Evidence for a Quantum Size Effect of the Conduction Electrons during Oxidation of Cs

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The transition from Cs to $Cs_{11}O_3$ leads to a twofold increase of the intensity of electron emission from the valence band (and to a substantial decrease of the emission from the Cs $5p$-core levels) as probed by metastable deexcitation spectroscopy, although the concentration of conduction electrons is reduced by about 50%. This phenomenon is attributed to a quantum size effect of the conduction electrons as proposed in a theory by Burt and Heine.

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The work function of the cesium suboxide $Cs_{11}O_3$ is considerably lower than that of pure Cs,[1] a fact which plays a role in the activation of photocathodes.[2] Based on the structural and bonding properties of $Cs_{11}O_3$,[1] Burt and Heine[3] developed a simple model according to which the lowering of the work function may be attributed to a quantum size effect: In the structural unit of $Cs_{11}O_3$ (Fig. 1) each of the three O^{2-} ions is octahedrally surrounded by Cs atoms; six of the Cs valence electrons are used up for the formation of the oxygen ions, while the remaining five form the metallic system of conduction electrons. Because of the strong repulsion by the O^{2-} ions the latter are essentially excluded from the inner space of the structural unit and confined to the outer range which will exhibit an atomic as well as electronic density close to that of pure cesium. As a consequence of the uncertainty principle, confinement of conduction electrons in space will be associated with an increase of their momentum and hence of the Fermi energy. The rise of E_F was calculated to be 0.9 eV for $Cs_{11}O_3$ with respect to Cs,[3] which number is to be compared with the 0.6-eV difference of the work functions.[1]

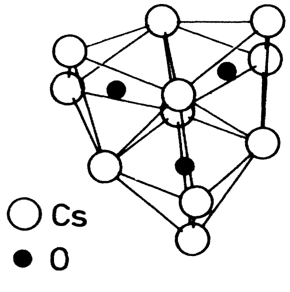

FIG. 1. Building block of $Cs_{11}O_3$ (Ref. 4).

To equate the increase of E_F with the decrease of the work function $\Delta\phi$ is, however, only justified if the dipole layer at the surface remains unaffected which might be well the case, e.g., by the presence of adsorbates. In the present case that means that the surfaces of both Cs and $Cs_{11}O_3$ should consist merely of (metallic) cesium atoms. The present work will demonstrate that this is indeed the case if a thin layer of $Cs_{11}O_3$ is created by exposing a clean Cs surface to small amounts of O_2. The resulting work functions are $\phi = 2.0$ eV for Cs-poly and $\phi = 1.5$ eV for $Cs_{11}O_3$-poly, in good agreement with the data for the bulk materials (1.95 and 1.35 eV, respectively).[1] But even now $\Delta\phi$ might still be affected by variations of the crystallographic surface structure. The use of metastable deexcitation spectroscopy (MDS) as a probe for the surface electronic properties will, however, bring direct evidence for the operation of the suggested quantum size effect. Further support for the model proposed by Burt and Heine[3] is found from experimental data for a monolayer of Cs adsorbed on a Cu (110) substrate.

The experimental system has been described elsewhere.[5] It contains MDS facilities,[6] for metastable deexcitation spectroscopy (MDS),[6] ultraviolet photoemission spectroscopy (UPS) ($h\nu = 21.2$ eV), LEED, Auger electron spectroscopy (AES), etc., and is operated at a base pressure of 5×10^{-11} Torr. Clean polycrystalline Cs films of at least ten atomic layers thickness were prepared by evaporation from a SAES getters source onto a clean Cu (110) surface kept at 140 K. Continuous transformation into the various Cs oxides was achieved by admission of small doses of O_2, for which work a full account will be given in a forthcoming paper.[7] The results on the electronic properties of clean Cs surfaces obtained by MDS and UPS are published elsewhere.[8]

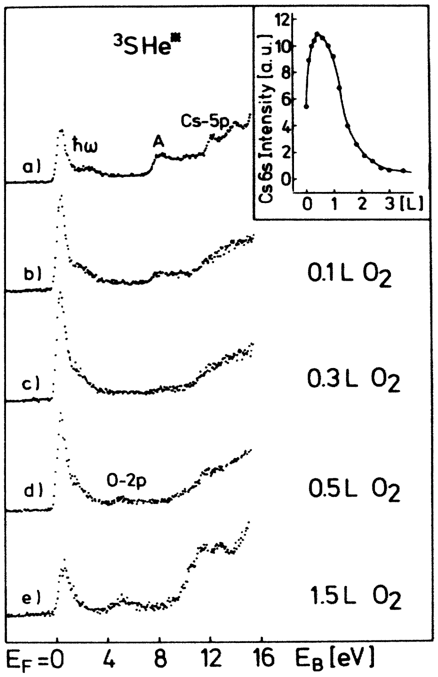

FIG. 2. Metastable deexcitation spectra (a) from clean Cs and (b)–(e) after increasing exposure to O_2. The inset shows the variation of the intensity of valence-band emission with oxygen exposure.

