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High-resolution 4f photoemission spectra from clean W(110) show that the natural lifetime width and the (electron-hole)-pair singularity index are both larger in the first atomic layer than in the bulk. Photon broadening for the surface and bulk components are smaller than theoretical estimates, and little excess broadening is detected in the surface layer. These findings are very different from the conventional picture of surface-atom core-level line shapes and have implications extending to other systems.

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It is now well established that core-level photoemission is a sensitive probe for studying the effects of the reduced coordination at the surface.1 With this spectroscopy the primary focus has been on the shift of the surface-atom core-level binding energy, whose sign and magnitude have been shown to be directly related to the narrowing and shape of the surface density of states.2-4 Studies of this shift as a function of material, crystal orientation, reconstruction, depth below the surface (i.e., subsurface layer shifts), adsorbate, and coverage exemplify the wide range of activity and interest in this area.1,5,6 However, the investigation of other manifestations of the reduced coordination at the surface, such as changes in core-hole lifetime, conduction-electron screening, and phonon broadening has been hampered by a lack of adequate experimental resolution and statistics. Indeed, while the excess width of the surface-atom core level in just a single metal, W, has been tentatively ascribed to additional surface phonon broadening, crystal-field splitting, reconstruction, and subsurface contributions,5,7,8 no measurement has yet succeeded in clearly identifying the broadening mechanisms operative at the metal surface.

In this Letter we report on high-intensity, high-resolution core-level photoemission measurements from a clean W(110) surface. We find that the major contribution to the increased surface linewidth in this metal involves none of the previous suggestions, but is, instead, enhanced lifetime broadening resulting from the more localized 5d electrons in the narrowed surface conduction band. In addition, we find differences in core-hole screening between the surface and bulk components which are manifest as a measurable difference in the shape of the (e-h)-pair excitation tail of the photopeak. These novel results are not specific to W, and should apply to a large number of systems in which conduction electrons dominate the core-hole decay.

The single-crystal sample of dimensions 4×20×0.2 mm³ was cleaned by resistive heating to 1520 K in 10⁻⁷ Torr of oxygen followed by flashing to 2300 K in a vacuum of 1×10⁻¹⁰ Torr. After cooling to either 210 or 310 K, which took only seconds due to the large difference in thermal mass between the sample and its mount, photoemission data were collected using the AT&T Bell Laboratories 6-m toroidal-grating monochromator (TGM) on the vacuum-ultraviolet ring of the National Synchrotron Light Source. A 100-mm voltage standing-wave hemispherical analyzer was used with a pass energy of 2 V, which gives a resolution of 40 meV (FWHM). The high intensity of the monochromatized radiation (70 eV for all measurements reported here) allowed single 2.5-eV scans with high statistics to be obtained in only 4 min, during which time the average surface H contamination is estimated not to exceed 0.01 monolayer.

The total instrumental resolution was determined from thirteen independent measurements of the Fermi cutoff of the W(110) crystal, yielding an average value of 83±3 meV FWHM. (The error bars quoted here and throughout the paper represent a 95%-confidence level, based on deviations from the mean of results obtained from fitting a large number of independent data sets.) Subtraction of the electron analyzer width yields a photon resolution of 73 meV, which is consistent with earlier determinations based on the much sharper Fermi edge of Cu at 90 K. Analysis of both Cu and W Fermi edges confirms that the resolution function is very well approximated by a Gaussian.

The clean W(110) surface is ideally suited for studying the broadening mechanisms of surface-atom core levels. The 4f states are long lived (i.e., the photopeaks are narrow) and there is no surface reconstruction.9 Moreover, for this close-packed surface, photoemission from subsurface layers should be indistinguishable from that from the bulk because the nearest- and next-nearest-neighbor coordinations of the subsurface atoms are identical to the bulk values. A complete photoemission spectrum of the W 4f lines from a freshly cleaned surface (see inset in Fig. 1) shows four lines. The >2 eV separation of the j=½ and ½ spin-orbit doublet allows the individual components to be analyzed separately. Furthermore, the bulk and surface lines in the 4f⁷/₂ data are so well resolved and have such high statistics that independent values of the natural Lorentzian lifetime width, the Gaussian phonon and instrumental broadening, and the core-hole screening singularity index for each of the lines can be readily obtained.

