Photoelectron Spectroscopy Studies of Cr(001) Near-Surface and Surface Magnetism

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ABSTRACT

Angle-resolved photoelectron spectroscopy (ARPES) studies of Cr(001) near-surface and surface electronic structure are reviewed. The near-surface energy band dispersions were investigated along the [010] direction parallel to the crystal surface. The periodicity of these band dispersions indicates that the valence electrons experience and self-consistently establish antiferromagnetism in the near-surface layers of Cr(001). Two surface-sensitive photoelectron peaks are observed in normal-emission ARPES. The spectral characteristics of these surface-related states are consistent with calculations that predict a ferromagnetic Cr(001) surface phase. The temperature dependence of one of these features is interpreted as evidence for a Cr(001) surface magnetic phase transition.

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I. INTRODUCTION

We review here recent angle-resolved photoelectron spectroscopy (ARPES) studies of Cr(001) surface[1,2] and near-surface[3] electronic structure. Prior to these experiments, the nature of the Cr(001) surface magnetization had attracted considerable theoretical interest.[4-7] Recently, more comprehensive calculations[8] have been made of Cr(001) surface electronic structure and magnetism. The comparison of the ARPES results with these theories provides insight into the Cr(001) surface and near-surface magnetism.

The nearly half-filled 3d band of Cr produces unique electronic and magnetic properties in the bulk metal. Neutron diffraction measurements[9] on Cr reveal the existence of a spin-density wave[10] (SDW) whose periodicity is incommensurate with the body-centered cubic (bcc) crystal lattice. The true incommensurate SDW ground state of bulk Cr is too complicated to be treated easily with band-structure theory. However, several calculations[11-14] have been made of a commensurate SDW state corresponding to perfect itinerant antiferromagnetism. An antiferromagnetic (AF) arrangement defines a simple cubic (sc) magnetic lattice in which the spin polarization at the corners and at the center of the bcc crystal lattice are of equal magnitude but opposite orientation. Consequently, the reciprocal space lattice is sc, and the associated AF Brillouin zone is a volume of simple cubic symmetry.[14] This differs fundamentally from the symmetry of the paramagnetic (PM) phase, for which the reciprocal space lattice is face-centered cubic. The associated PM Brillouin zone is a regular rhombic dodecahedron with twice the volume of the AF Brillouin zone. The relationship between the AF and PM Brillouin zones is shown in Fig. 1. A commensurate spin structure would render equivalent the two symmetry points in reciprocal space labelled (Γ) and (H) in the PM Brillouin zone.[14]

The existence of a magnetic lattice affects the periodicity of the valence-band dispersions. In the absence of antiferromagnetism, the bands would disperse with a periodicity consistent with the PM Brillouin zone. A magnetic potential with commensurate wavevector $2\pi/a$ would mix PM states with wavevectors k and $k \pm 2\pi/a$. Thus the energy-band structure for commensurate AF chromium arises[14] from the translation of the PM energy bands by $2\pi/a$. The periodicity of the valence-band dispersions would then be consistent with the sc Brillouin zone.

We expect from these considerations that the energy bands of the ideal AF state would disperse symmetrically about the X point of the sc Brillouin zone in Fig. 1. In the absence of commensurate antiferromagnetism, the energy-band dispersion need not show this periodicity. In a PM state, the Cr valence bands would disperse about the (H) point, since this point corresponds to a zone boundary in the PM Brillouin zone. The marked difference between the AF and PM Brillouin zones in Fig. 1 suggests that antiferromagnetism might be distinguishable from paramagnetism in chromium by a measurement of the valence-band dispersions along the [001] or [010] axes of Fig. 1.

ARPES has proved to be a powerful probe of valence-band dispersion relations. Most ARPES experiments probe within the first ~10 atomic layers near a metal surface. Despite this surface sensitivity, for many metals semi-quantitative agreement exists between ARPES results and bulk valence-band theory. This suggests that in these metals, the electronic structure is already "bulklike" by the second or third layer. However, Allan predicted[4-6] that the reduced coordination number (4) for the Cr(001) surface atoms would produce energy-band narrowing resulting in the formation of an unusual Cr(001)

surface magnetic order. His tight-binding calculation[6] for Cr(001) predicted a ferromagnetic surface phase characterized by an exchange-split surface spin density of states (SSDOS), and large ($2.8\mu_B$) localized surface magnetic moments. The magnitude of the Cr(001) surface moment is thought to be much larger than the maximum value $0.59\mu_B$ found[9] for the bulk chromium magnetic moment.

