Surface Structure of Thermionic-Emission Cathodes

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(Received 20 May 1986)

We have used surface extended x-ray-absorption fine structure (SEXAFS) to study the local geometry around barium atoms on thermionic cathodes. On the surfaces of tungsten and tungsten-osmium alloy dispenser cathodes, Ba is bonded to oxygen with a well-defined short-range order. The Ba-O distance is similar (2.62 ± 0.04 Å) for the two cathodes, with oxygen atoms occupying hollow sites of the substrate. However, the alloy cathode has Ba bonded to two oxygen near neighbors (compared to one for the tungsten cathode), which will enhance the surface dipole, thus explaining the observed lower work function.

Surface extended x-ray-absorption fine structure (SEXAFS) has proved to be the best method for precise determination of the structure of adsorbates on surfaces.[1] The oscillatory part of the photon absorption coefficient above an absorption edge contains information on the radial distance and type of neighboring atoms near to the absorber. Earlier SEXAFS studies concentrated on atomic adsorption on single-crystal surfaces[2] and thus established the technique on a sound footing. More recent work has exploited the local nature of SEXAFS to investigate, for example, amorphous surfaces,[3] molecular adsorbates,[4] and atomic adsorption systems without long-range order in the surface plane.[5] Here we describe an extension of the technique into a new area of application: the geometry of a surface complex on a polycrystalline substrate. In this study the bond lengths and orientation have been determined for the barium-oxygen-substrate complex on the surfaces of real thermionic dispenser cathodes. This information had not been obtained before, largely because the surface structure has no long-range order, precluding study by low-energy electron diffraction (LEED) or similar techniques. SEXAFS, being sensitive only to the local geometry, is the technique of choice to probe such surfaces.

Dispenser cathodes[6] are widely used in devices which require high electron-current densities, such as microwave tubes. These cathodes are constructed from a porous matrix of polycrystalline tungsten (with crystallites a few micrometers in size), which is impregnated with barium calcium aluminate, and surrounds an internal heater. In the working temperature (T_w) range of 1100 to 1400 K, the impregnant dissociates and a mixture of Ba and BaO diffuses through the pores between the tungsten crystallites and across the surface. This forms a submonolayer low-work-function coating which is dynamically in equilibrium with the barium-containing evaporants being thermally desorbed from the surface. The performance of dispenser cathodes has been improved by coating of the surface with third-row transition metals or their alloys with tungsten. The best such metals are Re, Os, and Ir, reducing the work function (ϕ) of the cathode by up to 0.2 eV (giving a factor-of-10 increase in emission); Pt and Au are notably bad, with ϕ for W-Pt-coated cathodes 0.2 eV higher than for a pure W matrix cathode. Various theories[6] have been advanced for the mechanism by which alloy coatings lower ϕ.

SEXAFS spectra were measured with use of an apparatus[7] at the Daresbury Laboratory Synchrotron Radiation Source, with the absorption coefficient above the Ba L_3 edge at around 5247 eV being recorded by our collecting the total electron yield in a Faraday-cup detector. The samples were real dispenser cathodes, chosen to be representative of the best uncoated W matrix cathodes (B-type), an improved alloy-coated cathode (CD-type), and a coated cathode with poor electron emission (W-Pt alloy). The emission characteristics and Auger-electron spectra (AES) were checked before and after the SEXAFS measurements, and found to be indistinguishable from those obtained from batches of normal working cathodes. SEXAFS spectra were recorded with the photon beam incident at approximately 35° to the sample normal, to avoid any possible problems[8] of polarization-dependent phase and amplitude effects due

to interference between scattered photoelectron waves of s and d symmetry. Measurement of the Ba L_3-absorption-edge jump, and the lack of Ba absorption signal after Ar^+ sputtering of the surface, showed that there was a negligible contribution to the Ba extended x-ray-absorption fine structure (EXAFS) from intergranular Ba compounds and that the SEXAFS signal was indeed overwhelmingly from a *surface* species. The best quality SEXAFS data were collected with the cathodes at ambient room temperature (T_a), with the cathode being flashed to at least 1300 K before recording each spectrum, to ensure the cleanliness of the emitter surface. However, many SEXAFS measurements were performed with the samples at temperatures between 1100 and 1155 K, where they are actually working as good cathodes, emitting about 1 A of electrons. The cathodes were biased to suppress this, so that the detector received only the current due to photon absorption ($\lesssim 10^{-9}$ A).

