Momentum-Dependent Line Shapes in Photoemission

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(Received 23 September 1983)

The crystal-momentum dependence of the line shapes appearing in photoexcitation from the valence levels of ordered S on Fe(100) has been measured with angle-resolved photoelectron spectroscopy. The variation in line shape with $\vec{k}$ is a consequence of the hybridization of the energy bands of the two-dimensional overlayer with those of the three-dimensional solid. This observation, predicted theoretically by Liebsch, yields detailed information about the bonding interactions of ordered chemisorption systems.

PACS numbers: 73.20.Hb, 79.60.Gs

The physical origin of line shapes in the photoexcitation process has been a subject of great interest for many decades. This has led to a number of descriptive models. The simplest mechanism for line broadening in photoelectron spectroscopy is the hole lifetime. A hole created by the absorption of a photon can decay, primarily by the Auger process or by photon emission, leading to a Lorentzian line shape.[1] Additional broadening may occur by the coupling of the photoexcitation process to many-electron excitations (electron-hole pair creation) or phonons of the system. The phonon coupling leads to a temperature-dependent Gaussian broadening,[2,3] while creation of electron-hole pairs in a metal produces an asymmetric line shape as a result of the Mahan–Nozières–De Dominicis[4] x-ray edge singularity.

In a recent angle-resolved experiment, Kevan has argued that the observed anomalous $k_{\parallel}$ dependence ($k_{\parallel}$ is crystal momentum parallel to the sample surface) of the linewidth of the sp surface state on Cu(111) is a ground-state phenomenon resulting from surface defects.[5] We report in this Letter the first observation of momentum-dependent linewidths for photoemission from the valence levels of an ordered two-dimensional overlayer on a single-crystal substrate. The chemisorption system used for this work was $c(2\times2)$S/Fe(100). The line-shape effect that we see is a one-electron property, originating in the interaction (hybridization) of the overlayer states with the substrate continuum. This effect, which is characteristic of the ideal ($k_{\parallel}$-conserving) surface, has been predicted by Liebsch,[6] and is reminiscent of the linewidths of intrinsic surface states versus surface resonances. It will be demonstrated that momentum-dependent linewidth data for an ordered overlayer yields new information concerning the bonding of adsorbate atoms to a surface.

Liebsch has calculated momentum-dependent linewidths for the system $c(2\times2)$ oxygen on Ni(100).[6] Figure 1 is taken from his paper and will be utilized to illustrate the physics of the

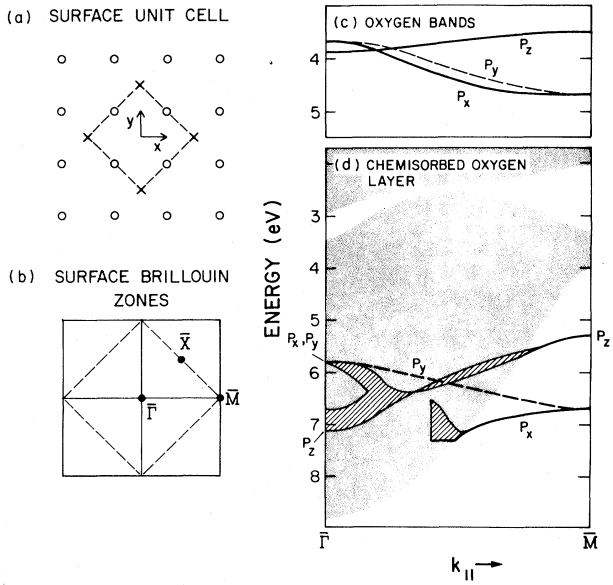

FIG. 1. (a) Real-space unit cell for $c(2\times2)$O on Ni(100) system (crosses are O atoms); (b) reciprocal-space Brillouin zone for clean Ni(100) (solid lines) and $c(2\times2)$O; (c) energy bands for isolated oxygen layer; and (d) energy levels for $c(2\times2)$O chemisorbed on Ni(100). The shaded regions indicate the projection of the even bulk bands.