Grempel's calculation[7] extended the theory to finite temperature using a spin-fluctuation formalism. His results predict the persistence of Cr(001) surface ferromagnetic order for temperatures up to 850 K, well above the bulk Néel temperature of 312 K. The transition from surface to bulk properties must encompass a finite number of near-surface layers. It is the surface and near-surface regions that are probed by the ARPES measurements summarized here. We review in Section II our ARPES investigation of the Cr(001) near-surface electronic structure and its implication for near-surface magnetism. In Section III we review our ARPES study of the Cr(001) surface electronic structure. A summary of the ARPES results is presented in Section IV.

II. Cr(001) NEAR-SURFACE ELECTRONIC STRUCTURE AND MAGNETISM

Figure 2 displays five ARPES spectra out of 50 that were taken of Cr(001) (at 298 K) to probe the [010] direction for binding energy (E_{IN}) values of 2-4 eV. The value $k_{\parallel}^{f}$ ($\AA^{-1}$) is the magnitude of the parallel component (along [010]) of the final-state wavevector for the peak marked with a tic. We use the direct-transition model[3] to associate $k_{\parallel}^{f}$ with an initial-state wavevector $\underset{\sim}{k}_i$ along the [010] symmetry line in the first Brillouin zone. For

the PM Brillouin zone of Fig. 1, $k_{\parallel}^{f} = 0$ probes $\underset{\sim}{k}_i$ at the (H) point. When viewed in the AF Brillouin zone of Fig. 1, direct transitions to $k_{\parallel}^{f} = 0$ arise from $\underset{\sim}{k}_i$ at the Γ point.

Figure 3 plots E_{IN} versus $k_{\parallel}^{f}$ for the features observed in the ARPES spectra. Three distinct bands of points are present. Band III is a feature that has been assigned[2] to the Cr(001) surface electronic structure. Band II is located at $E_{IN} = 2.4(1)$ eV for $k_{\parallel}^{f} = 0.15(8)$ Å^{-1} in Fig. 3. As $k_{\parallel}^{f}$ increases, Band II disperses toward E_F. At $k_{\parallel}^{f} \sim 1.06(8)$ Å^{-1}, Band II suddenly flattens out, with $E_{IN} = 1.5(1)$ eV. Band I is located at $E_{IN} = 3.2(1)$ eV for $k_{\parallel}^{f} = 0.20(8)$ Å^{-1}. As $k_{\parallel}^{f}$ increases, E_{IN} increases to a maximum of 4.1(1) eV at $k_{\parallel}^{f} = 1.07(8)$ Å^{-1}. This value of $k_{\parallel}^{f}$ corresponds to the X point (1.09 Å^{-1}) of the theoretical AF Brillouin zone (Fig. 1) to within the experimental uncertainty. As $k_{\parallel}^{f}$ increases beyond 1.07(8) Å^{-1}, Band I disperses symmetrically back toward E_F. In contrast to Band III, Bands I and II show comparatively little sensitivity to surface contamination. This suggests that Bands I and II arise from the Cr(001) near-surface electronic structure.

The smooth symmetrical dispersion of Band I about the X point in Fig. 3 is strong evidence that the X point is a Brillouin zone boundary for the [010] near-surface electronic structure. This periodicity is consistent with that expected for an AF electronic structure. The periodicity of Band I's dispersion is certainly inconsistent with our expectations for a PM phase. We therefore interpret the dispersion of Band I in Fig. 3 as evidence that the near-surface valence electrons feel, and self-consistently establish,

antiferrogmanetism in the near-surface layers of Cr(001). This conclusion is also consistent with the flattening of Band II at the X point, although the absence of symmetrical dispersion for Band II is not understood. These properties confirm the early theoretical predictions by Allan[4-6] and Grempel[7] that the Cr(001) near-surface region is antiferromagnetic.