The data were analyzed, after the usual background subtraction and conversion to **k** space, by a curve-fitting routine based on the rapid curved-wave computational scheme,[9] including a least-squares iteration to give the best theoretical fit to the experimental data. Electron-scattering phase shifts for Ba, O, and W were checked against our measured EXAFS spectra from BaO, $BaWO_4$, $BaMoO_4$, and samples of the impregnant compound. The results of this analysis for the B-type cathodes are given in Fig. 1, with, in addition, the Fourier transform (FT) of the raw SEXAFS data from the cathode at $T_w = 1155$ K shown as a bold solid line. The FT's of the T_w spectra exhibit a weaker signal and higher background level: This is in part caused by increased atomic vibration, smearing out EXAFS information, but partly reflects the difficulty of suppressing thermionic electron emission in a stable manner. For this reason, we concentrate here on the analysis of the T_a data: The derived coordination numbers and bond lengths are presented in Table I. Although the EXAFS technique is not particularly good at discriminating between different types of neighbor atoms, in this case the distinctly different backscattering signatures for Ba, O, and the substrate metal readily allow us to determine which atoms are involved in each shell of neighbors (although the small differences between W, Os, and Pt cannot be distinguished).

We make several simple observations from the SEXAFS results. There is a unique, well-defined surface complex at both temperatures, with Ba atoms coordinated directly to oxygen, and substrate atoms as next nearest neighbors, for the two types of good working cathodes studied here. The observed Ba-W or -Os next-nearest-neighbor distances rule out suggestions of suitably ionized Ba-O lying parallel to the surface (which would have Ba-W or -Os distances $\lesssim 3.3$ Å) or standing-up atop substrate atoms (expected Ba-W or -Os distances $\gtrsim 4.7$ Å). The Ba must be above O, as also
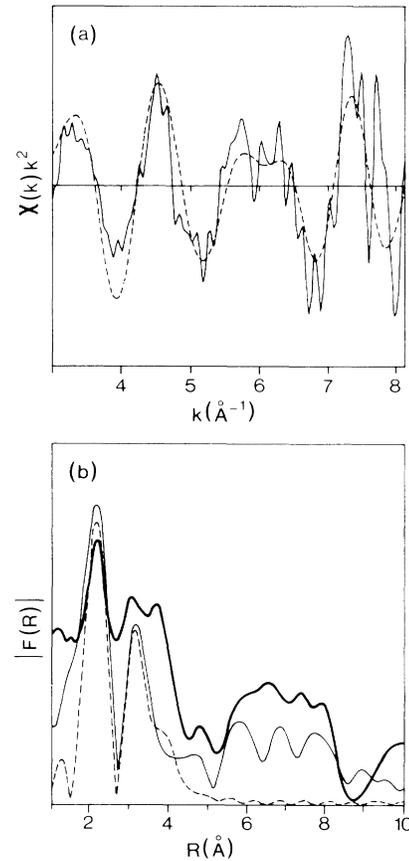

FIG. 1. SEXAFS results for the B-type cathode: (a) the EXAFS function $\chi(k)$, after background subtraction and weighting by k^2, for the raw data (solid line) and the best theoretical fit (dashed line); (b) absolute values of the Fourier transforms of the data in (a), with the data for the hot $(T = 1155$ K) cathode given as a bold line. The peak at ~ 2.2 Å (including the scattering phase shift) is due to O neighbors, and the peak at 3.2–3.9 Å is due to W: Because of the nature of its backscattering envelope, a single shell of W atoms gives an apparently split peak. The theoretically calculated spectra used the parameters given in Table I.

suggested by angularly resolved AES measurements,[10] and the O atoms must be lying in hollows of the substrate surface. The $T = 1155$ K spectra show the same types of atom in the first (O) and second (W or Os) shells, although it is impossible from these SEXAFS data to be sure of a consistent difference in coordination number at T_w between B- and CD-type cathodes. However, we believe that the difference found at T_a does persist to high temperatures,[11] and the model presented below is consistent with the observed difference in ϕ at T_w.