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phenomena described in this article. For the sake of brevity we will describe only the results of the calculation and our data along the $\bar{\Gamma}\bar{M}$ line in the surface Brillouin zone [SBZ—see Fig. 1(b)]. Figure 1(c) shows the calculated energy bands for the isolated oxygen layer with the spacing appropriate to the $c(2\times2)$O on Ni(100) geometry. The levels formed from the p_z and p_x oxygen wave functions are even with respect to the mirror plane defined by the $\bar{\Gamma}\bar{M}$ direction and the z axis (perpendicular to the plane), while the p_y levels are odd. Figure 1(d) illustrates the effect of the Ni substrate on the oxygen levels. The shaded regions of this panel indicate the projections of the three-dimensional (3D) Ni energy bands onto the SBZ. Only the even Ni bands are shown, since the odd-symmetry bands lie energetically above the smallest oxygen binding energy of Fig. 1(d). The cross-hatched regions indicate the broadening of the O $2p$-derived levels along the bands upon chemisorption. The basic results can be summarized as follows: (1) The bonding for this system is principally through the O(p_z)-Ni(sp) interaction. (2) The position and shape of the oxygen-derived bands have changed appreciably as a result of interaction with the Ni substrate. (3) The even p_z- and p_x-derived oxygen bands hybridize because the inversion symmetry of the O layer is broken by the presence of the Ni substrate. (4) The oxygen-derived levels exhibit an appreciable width when they overlap the projection of the bulk bands, because of hybridization with the Ni levels. The width of each level at a given $k_{\parallel}$ is then a direct measure of the hybridization of the adsorbate band with the substrate band. Note that $k_{\parallel}$ is a good quantum number for both the 2D and 3D systems, so only levels with the same energy and $k_{\parallel}$ can mix. For example, the p_z level at $\bar{\Gamma}$ has ~0.5 eV width. In contrast, the p_z level at $\bar{M}$ and the odd-symmetry p_y levels for all $k_{\parallel}$ lie outside of the projection of the bulk bands and are consequently discrete.

The measurements described here were made at the Tantalus I storage ring of the University of Wisconsin with use of the University of Pennsylvania beam line. The procedure for these types of experiments has been described in detail in other articles.[7] The sample was prepared by segregating sulfur to the surface of a clean Fe(100) single crystal in order to form a $c(2\times2)$ low-energy electron-diffraction (LEED) pattern.[8] Previous LEED measurements have determined that the S sits in a fourfold site at 1.1 Å above the Fe(100) plane.[9] Smooth backgrounds were subtracted from the measured photoemission spectra, and the S features were deconvoluted by Gaussian fitting. (The observed S peaks were well described by Gaussians, which were chosen for their computational simplicity. Lorentzian fitting does not alter the basic results of this study.) Corrections were made for line-shape broadening effects due to the finite angular acceptance of the electron analyzer. The recorded widths are believed to be accurate within ±10%.

Figure 2 shows the measured dispersion and level width at each $k_{\parallel}$ of the $3p_y$-derived S band, whose levels are of odd symmetry with respect to the $\bar{\Gamma}\bar{M}$ mirror plane. The odd-symmetry Fe bands lie energetically above the band of Fig. 2(a) and therefore cannot hybridize with it. Thus the measured linewidths must be a consequence of lifetime broadening and any additional many-particle effects associated with the photoexcitation process. Figure 2(b) plots the full width at half maximum (FWHM) of the levels along this band as a function of $k_{\parallel}$. The measured width is 1.0 eV ± 0.15, independent of energy or $k_{\parallel}$.

Figure 3(a) shows the measured dispersion of the even S bands from the zone center at $\bar{\Gamma}$ out to the second zone center. (The shaded region shows the projection of the even Fe bands.) It is easy to see the hybrization of the p_x and p_z bands along $\bar{\Gamma}\bar{M}$. The top band starts out with a pure p_x-derived level at $\bar{\Gamma}$ and disperses downward until it mixes with the p_z band. Thus, the top band level at $\bar{M}$ is pure p_z in character.[6] Figures 3(b) and 3(c) plot the hybridization contribu-

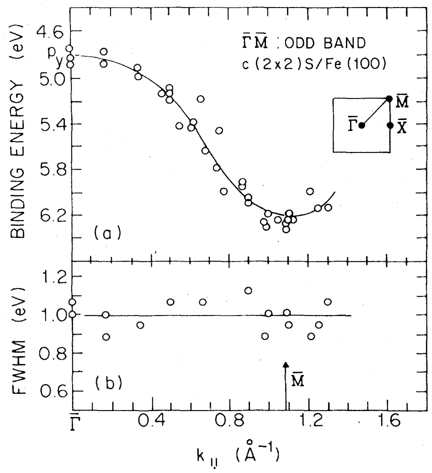

FIG. 2. Dispersion of the odd-symmetry S p_y band. (b) Linewidth (full width at half maximum) of the levels along the S p_y band.

