York, 1971), p. 23.
[22]G. D. Watkins and R. P. Messmer, to be published.
[23]G. D. Watkins, J. Phys. Soc. Jap. 18, Suppl. II, 22 (1963).
[24]R. Keown, Phys. Rev. 150, 568 (1966).
[25]K. H. Johnson, J. G. Norman, Jr., and J. W. D. Connolly, in *Computational Methods for Large Molecules and Localized States in Solids*, edited by F. Herman, A. D. McLean, and R. K. Nesbet (Plenum, New York, 1973), p. 161.
[26]J. Callaway and C. S. Wang, Phys. Rev. B 7, 1096 (1973).

Auger Observation of a Surface State on Tungsten

N. R. Avery
Commonwealth Scientific and Industrial Research Organization, Division of Tribophysics, University of Melbourne, Parkville, Victoria 3052, Australia
(Received 8 October 1973)

Fine structure in the N_7VV Auger spectrum from a W(100) surface has been observed and attributed to emission from a surface state, and from three peaks in the bulk density of states.

Recent theoretical work by Forstmann and coworkers[1] has proposed the existence of surface states on d-band metals. On the (100) surface of tungsten the presence of a surface state 0.4 eV below the Fermi level (E_F) has been demonstrated by total-energy analysis of field-emitted electrons,[2] and more recently by photoelectron-energy distributions.[3-5] The distinguishing feature of this state is its sensitivity to the presence of adsorbates on the surface. For example, it is almost completely eliminated by an exposure of 0.3 L (1 L = 10^{-6} Torr sec) to hydrogen. Taking the sticking coefficient as 0.23[4] this corresponds to only 2.5×10^{14} molecules cm^{-2}, or half a monolayer of dissociatively chemisorbed hydrogen. The purpose of this Letter is to report fine structure in the N_7VV Auger spectrum from a W(100) surface which can be attributed to emission from a surface state in addition to emission from prominent features in the bulk density of states (DOS).

The experiments were performed in a Vacuum Generators four-grid, low-energy electron-diffraction, Auger apparatus equipped with a side electron gun and a Riber quadrupole mass spectrometer. The residual gas consisted almost exclusively of hydrogen at a base pressure of 3×10^{-10} Torr (corrected for ionization-gauge sensitivity). Auger emission was excited by a finely focused 700-eV electron beam from the side gun at ~30° incidence. The crystal was in the form of a thin ribbon and was cleaned *in situ* by flashing in the presence of oxygen for many hours. Prior to recording the Auger spectra by the normal ac modulation technique the crystal was flashed clean at 2500 K and cooled to < 400 K in 30 sec.

Although the secondary-electron spectrum of tungsten revealed several peaks in the low-energy range (~60 eV) which may be conceivably due to Auger emission of the core-VV type,[6] only the strong N_7VV emission centered at ~22 eV contained fine structure when the modulation voltage was reduced to 1 V peak to peak. This fine structure was not resolved at, for example, 3 V peak to peak. As a result of the large secondary-electron cascade in this region, features in the spectrum could not be seen in the $N(E)$ trace. Instead, all spectra were recorded in the more usual differentiated form, viz., $N'(E)$ versus E. The N_7VV spectrum shows a maximum positive excursion at 13 eV and six resolvable inflexions during its negative excursion corresponding to peaks in the emission at 25.5, 23.3, 21.5, 20.2, 18.7, and ~17 eV. The 25.5-eV emission is identified as originating from a surface state (labeled S) and accordingly designated N_7SS, on the basis of its behavior with small exposures of hydrogen. Thus, Fig. 1 shows that an exposure of 0.18 L almost completely attenuated this emission which was then essentially eliminated when the exposure was increased to 0.48 L.

With S at -0.4 eV from the previously cited studies,[2-5] the emission edge corresponding to both the *up* and *down* electrons originating from E_F occurs at 26.3 eV and the total emission width is estimated to be ~15 eV. This emission edge is slightly lower than the 28.4 eV which was calculated using an N_7 binding energy of 32.5 eV[7] and a measured analyzer work function of 4.1 eV.

