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Electronic structure of clean and oxygen-exposed Na and Cs monolayers on Cu (111)

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The electronic structure of adsorbed Na and Cs monolayers and these alkalies coadsorbed with oxygen is studied via electron-energy-loss spectroscopy (EELS), work-function changes, Auger emission, and ultraviolet photoelectron spectroscopy. Interest is focused on the changes of the electronic structure due to a change of alkali coverage or to oxygen adsorption. Even at low coverage, when work-function values and core-level binding energies suggest that most of the alkali valence charge is transferred to the substrate, the EEL spectra show a peak due to alkali valence electron excitations. During continued alkali deposition the energy loss after an initial decrease passes a minimum and increases at high monolayer coverage. At high coverage the peak is ascribed to plasma oscillations in the monolayer. For Cs the monolayer plasmon energy loss can be varied in a continuous manner and over a wide range by changing the amount of adsorbed oxygen. We ascribe the energy-loss change to a dilution of the electron gas in the layer. The effect is observed for coverages above a critical value corresponding to around 60% of a close-packed monolayer.

I. INTRODUCTION

As examples of simple chemisorption systems, and because of their technically interesting properties such as low work function, alkali adsorption systems have been studied extensively.[1] From such work has emerged a picture of the electronic structure rather similar to that proposed by Friedel in his resonant-state model of the outer *d* electrons in a transition-metal atom when dissolved in a normal metal. While the Friedel model has been confirmed by direct spectroscopic observations,[2,3] the resonance picture for the valence level of an adsorbed alkali atom is based on indirect evidence. In principle more detailed information can be obtained by using a surface-sensitive probe such as photoemission to study the excitation of the alkali valence electrons, preferably at low surface coverage when effects due to the adatom-adatom interaction are small. A difficulty here is that the *ns* resonance state is nearly empty at low coverage due to a transfer of alkali valence electrons to the substrate. If the adsorbed amount is increased, the charge on an atom is reduced. A substantial photoemission intensity has so far been obtained only at relatively high monolayer coverages.[4] At low coverage the photoelectron energy spectra have provided information mainly about how the substrate states at the receiving end of the charge transfer are affected.

Electron-energy-loss spectroscopy (EELS) has been the main tool for probing the spectrum of collective as well as single-particle excitations of alkali adsorption systems. Following the early observations by MacRae *et al.*[5] that plasma oscillations can be excited in a Cs monolayer on W(100), this phenomenon has been studied for several other substrate-adsorbate combinations.[6-13] In quantitative terms the oscillations are poorly understood. The characteristic energy loss at full monolayer coverage is about half of the bulk plasmon energy for the alkali metal. Higher energies are predicted by continuum models, assuming that the sample can be regarded as a slab of one free-electron metal with reasonable thickness and electron density placed on top of another free-electron metal with an abrupt boundary between them. Poorly understood even qualitatively is a feature observed at low energy losses for small Na, K, and Rb coverages on Ni(100) (Ref. 8). This structure appears at a strongly coverage-dependent loss energy such that on a plot of energy loss versus coverage a curve drawn through the points joins smoothly to the plasmon energy losses measured at high coverage. We observe a similar coverage dependence for a loss peak induced by Na and Cs adsorption on Cu(111) which suggests that the excitation mechanism responsible for this structure is common to all alkali adsorption systems. EELS can also be used to investigate the charge transfer between adsorbate and substrate at different alkali coverages. This information is obtainted by measuring the threshold energy for alkali core-level excitations. Thus we may compare the Cs 5*p* threshold energies with the Cs 5*p* binding energies as measured by ultraviolet photoelectron spectroscopy (UPS). UPS observations of coverage-dependent binding energies have recently been reported for two other adsorption systems.[14,15]

In the present work we also use EELS together with work-function measurements, low-energy electron diffraction (LEED) observations, and Auger electron emission to investigate atomic structure and some electronic properties of Cs-or Na-covered Cu(111) samples which are exposed to oxygen. The reason for our interest in these more complicated systems is that we observe simple and regular changes of loss spectra on exposure of Cu(111)/Cs to oxygen. According to our interpretation the changes recorded at high Cs coverages can be explained by a dilution of the electron gas in the overlayer by the oxygen adsorption. We have previously given a brief account of the results obtained at full Cs monolayer coverage.[16] Here we show that the oxygen-adsorption-induced changes are qualitatively different below and above a coverage corresponding to approximately 60% of a close-packed monolayer.