III. Cr(001) SURFACE ELECTRONIC STRUCTURE AND MAGNETISM

Figure 4 compares room-temperature normal-emission ARPES spectra of clean Cr(001) and Cr(001) exposed to 5 L of CO.[15] Note the sharp attenuation of the features with binding energies 0.16(5) eV (labelled 1) and 0.75(5) eV (labelled 2). The surface sensitivity of the features 1 and 2 in Fig. 4 indicates that these photoelectron peaks arise from initial states in the Cr(001) surface electronic structure. Since the polar angle of electron detection θ_e is zero, $k_{\parallel}^f = 0$ Å^{-1} for all photoelectron peaks in the spectra of Fig. 4. Features 1 and 2 therefore arise from initial states at the $\bar{\Gamma}$ point of the Cr(001) surface Brillouin zone. Figure 5 contrasts two normal-emission ARPES spectra of Cr(001) that use the P-and S-polarization geometry.[2] For the P-polarization normal-emission spectrum 5(a), only Δ_1 and Δ_5 initial states are allowed by the dipole selection rules[16] governing the photoelectric transition. Consequently at $\bar{\Gamma}$, the initial states 1 and 2 have either Δ_1 or Δ_5 symmetry. That feature 1 has Δ_1 symmetry and feature 2 has Δ_5 symmetry are shown by spectrum 5(b). For this S-polarization, normal-emission spectrum, only Δ_5 initial states are allowed.[16]

Surface feature 2, and to a lesser extent feature 1, were observed to display a temperature dependence. The binding energies of 1 and 2, $E_{IN}(1)$ and $E_{IN}(2)$, are plotted against temperature in Fig. 6. The thermal modification of $E_{IN}(2)$ is larger in magnitude and different in character than that of $E_{IN}(1)$. We have scaled and graphed in Fig. 6 the temperature-dependent bulk exchange splitting in nickel Δ_{ex}^{Ni} as measured by ARPES.[17] Note that $E_{IN}(2)$ decreases with temperature in a manner very similar to that of a ferromagnetic exchange splitting.

The comparison of these ARPES results with theory provides insight into the magnetic properties of the Cr(001) surface. The observed characteristics of feature 1 and 2 have found overall agreement with the first comprehensive calculation of Cr(001) surface electronic structure recenty completed by Victora and Falicov.[8] In agreement with Allan[4-6] and Grempel,[7] Victora and Falicov predict a ferromagnetic Cr(001) surface characterized by a very large (~3.00 electrons) surface spin polarization and an exchange-split surface electronic structure. Their work also predicts the symmetry-, wavevector- and layer-dependence of the initial states contributing to the surface electronic structure. When discussing the layer dependence of the Cr(001) surface electronic structure, the terms "majority spin" and "minority spin" become ambiguous. The label (+)-spin is used in reference to electrons whose spin magnetic moments lie parallel to the magnetization of the surface layer. Electrons whose moments lie antiparallel to the surface magnetization (but parallel to the second-layer magnetization) are identified as (-)-spin electrons.

The theoretical Cr(001) surface-layer and second-layer electronic structures of $k_{\parallel} = 0$ ($\bar{\Gamma}$) are shown in Figs. 7(a) and 7(b), respectively. A prominent Δ_5-symmetry (+)-spin surface state is predicted with energy 1.30 eV below (to the left of) E_F in Fig. 7(a). This is accompanied by a Δ_5-symmetry (-)-spin surface state with binding energy 1.2 eV in Fig. 7(b). Both surface states are located in a Δ_5-symmetry band gap of the surface-projected theoretical AF band structure.[11-14] A small Δ_1-symmetry (+)-spin surface state is also prediced with energy 0.68 eV above (to the right of) E_F in Fig. 7(a).

These aspects of the theoretical Cr(001) surface electronic structure at $\bar{\Gamma}$ are consistent with the ARPES results. We believe that the Δ_5-symmetry surface states in Figs. 7(a) and 7(b) can be associated with the photoelectron feature 2. The nearly degenerate theoretical surface states have binding energies near that observed for the Δ_5-symmetry surface feature 2. Victora and Falicov predict that as $k_{\parallel}$ increases along the $\bar{\Gamma}$-$\bar{X}$ line in the surface Brillouin zone both the (+)-spin and (-)-spin Δ_5-symmetry surface states will disperse toward larger binding energies. This dispersion is observed for the surface feature 2 in off-normal ARPES measurements.[2] Since the symmetry, binding energy, and binding energy variation with $k_{\parallel}$ of the surface feature 2 are consistent with the theory of Falicov and Victora, we assign the surface feature 2 to nearly degenerate Δ_5-symmetry (+)-spin and (-)-spin surface states at $\bar{\Gamma}$. As such, feature 2 would have d_{xz} and d_{yz} orbital character.