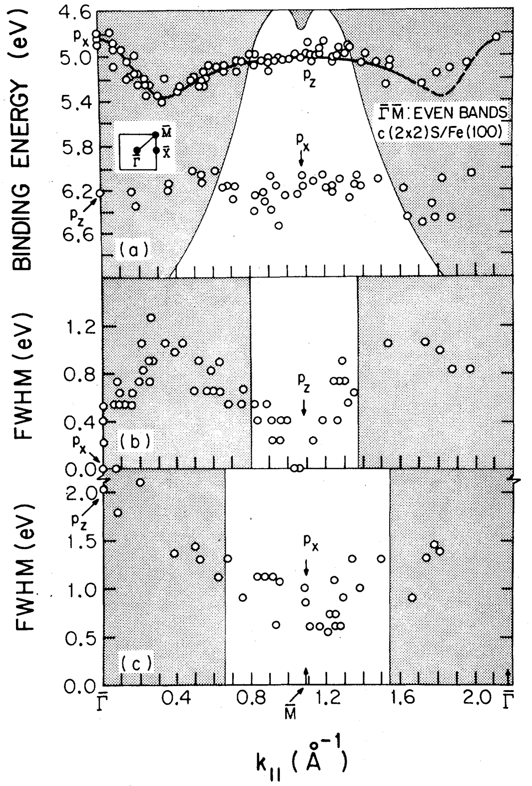

FIG. 3. (a) Dispersion of the two even S bands. The shaded region is the projection of the bulk bands. (b) Hybridization widths along the upper band in (a). (c) Hybridization widths along the lower band in (a).

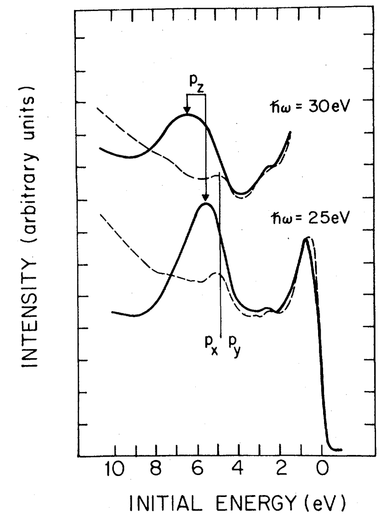

FIG. 4. Normal emission spectra of $c(2\times2)$S on Fe(100) illustrating the $\hbar\omega$ dependence of the S $3p_z$ line shape at $k_{\parallel}=0$. (Dashed and solid lines indicate s- and p-polarized incident radiation, respectively.)

tion to the widths after removal of a constant width of 0.85 eV. This width was assumed to be constant for all $k_{\parallel}$ based on the odd-band results of Fig. 2(b). The value of 0.85 eV was selected to yield zero hybridization broadening at $\bar{M}$, where the narrowest levels (even and odd) are observed. The shading in these figures indicates where the bands lie on top of the projected Fe *sp* bands, as determined from Fig. 3(a). The functional behavior of the linewidths can be qualitatively explained by use of Liebsch's model:

(1) Figure 3(b) shows the hybridization width for the top band of Fig. 3(a). At $\bar{\Gamma}$, the p_x-derived level is not broadened since it cannot mix with the substrate s-p band for symmetry reasons.[6] Upon leaving $\bar{\Gamma}$, this level no longer has the full p_x symmetry and broadens by mixing with the Fe *sp* levels. Once it has crossed out of the projected Fe bands, however, the level returns at $\bar{M}$ to the intrinsic width seen for the odd-band levels.