Figure 2 shows a series of electron energy distributions recorded by deexcitation of $He^*(^3S)$ atoms at Cs surfaces after increasing exposures to O_2. These spectra are caused by Auger deexcitation of the metastable atom

$$T+\mathrm{He}^* \rightarrow T^+ + \mathrm{He} + e(\epsilon_{\mathrm{kin}}),$$

whereby ϵ_{kin} is related to the binding energy E_B (with respect to the Fermi level E_F) of the emitted electron through

$$\epsilon_{\mathrm{kin}} = E^*_{\mathrm{eff}} - E_B - \phi .$$

E^*_{eff} is the effective excitation energy of the metastable atom in front of the surface (19.5 eV in the present case[8]), and ϕ is the work function, so that the data can simply be converted onto an E_B scale. Curve 2*a* from a clean Cs surface exhibits[8] (with increasing E_B) (i) a pronounced signal from the valence band, (ii) a peak ($\hbar\omega$) arising from surface plasmon losses, (iii) an Auger peak A from O_2VV transitions, and (iv) two peaks arising from ionization of the Cs $5p_{3/2}$- and $5p_{1/2}$-core levels, respectively.

MDS is an extremely surface-sensitive technique, and deexcitation occurs at a distance of about 5 Å from the Cs surface.[8] The relative intensities of the various peaks are governed by the overlap between the He* 1*s* hole and the tail of the wave function of the respective level. With the clean Cs surface obviously both the valence levels as well as the 5*p*-core levels exhibit comparable intensities. The Auger peak A requires ionization of the $5p_{3/2}$ level and is therefore linked to the presence of the latter peak. (The $5p_{1/2}$ hole is rapidly quenched by a Coster-Kronig transition and does not therefore give rise to a corresponding Auger signal).

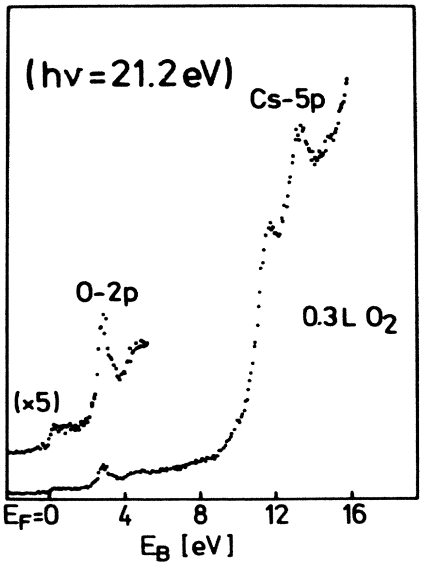

FIG. 3. He I photoelectron spectrum from a Cs surface exposed to 0.3 L O_2 which is characteristic for the formation of $Cs_{11}O_3$.

Admission of 0.1 L O_2 (1 L$=10^{-6}$ Torr sec) causes substantial changes of the spectrum (curve 2*b*): The valence-band emission has gained in intensity, while that from the Cs 5*p* levels and from the Auger transition is strongly reduced. The plasmon loss has been shifted closer to the valence-band peak. This tendency continues up to 0.3-L O_2 exposure (curve 2*c*), where the intensity of valence-band emission reaches a maximum and the Cs 5*p* levels as well as the Auger peak are almost indistinguishable from the background. So far no oxygen-derived spectral features can be detected by MDS, which would—in view of the extreme surface sensitivity of this technique—be clearly discernible if this species were *on* the surface. That oxygen atoms have in fact been incorporated *below* the surface becomes evident from UPS which method has a finite information depth. Figure 3 shows the He I photoelectron spectrum recorded after 0.3-L O_2 exposure which is identical to that reported for $Cs_{11}O_3$.[1] Apart from pronounced Cs 5*p* structures it exhibits in particular a narrow peak at $E_B=2.8$ eV which is characteristic for the O^{2-} ions in the $Cs_{11}O_3$ structural unit.[1] Since these ions are octahedrally surrounded by Cs atoms (see Fig. 1) they are obviously completely shielded from ionization in MDS.