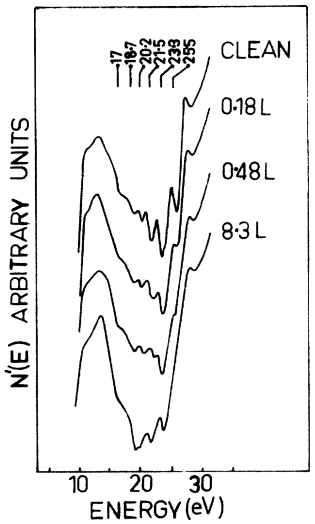

FIG. 1. $N_{6,7}VV$ Auger spectra recorded in the derivative mode [$N'(E)$ versus E] for a clean W(100) surface and with increasing exposure to hydrogen (1 L $\equiv 10^{-6}$ Torr sec).

The remaining five approximately evenly spaced features in the spectrum of clean W(100) are attributed to emission from structure in the DOS in the manner originally proposed by Lander.[8] In the absence of initial- and final-state effects or a dependence of transition probability on band energy, such core-VV Auger spectra should be given simply by the derivative of the self-convolution of the DOS, which may then be broadened by lifetime or instrumental effects. A best fit with the position of these features in the spectrum is obtained from three approximately equally spaced peaks in the DOS at -1.5, -3.1, and -4.5 eV, which are designated V_1, V_2, and V_3, respectively (Table I).

The experimental spectrum for clean W(100) may be compared with that expected from the theoretical bulk DOS computed by Mattheiss[9] with a $V_1(r)$ potential which shows three peaks in the DOS at -1.5, -3.2, and -4.6 eV in close agreement with the present estimates. Furthermore, the computed DOS shows that the two peaks corresponding to V_1 and V_2 are sharp (full width at half-maximum, 0.6 eV) leading to conspicuous $V_1'*V_1$, $V_1'*V_2$, and $V_2'*V_2$ features, whereas the $V_1'*V_3$, $V_2'*V_3$, and $V_3'*V_3$ features are broadened by the V_3 level (full width at half-maximum, 1.3 eV). This trend is in agreement with the observed spectrum where the higher-energy features are more conspicuous than those at lower energies.

TABLE I. Comparison of calculated and observed features of the N_7VV Auger spectrum.

Transition	Calculated[a] (eV)	Observed (eV)
N_7SS	25.5	Reference[b]
$N_7V_1V_1$	23.3	23.3
$N_7V_1V_2$	21.7	21.5
$N_7V_1V_3$	20.3	20.2
$N_7V_2V_2$	20.1	
$N_7V_2V_3$	18.7	18.7
$N_7V_3V_3$	17.3	~17

[a]For S at -0.4, V_1 at -1.5, V_2 at -3.1, and V_4 at -4.5 eV.

[b]The N_7SS emission at 25.5 eV was taken as a reference from which the other transitions were calculated.

The theoretical self-convolution of the DOS did not show the large positive excursion that was exhibited by the experimental curve at 13 eV which consequently must be attributed to increased emission from the bottom of the band. This may arise as a result of a modification of the bulk DOS at the surface, or alternatively as a result of enhanced emission from the s-like states near the bottom of the band as has been proposed for aluminum.[10] The total width of the spectrum (~15 eV) is also in good agreement with the value of 13.6 eV that was obtained from the theoretical DOS. When compared with Mattheiss's bulk DOS this portion of the W(100) Auger spectrum shows satisfactory agreement with the criteria of (1) φ threshold, (2) linewidth, (3) $2E$ peak shift, and (4) two-peak multiplication, as proposed by Sickafus.[11] The associated Auger emission involving the N_6 core level at -34.5 eV[7] produced a very weak emission at 27.5 eV. Although this N_6VV transition should be almost as strong as the N_7VV transition on the basis of relative populations,[12] it is suggested here that its low intensity is due to a depopulation of the N_6 hole by an N_6N_7V Coster-Kronig transition. In addition to eliminating the N_7SS emission, hydrogen adsorption also produced changes in the N_7VV part of the spectrum (Fig. 1). Integration of the $N'(E)$ traces showed that the energy distribution curve, $N(E)$, developed a broad region of enhanced emission at 13–21 eV, which may be attributed to an increase in the DOS between -2.5 and -6.2 eV. The $N'(E)$ curves indicate that in this region a peak in the emission at ~18 eV developed which may be due to a new adsorbate-induced level at -4.2 eV if both the *up* and

down electrons originate from this level.