Figure 5 demonstrates that the surface feature 1 possesses Δ_1-symmetry. The only theoretical Δ_1-symmetry initial state near E_F is the unoccupied (+)-spin surface state with energy 0.68 eV above E_F in Fig. 7(a). Note that a companion Δ_1-symmetry (-)-spin surface state is not found in the second-layer electronic structure, Fig. 7(b). The true energy position of the (+)-spin surface state may be closer to E_F than predicted. This possibility, combined with the very sharp onset of the feature 1 spectral intensity at E_F, leads us to assign the Δ_1-symmetry surface feature 1 to a peaked spectral profile produced by the truncation of a Δ_1-symmetry (+)-spin surface state by the Fermi level. As such, feature 1 would have d_z2 orbital character. The overall agreement between theory[4-8] and the ARPES data indicate that the Cr(001) surface is in fact ferromagnetic. This interpretation, and the resemblance of feature 2's temperature dependence to Δ_{ex}^{Ni} (T) suggests that the temperature dependence of $E_{IN}(2)$ signals a Cr(001) surface magnetic phase transition.

IV. SUMMARY

Photoelectron spectroscopy measurements of Cr(001) have revealed the periodicity of the near-surface valence-band dispersions along the [010] direction parallel to the crystal surface. The results indicate that the valence electrons feel, and self-consistently establish, antiferromagnetism in the Cr(001) near-surface layers.

Two surface electronic features are observed in normal-emission ARPES. The binding energy, symmetry and dispersion of each feature is consistent with the latest theoretical calculations that predict a ferromagnetic Cr(001) surface phase on an otherwise antiferromagnetic Cr crystal. The temperature dependence of $E_{IN}(\underline{2})$ resembles a temperature-dependent ferromagnetic exchange splitting (Fig. 6). This behavior is interpreted as evidence for a surface magnetic phase transition on Cr(001).

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FIGURE CAPTIONS

FIG. 1. The AF (solid line) and PM (dashed line) Brillouin zones in the (100) mirror plane (defined by the [001] and [010] vectors). High symmetry points in the AF Brillouin zone are labelled with the conventional greek letters; those in the PM Brillouin zone are labelled with the appropriate letters enclosed by parentheses.

FIG. 2. ARPES specta of Cr(001) at 298 K. The photon energy $h\nu$ (eV) and the polar angle of electron detection θ_e (degrees), measured from the surface normal, are listed for each spectrum. The values $k_{\parallel}^{f}$ ($\AA^{-1}$) are the components of the final-state wavevectors parallel to the surface for the peaks labelled with a tic mark. The intensities of the spectra have been scaled to clarify the presentation.

FIG. 3. Experimentally observed band dispersions along the [010] symmetry line. Values of E_{IN} (eV) are ploted versus $k_{\parallel}^{f}$ ($\AA^{-1}$) for the features observed in our ARPES spectra. The size of the symbol gives the experimental error in E_{IN}. The greek letters at the top of the figure label the [010] symmetry line in the manner appropriate for simple cubic symmetry. The solid lines are the Γ-X-Γ band dispersions for commensurate AF chromium as calculated by Skriver (Ref. 12). Arabic numerals label the symmetry of these theoretical bands. A peak is observed at $E_{IN} \sim 0.25$ eV for many values of $k_{\parallel}^{f}$. A feature is also present for $k_{\parallel}^{f} < \sim 0.3$ $\AA^{-1}$ with $0.7 \leq E_{IN} \leq 0.9$ eV. Both have been previously assigned (Ref. 2) to the ferromagnetic surface electronic structure and are omitted from this figure for clarity.

FIG. 4. Normal-emission P-polarization ARPES spectra ($h\nu$ = 23.00 eV) of Cr(001) before (line) and after (dots) 5L CO exposure. The

contamination-induced peak at 6.7 eV binding energy is assigned to impurity (carbon and oxygen) 2p photoemission.

FIG. 5. The polarization dependence of surface features 1 and 2. (a): Normal-emission ARPES spectrum of Cr(001) (at 298 K) using the P-polarization geometry. (b): Normal-emission spectrum in S-polarization. The intensities of the spectra have been scaled to clarify the presentation. The photon energy is 21.22 eV for spectra (a) and (b).

FIG. 6. The binding energies of the surface features 1 and 2 plotted vs. temperature. The solid line is the temperature dependence of the bulk exchange splitting in nickel as measured by ARPES. This curve, reproduced from Fig. 2 of Ref. 17 and scaled in energy for comparison, should only be compared with the temperature dependence of feature 2.

FIG. 7. The theoretical Cr(001) surface-layer (a) and second-layer (b) electronic structure at $\bar{\Gamma}$, as calculated by Victora and Falicov (Ref. 2). For both (a) and (b) the (+)-spin surface electronic structure is indicated by the solid line; the (-)-spin surface electronic structure is drawn with the dashed line. The theory has been broadened in energy by a 0.6 eV Gaussian to simulate experiment. States to the left of E_F are occupied.