The same samples used in these measurements were

TABLE I. Nearest- and next-nearest-neighbor distances (R in angstroms) and coordination numbers (N) derived by SEXAFS for Ba atoms on the surfaces of three types of thermionic-emission cathodes. The experimental noise level prevents observation of shells at greater distances than about 4.5 Å. The error bars on the distances arise mainly from random statistical fluctuations between successive runs, and are somewhat worse than those attainable with state-of-the-art SEXAFS on well-defined single-crystal surfaces.

	Nearest neighbor Ba-O		Next-nearest neighbor Ba-W[a]	
Cathode type	$R(\pm 0.04$ Å$)$	$N(\pm 0.5)$	$R(\pm 0.12$ Å$)$	$N(\pm 1.5)$
B (W matrix)	2.62	1	3.59	4
CD (W-Os alloy)	2.61	2	3.75	4
W-Pt alloy	2.72	1	. . . [b]	. . .

[a] The technique cannot distinguish between W, Os, and Pt neighbors.
[b] No well-defined Ba-metal distance was observed for this surface.

also analyzed by x-ray diffraction (XRD) in a grazing-incidence geometry to emphasize the contribution of substrate planes near to the surface. The B-type cathode (pure W matrix) gave a body-centered-cubic diffraction pattern, almost randomly oriented. The CD-type (W-Os alloy) was found to be mainly hexagonal close packed, as might be expected from the bulk phase diagram for W-Os,[12] with a strong preponderance of $\langle 10\bar{1}0 \rangle$ planes parallel to the surface. For the platinum-tungsten alloy cathode, the surface was found to consist almost entirely of Pt face-centered-cubic $\langle 111 \rangle$ planes.

To deduce surface structural models for the cathodes,

we combine information on local structure (SEXAFS), the predominant morphology (XRD), surface composition (AES), and work function. ϕ can be related semiquantitatively to the dipole strength of the oriented Ba-O surface layer, which depends on the ionicity of the Ba and O via the well-known Helmholtz relationship. The observed values of ϕ can therefore be used to estimate the appropriate Ba and O ionicities and hence their atomic radii.[13] Numerous models of Ba-O-W surface complexes on the exposed crystal planes of the cathodes were considered. For the B-type and CD-type cathodes, the results of our modeling exercise strongly favor sur-