The fine structure in the N_7VV Auger spectrum of W(100) has been interpreted as arising from emission from a valence band with three prominent peaks in the bulk DOS and a surface state which does not interact with the bulk states, i.e., Auger transitions of the type N_7SV are not important. Whereas previous observations of the surface state by the one-electron photoemission and field-emission processes were based on its sensitivity to adsorbates, the two-electron Auger process has demonstrated more directly that S is a localized state. Although the emissions at 21.5 and 23.3 eV were attenuated by the same low exposures to hydrogen that attenuated the N_7SS emission at 25.5 eV, the possibility of these emissions being dominated by processes involving both S and V levels was rejected for the following reasons. (1) Although increasing hydrogen exposure should attenuate an N_7SV emission more slowly than the N_7SS emission, the 21.5- and 23.3-eV emissions are still conspicuous when S has effectively been eliminated with exposures in excess of ~0.3 L. (2) The equivalent N_7VV spectrum from a clean W(110) surface, which does not exhibit a surface state, was very similar to that of a W(100) surface with the exception that the 25.5-eV emission was absent. The 21.5- and 23.3-eV emissions were as conspicuous as those observed from W(100) surface indicating that they are probably of a common origin. With the exception of the localized surface state on the W(100) surface the valence bands of the W(100) and W(110) surfaces seem to be similar to each other and to the bulk valence band. Although recent electron-energy-loss spectroscopy studies[13,14] have suggested differences in valance bands at the two surfaces, a reexamination of the W(100) surface in this laboratory has shown a similar loss spectrum to that reported for the W(110) surface provided that the incident electron beam is at normal incidence.

Recent high-resolution studies of Auger transitions involving the valence band of conductors have proposed that the additional fine structure, which cannot be explained on a pure jj coupling scheme, arises from multiplet splitting of an atomiclike final state[10,15-18]. The present results for tungsten suggest that the pertinent features of the N_7VV spectrum can be adequately accounted for by a simple bulk DOS and a surface state model with an increase in emission towards the bottom of the band, without recourse to final-state effects. The sensitivity of the fine structure to the presence of adsorbates on the surface should argue against an atomiclike final state, which instead appears to reflect more the role of the band in the emission of N_7VV Auger electrons from tungsten.

[1]F. Forstmann and V. Heine, Phys. Rev. Lett. 24, 1419 (1970), and references therein.
[2]E. W. Plummer and J. W. Gadzuk, Phys. Rev. Lett. 25, 1493 (1970).
[3]B. J. Waclawski and E. W. Plummer, Phys. Rev. Lett. 29, 783 (1972).
[4]B. Feuerbacher and B. Fitton, Phys. Rev. Lett. 29, 786 (1972).
[5]J. M. Baker and D. E. Eastman, J. Vac. Sci. Technol. 10, 223 (1973).
[6]E. J. Scheibner and L. N. Tharp, Surface Sci. 8, 247 (1967).
[7]T. A. Carlson and G. E. McGuire, J. Electron Spectrosc. Relat. Phenomena 1, 161 (1972).
[8]J. J. Lander, Phys. Rev. 91, 1382 (1953).
[9]L. F. Mattheiss, Phys. Rev. 139, A1893 (1965).
[10]C. J. Powell, Phys. Rev. Lett. 30, 1179 (1973).
[11]E. N. Sickafus, Surface Sci. 36, 472 (1973), and Phys. Rev. B 7, 5100 (1973).
[12]W. A. Coghlan and R. E. Clausing, At. Data 5, 317 (1973).
[13]D. Edwards and F. M. Propst, J. Chem. Phys. 55, 5175 (1971).
[14]N. R. Avery, Surface Sci. 32, 477 (1972).
[15]C. J. Powell, Phys. Rev. Lett. 29, 1153 (1972).
[16]L. Yin, T. Tsong, I. Adler, and E. Yellin, J. Appl. Phys. 43, 3464 (1972).
[17]P. J. Bassett, T. E. Gallon, J. A. D. Matthew, and M. Prutton, Surface Sci. 35, 63 (1973).
[18]S. P. Kowalczyk, R. A. Pollak, F. R. McFeeley, L. Ley, and D. A. Shirley, Phys. Rev. B 8, 2387 (1973).