing the probability of direct bulk-band transitions, using the wave functions generated in the LAPW band-structure calculation,[7] and by performing a matching to the surface. Broadening parameters of 0.2 and 2.0 eV were used in the calculations for the low- and high-energy states, respectively. Linearly polarized radiation incident at $\theta_i = 45°$, but with the electric field vector

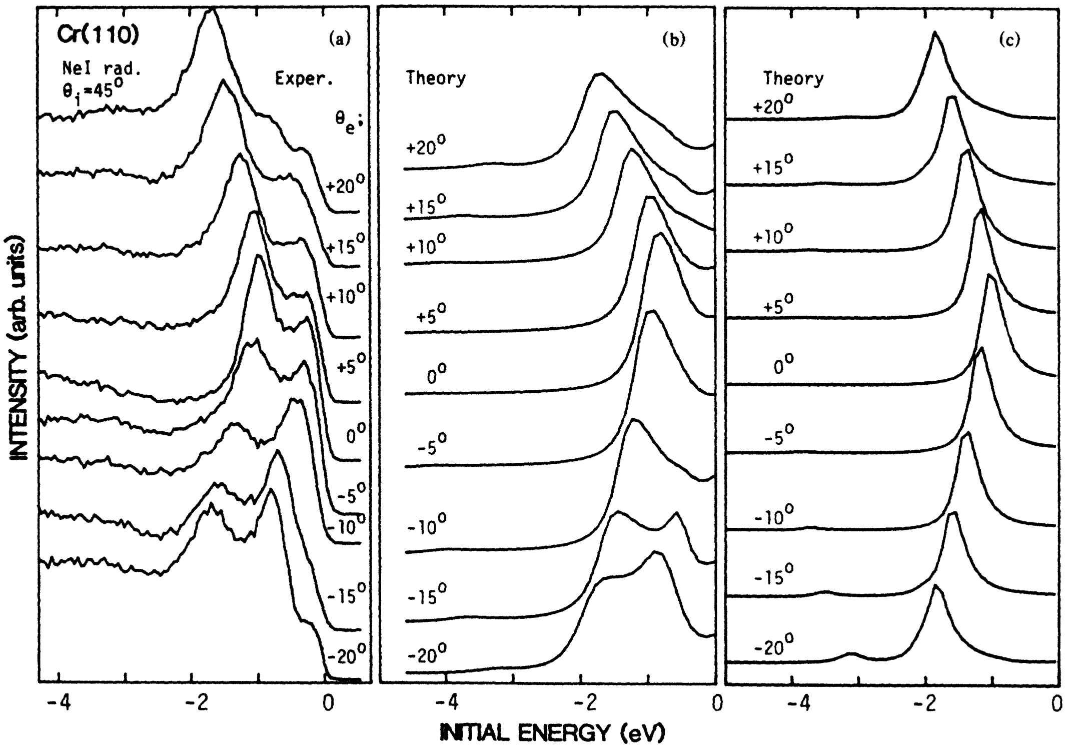

FIG. 3. Angle-resolved photoemission spectra of Cr(110) for different emision angles, θ_e, and 16.8-eV radiation incident at $\theta_i = 45°$ in the $(1\bar{1}0)$ mirror plane. (a) Experimental spectra, (b) theoretical spectra calculated using the time-reversed LEED scheme (Ref. 12), and (c) theoretical spectra calculated using the LAPW bulk-band-structure results (Ref. 7).

at an angle of 45° relative to the plane of incidence, was assumed in the calculation for simulating unpolarized incident radiation. The spectra shown in Fig. 3(c) model the contributions from direct bulk-band transitions while those in Fig. 3(b) also contain contribution from surface-induced states. In the spectra calculated from emission angles of $|\theta_e| > 10°$, a surface-induced structure is clearly resolved between -0.4 and -0.6 eV in Fig. 3(b). The calculated photocurrent for this structure was found to originate essentially from the first two layers, and its position was found to be sensitive to the location of the surface barrier. The theoretical spectra are found to model the dispersion and intensity variation of the bulk and surface contributions in the experimental spectra very well, as seen in Fig. 3. The surface state is best resolved at negative emission angles also in the calculated spectra.

In the spectra recorded using He I (21.2 eV) radiation, contribution from surface-induced states could not be identified unambiguously. At this photon energy and normal emission there are two initial state bands available[7] within 1 eV below the Fermi level (a Σ_1 and a Σ_2 band). The calculated contributions from these two bulk bands were found to reproduce the experimental spectra quite well. No significant changes were observed in the near normal emission spectra for oxygen exposures of 2 L. These findings cast some doubt on the assignment of a surface state close to the Fermi level in previous investigations.[1,13] One of those studies[1] was made along the $\langle 1\bar{1}0 \rangle$ azimuth and there the bulk bands interfere strongly with the assigned surface state since the bulk bands disperse towards the Fermi level when increasing the emission angle from normal emission. For Ne I radiation, that interference does not exist, which also is true along the $\langle 001 \rangle$ azimuth.

In summary, strong contribution from a surface-induced state was observed in angle-resolved photoemission spectra of Cr(110) recorded using Ne I radiation. The band structure of the paramagnetic phase of chromium, calculated using the LAPW method (and a fully relativistic calculation made to check the nonrelativistic results), showed that a band gap exists along lines parallel to the Σ line in the *TNP* plane, which can explain the occurrence of a *d*-band surface state. Calculations made for complex **k** values supported this interpretation and indicated an energy position of about -0.5 eV, in good agreement with the experimental value. At small $k_{\parallel}$ values, i.e., before the band gap opens up, the calculations indicated that a surface resonance may exist, which is believed to give rise to the experimentally observed structure at small emission angles (for $|\theta_e| < 10°$ when using Ne I radiation). The photocurrent calculations made, using two different methods, were found to reproduce the dispersion and intensity variation of both the bulk and surface-state contributions very well, thus giving firm support to our interpretation.

[1] P. L. Wincott, N. B. Brookes, D. S. Low, G. Thornton, and H. Padmore, Vacuum **33**, 815 (1983).

[2] G. Gewinner, J. C. Peruchetti, A. Jaegle, and R. Pinchaux, Phys. Rev. B **27**, 3358 (1983).

[3] D. Aitelhabti, G. Gewinner, J. C. Peruchetti, R. Riedinger, D. Spanjaard, and G. Treglia, J. Phys. F **14**, 1317 (1984).

[4] L. E. Klebanoff, S. W. Robey, G. Liu, and D. A. Shirley, Phys. Rev. B **30**, 1048 (1984).

[5] R. H. Victoria and L. M. Falicov, Phys. Rev. B **31**, 7335 (1985).

[6] L. E. Klebanoff, R. H. Vicotria, L. M. Falicov, and D. A. Shirley, Phys. Rev. B **32**, 1997 (1985).

[7] P. E. S. Persson and L. I. Johansson, Phys. Rev. B (to be published).

[8] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[9] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[10] T. L. Loucks, *Augmented Plane Wave Method* (Benjamin, New York, 1967).

[11] J. F. Cornwell, *Group Theory and Electron Energy Bands in Solids* (North-Holland, Amsterdam, 1969).

[12] J. F. L. Hopkinsson, J. B. Pendry, and D. J. Titterington, Comput. Phys. Commun. **19**, 69 (1980).

[13] L. I. Johansson, L. G. Petersson, K. F. Berggren, and J. W. Allen, Phys. Rev. B **22**, 3294 (1980).