The fit to the 4f⁷/₂ data is shown in Fig. 1. Its quality
FIG. 1. Analysis of the W 4f \( \frac{7}{2} \) photoemission spectrum of a clean W\((110)\) surface. The data, taken with 70-eV photons, are fitted with a linear background and two fully independent lines, representing the surface (right) and bulk (left) contributions. The residuals of the fit are shown in the bottom panel. Inset: A scan encompassing the W 4f \( \frac{7}{2} \) and 4f \( \frac{5}{2} \) components.

can be critically assessed by the residuals, which exhibit no systematic deviations and show only the fluctuations due to counting statistics. This immediately demonstrates that one cannot hope to isolate a third component, viz., the signal from the second atomic layer, by least-squares analysis because its binding-energy shift is much smaller than the Gaussian width. Accordingly, we have restricted ourselves to a two-component analysis. Eighteen independent data sets were analyzed using two fully independent Doniach-Šunjic\(^{10}\) (DS) lines convolved with independent Gaussians to test the reproducibility of the output parameters. The resulting width and shape parameters for the bulk and surface lines contain a number of surprises.

(1) The surface-atom core-level shift is 321 ± 1 meV. This value is decidedly larger than the splitting of 300 meV obtained from earlier data with lower resolution.\(^{11}\) In a related experiment we found that this splitting is reduced by adsorbed hydrogen [initially changing by about −50 meV/L, 1 L (Langmuir) = 10\(^{-6}\) Torr sec, of H\(_2\) exposure], demonstrating that great care must be exercised to maintain a clean surface during the measurement.

(2) We find that the independently determined Gaussian widths of the bulk and surface components are very similar at 210 K: 94.5 ± 2.7 and 96.0 ± 1.4 meV, respectively. At 310 K the difference is only slightly larger, 100.8 ± 4.4 meV for the bulk and 105.7 ± 1.4 meV for the surface. Subtracting the instrumental resolution in quadrature from the total Gaussian width results in an excess width for the bulk (surface) of 45.4 ± 7.6 (48.4 ± 5.5) at 210 K and 57.3 ± 8.7 (65.6 ± 4.2) at 310 K. The temperature dependence immediately identifies these widths, which are plotted in Fig. 2, as being due to phonons excited during the photoemission process.\(^{12}\) The room-temperature values are significantly smaller than the semiempirical estimate of 109 meV,\(^{13}\) and both values are smaller than the theoretical estimates of 76 and 88 meV\(^{14}\) for bulk W at the corresponding temperatures (also shown in Fig. 2).

Although the measured phonon broadening is less than that expected from either calculation above, the results for the temperature dependence, along with the slight difference in surface and bulk values, are both consistent with an estimation based on the bulk and surface Debye temperatures of W\((110)\). Using the bulk width at 310 K as the reference point and a bulk Debye temperature of 310 K\(^{15}\) gives the dashed line in Fig. 2. Keeping the coupling strength to the phonons constant but lowering

FIG. 2. Experimental phonon widths of the bulk and \((110)\) surface W 4f \( \frac{7}{2} \) levels compared with the results of two theoretical calculations.

the Debye temperature to 250 K, a value appropriate for
the W(110) surface,\(^{16}\) produces the dot-dashed curve
which just intersects the error bars on the surface data.
Thus, although the difference in phonon broadening is
too small to discern any significant difference between
the surface and the bulk, the data are consistent with a
simple interpretation of a Debye-phonon excitation spec-
trum in the limit of a Gaussian line shape.

(3) In contrast to the small difference observed in the
phonon broadening, the data clearly show that the core-
hole lifetime width is distinctly larger at the surface than
in the bulk. Figure 3 demonstrates that there is no dif-
ficulty in separating the Gaussian and Lorentzian contri-
butions to the linewidth. Analysis of the eighteen data
sets yields a width of 60 ± 3 meV for the bulk and 84 ± 3
meV for the surface. The value for the lifetime width of
the bulk line is in satisfactory agreement with earlier
determinations,\(^{7}\) which were 55 and 61 meV.