(2) Figure 3(c) shows the hybridization widths for the levels along the bottom band of Fig. 3(a). At $\bar{\Gamma}$, the width is very large (~2 eV) because of the large hybridization of the S p_z level with the Fe *sp* levels of the same $k_{\parallel}$. The width becomes gradually smaller in proceeding across the SBZ as more p_x character is introduced, and less hybridization with the bulk levels occurs. Finally, the band crosses out of the projected Fe bands and the levels show almost no hybridization broadening at $\bar{M}$, indicating that lifetime broadening is responsible for the widths near this point.

When the above results for $c(2\times2)$S/Fe(100) are compared with a previous photoemission study of $c(2\times2)$S/Ni(100),[10] and the theoretical calculation for $c(2\times2)$O/Ni(100),[6] it can be concluded that the S($3p_z$)-Fe(*sp*) interaction is much more pronounced in this system. Thus the observation of $k_{\parallel}$-dependent linewidths can provide important information about the nature of the chemisorption bond.

There are two observations that we made about this system that were not anticipated by Liebsch's calculation.[6] The first is that the hybridization linewidths shown in Fig. 3 continue to vary with $k_{\parallel}$ even after the S level has moved out of the bulk band projections, qualitatively similar to Kevan's observation for the surface state on Cu(111).[5] The effect we observe is too large to attribute to $k_{\parallel}$ smearing due to surface defects, however. This effect could result from the coupling of the hole lifetime width with the $k_{\parallel}$-resolved hybridization width. In an independentparticle picture similar to the one used by Liebsch,[6] the S levels are discrete when they lie outside of the projection of the bulk bands. In Fig. 2, however, there is ~1 eV width in these regions due to the hole lifetime. This finite lifetime for the state characterized by $E(k_\parallel)$ implies an uncertainty in $k_\parallel$ and E allowing bulk 3D states to hybridize with surface 2D states even when they appear to be separated in E-$k_\parallel$ space.

The second observation is depicted in Fig. 4, where we show two measured energy distributions. The collection geometry is normal to the crystal ($\bar{\Gamma}$ in the SBZ), and the photon energy and polarization of the incident light have been varied. The dashed curves are for nearly s-polarized light where only the $p_x p_y$ levels can be excited, while the solid curves are for p-polarized light where all levels can be excited. As the photon energy is changed, the energy position and width of the $p_x p_y$ level is unchanged as it should be for a two-dimensional system.[7] In contrast, the p_z level moves in energy and its width increases appreciably as $\hbar\omega$ is changed from 25 to 30 eV. At first glance, this observation seems to violate the contention that we are looking at a 2D band structure where the levels are described by $E(k_\parallel)$. The origin of this shift in the p_z level with photon energy is the large hybridization of the S p_z with the Fe s-p bands. This feature in the photoemission spectra contains large admixtures of S p_z and Fe s and p wave-function character, with each having a slightly different local density of states. As the photon energy is changed the cross-sectional variation of each component is different resulting in apparent changes in the line shape and position.

This work was supported by the U. S. Office of Naval Research. The University of Pennsylvania beam line is supported by the National Science Foundation through Materials Research Laboratories Contract No. DMR-8216718. We would like to thank the staff of the Synchrotron Radiation Center at the University of Wisconsin for their assistance, and Professor P. Soven for his helpful comments.

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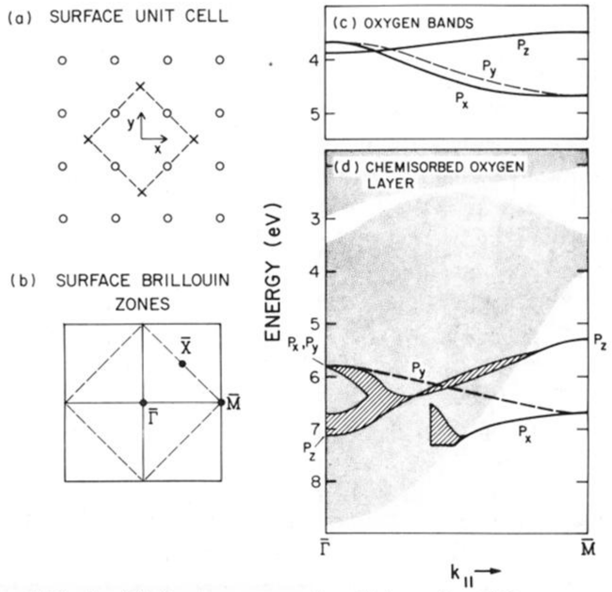

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