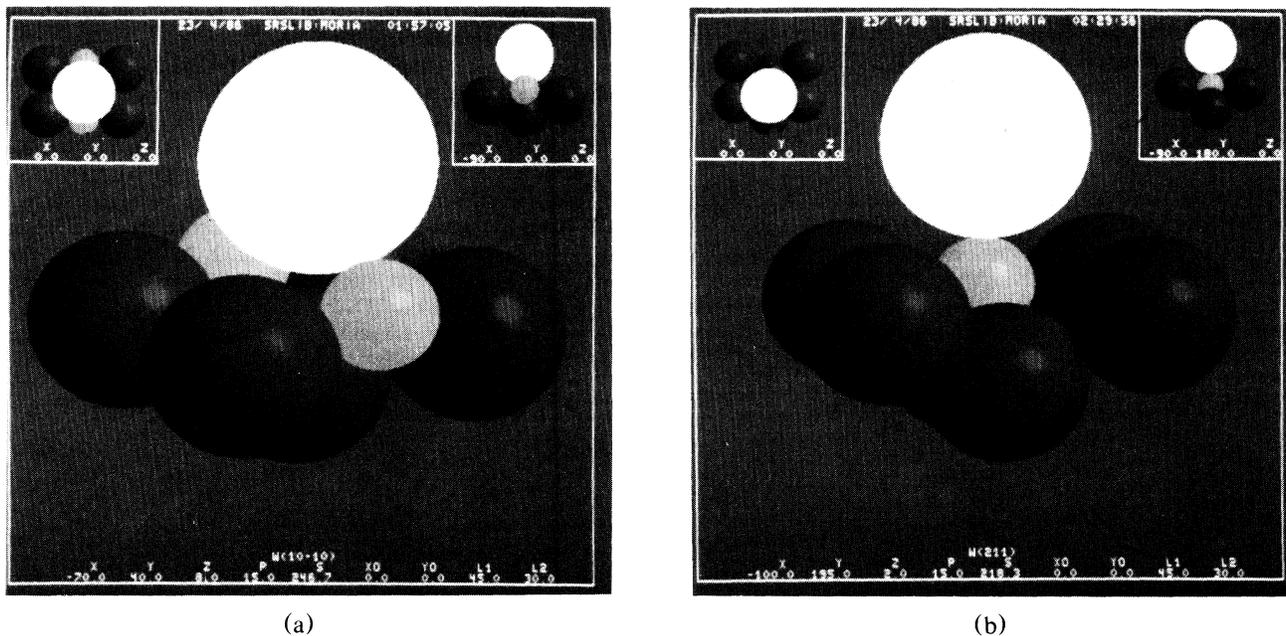

(a)   (b)

FIG. 2. The surface structural local units derived for (a) a $\langle 10\bar{1}0 \rangle$ face of the W-Os alloy (CD-type) and (b) a $\langle 211 \rangle$ face of the W matrix (B-type) cathode. The inset figures show the same models viewed from different directions. The Ba atoms are depicted as white, O atoms grey, and substrate atoms black, with no distinction being made in these models between the W and Os substrate atoms. The choice of atomic radii is described in the text.

face complexes of the type shown in Fig. 2. Similar structures can be derived for all crystal planes present in significant proportions at the B-type cathode surface, giving a weighted mean value of next-nearest-neighbor distance equal, within experimental error, to the SEX-AFS result.

While electronic effects are undoubtedly important, we propose that the morphology of the surface plays a similarly important role in the determination of the efficiency of cathodes. The more open structure of the CD-type surface planes has a Ba atom bridging two O atoms.[14] This will result in greater electron transfer towards the surface, a larger surface dipole, and a smaller work function. In addition, an open structure allows the O atoms to sit in the surface layer, below the Ba atom. In this configuration, any *adverse* dipole caused by electron transfer from the substrate to oxygen will be minimized. By the same argument, this adverse dipole will be maximized for the close-packed surface of the W-Pt alloy. It appears that there may be an optimum surface crystallography which could hold the key to development of even more efficient cathodes.

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[1]For a review, see D. Normal, J. Phys. C. **19**, 3273 (1986).

[2]For example, P. H. Citrin, P. Eisenberger, and R. C. Hewitt, Phys. Rev. Lett. **41**, 309 (1978); S. Brennan, J. Stöhr, and R. Jaeger, Phys. Rev. B **24**, 4871 (1981).

[3]F. Comin, L. Incoccia, P. Lagarde, G. Rossi, and P. H. Citrin, Phys. Rev. Lett. **54**, 122 (1985).

[4]J. Stöhr, E. B. Kollin, D. A. Fischer, J. B. Hastings, F. Zaera, and F. Sette, Phys. Rev. Lett. **55**, 1468 (1985).

[5]G. M. Lamble, R. S. Brooks, S. Ferrer, D. A. King, and D. Norman, Phys. Rev. B **34**, 2975 (1986).

[6]Reviewed by R. A. Tuck, Vacuum **33**, 715 (1983).

[7]A. A. MacDowell, D. Norman, and J. B. West, Rev. Sci. Instrum. **57**, 2667 (1986).

[8]J. Stöhr and R. Jaeger, Phys. Rev. B **27**, 5146 (1983); P. H. Citrin, Phys. Rev. B **31**, 700 (1985).