The continuous lowering of the plasmon energy indicates a progressing reduction of the density of conduction electrons, n_c.[9] Analysis of the shift of the plasmon loss[6] reveals that n_c decreases from 1.0 (per Cs atom) for pure Cs to a value of 0.5 after 0.3-L O_2 exposure, in perfect agreement with the data obtained for bulk Cs and $Cs_{11}O_3$, respectively.[1] We have, therefore, to conclude that 0.3 L O_2 causes the creation of a "monolayer" of $Cs_{11}O_3$, consisting of the three topmost layers of Cs atoms between which two layers of O_2^- ions are embedded—corresponding to the structure shown in Fig. 1. The derived conduction-electron density of about 0.5 confirms the model, whereafter in this compound 6/11 of the Cs valence electrons are consumed by the formation of the O^{2-} ions.[1]

If the O_2 exposure is further increased [Fig. 2(d)], the MDS data show the appearance of a new peak at $E_B = 5.6$ eV which is attributed to O atoms adsorbed *on* the surface preceding the formation of the higher Cs oxides. (The energy of this peak is in the same range as found for O adsorbed on numerous other metals.[10]) Further oxidation leads to continuous complete ionization of Cs atoms; the valence-band emission decreases in intensity and finally disappears completely. An intermediate state reached after 1.5-L O_2 exposure is represented by curve *e* of Fig. 2. Note that the intensity of the Cs $5p$ level emission has increased substantially: The removal of the Cs valence electrons renders the $5p$-core levels more accessible to the overlap with the He* $1s$ hole, and hence their spectral features increase in intensity.

Obviously a puzzle consists now in the fact that the transition from Cs to $Cs_{11}O_3$ leads to an increase of the emission from the valence band and to a decrease of that from the $5p$ levels [cf. Figs. 2(a)-2(c)], although the valence electron density decreases. The only solution for this apparent discrepancy is that the wave functions of the conduction electrons in $Cs_{11}O_3$ "leak" farther into the vacuum than in Cs, while the localized $5p$ levels are not affected in such a way. As a consequence, the average distance from the surface from where deexcitation occurs is increased, and the valence-band emission gains at the expense of the reduced overlap of the $5p$ levels with the He* $1s$ hole. This explanation would be exactly a consequence of the model proposed by Burt and Heine[3]: The increase of the Fermi energy increases the extension of the "tails" of the free electrons close to E_F reaching into the vacuum and hence the overlap with the He* $1s$ hole, while the localized $5p$ levels are not affected in such a way. The observed phenomena are therefore considered as direct confirmation of the proposed quantum-size effect.

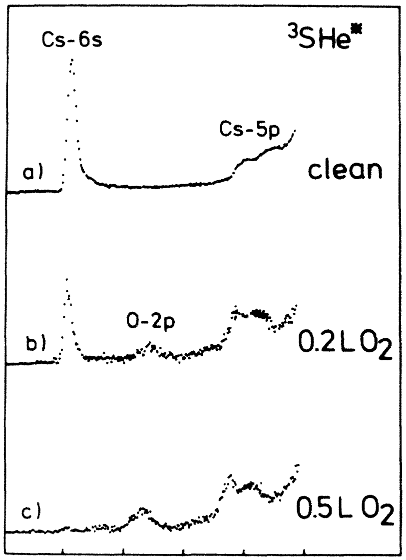

FIG. 4. MDS data from (a) a clean monolayer of Cs adsorbed on a Cu(110) surface, and after exposure to (b) 0.2 and (c) 0.5 L of O_2.

Further support for the proposed model is believed to be obtained from the MDS data recorded with a Cs monolayer adsorbed on the Cu (110) substrate as reproduced in Fig. 4. The spectrum from the pure Cs overlayer (curve *a*) exhibits an intense peak from Cs $6s$ derived valence states which now, however, have widely lost their free-electron character, presumably because of their involvement in the bond formation with the substrate[11]: The plasmon loss as well as the Auger transition is no longer discernible in the spectrum. Admission of O_2 causes now a continuous decrease of the intensity of valence-band emission and an increase of the $5p$-peak intensities (curves *b* and *c*). $Cs_{11}O_3$ is no longer formed (which would need at least three Cs layers), and the peak due to O atoms *on* the surface appears already after the lowest exposures.

Since the valence electrons have lost their free-electron character the quantum-size effect is no longer operating: The reduction of the valence electron density is now associated with a continuous decrease of their emission intensity, while the Cs $5p$ levels become increasingly accessible for ionization.

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