Since the \(4f_{7/2}\) hole state decays almost entirely by
\(N_{2}O_{4.5}\) Auger transitions [the fluorescence yield is
only \(7 \times 10^{-6}\) (Ref. 17)], one can look for an explanation
of the increased width at the surface by focusing on the
properties of the metal 5d band. Starting with the free
W atom, there will be two opposing effects on the \(4f_{7/2}\)
lifetime in forming the metal. On the one hand, the
Auger decay rate will be enhanced because the \(d\)-band
occupancy is increased both by reconfiguration in the ini-
tial state and by metallic 5d core-hole screening in the
final state. On the other hand, the Auger decay rate will
be reduced by the delocalization of the 5d conduction
electrons, which decreases the overlap between the 4f
and 5d orbitals. The larger lifetime width observed in
the surface relative to the bulk, then, clearly implies that
the reduced delocalization in the narrowed, more atomic-
like surface 5d band is the dominant mechanism.

(4) The singularity index, \(\alpha\), of the bulk and surface
lines are also different, 0.035 ± 0.003 and 0.063 ± 0.003,
respectively (the rms deviations from the mean are small
because the coupling of \(\alpha\) to the other parameters is very
weak). The small absolute values of \(\alpha\), compared to,
e.g., the simple metals Na, Li, Mg, and Al,\(^{12}\) are a con-
sequence of the larger fraction of screening charge
residing in orbitals of higher angular momentum. The
bulk value of \(\alpha\) is close to the minimum value of \(\frac{1}{3}\) ob-
tainable for screening by \(s, p, d,\) and \(f\) orbitals. By
showing that the valence-band excitation spectrum is ap-
proximately constant from 0 to 5 eV, Sébilleau et al.\(^{14}\)
have demonstrated that the DS line shape is appropriate
for W. Their calculated values for \(\alpha\) are, however, ap-
proximately the same for bulk and surface and are in
agreement only with our surface value.

Our results for the W(110) surface have significant
implications on some of the earlier interpretations of
surface-atom core-level measurements.\(^{1,2,8}\) For ex-
ample, the present findings indicate that the excess width
of the surface signal from Ta and other W surfaces is due
almost solely to the increased natural width of the core
hole, \(\sigma\), the other broadening mechanisms which have
been proposed. For the W(111) surface we have con-
firmed that the extant data are compatible with this con-
clusion, but the resolution of the data does not allow in-
dependent Gaussian- and Lorentzian-width parameters
to be determined for the bulk and surface lines. In gen-
eral, it should certainly not be assumed, as has been done
in the past, that the natural width is the same in the bulk
and surface, especially when it is determined primarily
by Auger processes involving valence electrons. More-
over, the singularity index should not be assumed to be
unchanged at the surface, even when the absolute bulk
value is small.

FIG. 3. Distinguishing between Gaussian and Lorentzian
broadening. The bottom panel shows a cut through the \(\chi^2\) sur-
face of a least-squares analysis of the data in Fig. 1. For
the purpose of this demonstration only, a common Gaussian width
was used for both surface and bulk photopeaks, leaving the
other parameters unconstrained. (The use of a common
Gaussian width in these data is justified by the fact that the
bulk and surface lines are so well separated.) The correspond-
ing natural Lorentzian widths and singularity indices are
shown above. The clearly defined minimum in \(\chi^2\) demonstrates
that the Lorentzian lifetime and Gaussian phonon broadenings
are readily distinguishable in these data.
In summary, we have shown that the modification of the electronic properties at the surface readily accounts for the changes in the core-electron photoemission spectra from the first atomic layer of W(110). There is no anomalous phonon broadening, no evidence for crystal-field splitting, and no need to postulate unresolved lines from subsurface layers. The important phenomena at the surface are the changes in the natural width and the conduction-electron screening. These conclusions depart from all previous interpretations of surface-atom core-level spectra and are not limited to W(110). We anticipate that the higher-energy resolution and beam intensities now obtainable from improved synchrotron sources and beam-line optics should open up a variety of systems from which new conclusions about surface photoemission will emerge.

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