[9]S. J. Gurman, N. Binsted, and I. Ross, J. Phys. C **17**, 143 (1984).
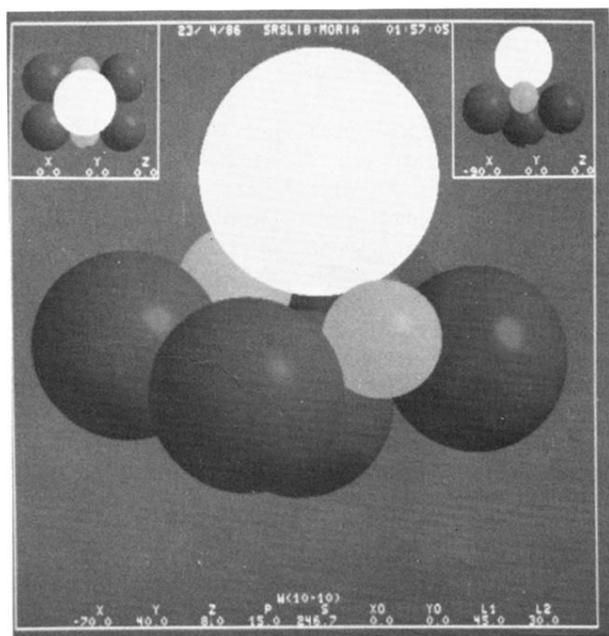
[10]H. B. Skinner and R. A. Tuck, Final Report on Contract DAJA 45-83-C-0009-U.S. Army, 1984 (unpublished).

[11]Our AES data support this: Under the UHV conditions of this experiment ($< 10^{-10}$ Torr) Ba and O Auger signals show only small changes [D. Brion, J. C. Tonnerre, and A. M. Shroff, Appl. Surf. Sci. **16**, 55 (1983)] between T_a and T_w. Such changes are, in our experience, attributable to adsorption of CO from the residual gas background, which does not affect the work function of cathodes [R. A. Tuck, *Proceedings of the Fourth International Conference on Residual Gases in Electron Tubes* (Academic, New York, 1972) p. 277], and thus probably has little, if any, effect on the structure of the surface complex.
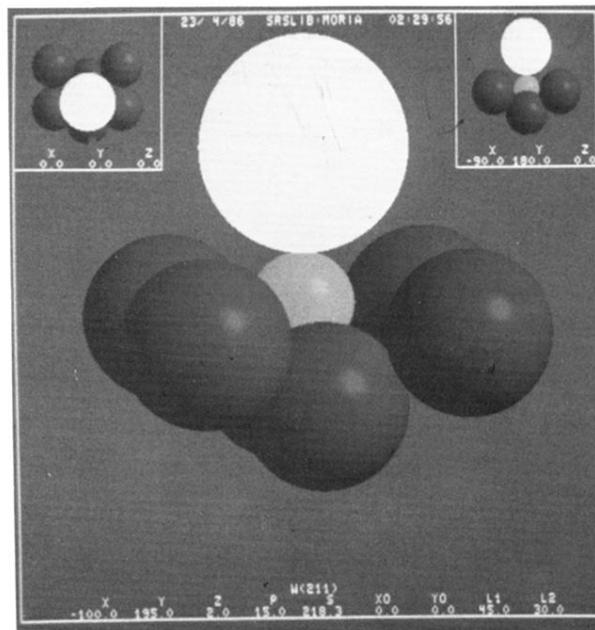
[12]M. C. Green, H. B. Skinner, and R. A. Tuck, Appl. Surf. Sci. **8**, 13 (1981).

[13]L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, New York, 1960).

[14]This is consistent with Auger data for the O/Ba ratio on hot CD cathodes, by use of standard sensitivity factors [A. Shih, C. Hor, and G. A. Haas, Appl. Surf. Sci. **2**, 112 (1979)] and the density corrections of J. Hasker and H. J. H. Stoffelen, Appl. Surf. Sci. **24**, 330 (1985). The O/Ba Auger ratio on B-type cathodes is invariably measured to be higher than on CD-type, but there is considerable evidence in the literature [e.g., C. R. K. Marrian, A. Shih, and G. A. Haas, Appl. Surf. Sci. **16**, 1 (1983)] that this is due to excess oxygen not bonded to barium: Our SEXAFS measurements detect only oxygen atoms immediately adjacent to Ba.

FIG. 2. The surface structural local units derived for (a) a ⟨10$\bar{1}$0⟩ face of the W-Os alloy (CD-type) and (b) a ⟨211⟩ face of the W matrix (B-type) cathode. The inset figures show the same models viewed from different directions. The Ba atoms are depicted as white, O atoms grey, and substrate atoms black, with no distinction being made in these models between the W and Os substrate atoms. The choice of atomic radii is described in the text.