II. EXPERIMENTAL

We use a standard LEED display system to observe the diffraction pattern and to record the work-function changes by the retarding field method. The energy distribution of electrons leaving the sample is obtained by using the three-grid LEED optics as a retarding field energy analyzer or by using a 180° segment cylindrical mirror analyzer (CMA) with inner and outer radii of 14 and 41 mm, respectively, and a length of about 100 mm. The analyzer entrance accepts electrons emitted within a cone having an opening angle of 2°. The cone axes makes an angle of 42.3° with the axes of the mirror cylinder. Electrons from the LEED electron gun approaching the sample at 68° incidence angle are reflected specularly into the analyzer. Angle-resolved photoelectron spectra are measured using a rare-gas discharge lamp attached to the chamber via a straight-through valve. Before reaching the cylindrical field region the electrons are retarded between two circular apertures ($\phi = 1$ mm). The electrons passing the circular ($\phi = 1$ mm) exit aperture enter a channeltron. The analyzer has a resolution of some 2.5% and is usually operated at a constant pass energy of between 5 and 10 eV. The EELS resolution is therefore mainly determined by the energy spread of the electrons from the electron gun.

The 1 mm thick Cu(111) crystal is spark cut from a rod ($\phi = 18$ mm) and then mechanically and electrolytically polished as described by Tegart.[17] After an experimental run, when both alkali and oxygen have been adsorbed, a clean Cu(111) surface is prepared by Ar-ion bombardment (2 μA, 250 eV, 10h) followed by heating to 400 °C for 1 h. The heating is achieved by passing a current through a Mo ribbon serving as a sample holder. Four holes ($\phi = 1$ mm), spark cut through the crystal, and thin Mo wires are used to fix the sample to the ribbon. The temperature is measured by a platinel thermocouple junction pressed into one of the four holes. The section containing the alkali ampoule can be sealed off from the rest of the UHV chamber by closing a straight-through valve. During an experimental run the ampoule is kept at constant temperature. The evaporated metal reaches the substrate when a shutter placed in front of the ampoule is removed. The alkali coverage values given below are obtained from the evaporation times assuming a constant sticking probability and using as a reference the time required to form the ordered overlayers observed for both Na and Cs on Cu(111). In the first series of experiments the coverage dependence of the work function is measured. In later runs the coverage values are determined by measuring the change of the work function.

The oxygen exposures of the alkali-covered Cu(111) surface are made dosewise using gas pressures in the 10^{-9}-torr range. The base pressure is ca. 1×10^{-10} torr. The exposure values may be wrong by approximately a factor of 2, mainly due to uncertainties in the pressure values obtained from the ion gauge. The purity of the gas may be checked by a mass spectrometer (V. G., model Q7) mounted on the chamber.

III. RESULTS

A. Work function and structure

Both for Na and Cs on Cu(111) the work function shows the coverage dependence typical of alkali adsorbates on metals. During continued evaporation the work function after an initial rapid decrease passes a minimum and then increases to a nearly stable level attained when approximately one full monolayer is adsorbed. For Cs the maximum work-function reduction is 3.4 eV and occurs at a converge $\Theta \approx 0.16$ (Fig. 1). We define Θ as the number of adsorbed atoms divided by the number of atoms in the outermost substrate layer. Since

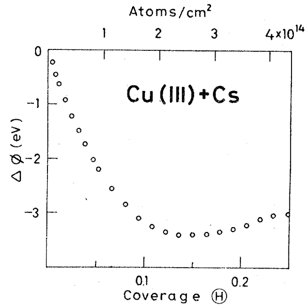

FIG. 1. Work-function change of a Cu(111) substrate versus Cs coverage, Θ. $\Theta = 0.25$ corresponds to a close-packed Cs monolayer.

for clean Cu(111) $e\phi \approx 4.9$ eV (Ref. 18) the minimum work-function value is 1.5 eV, whereas the value for a close-packed layer is 1.9 eV. The LEED pattern shows that the full monolayer has a $p(2\times2)$ structure. At lower coverages a diffraction ring around the specular spot indicates uniform adatom distribution. The maximum Cs coverage which can be studied at room temperature corresponds to a close-packed monolayer, $\Theta = 0.25$.

If the Cs-covered Cu(111) crystal is exposed to oxygen and the coverage is less than 0.15, the work function increases monotonically with increasing exposure (Fig. 2). At higher Cs coverages there is an initial decrease of the work function to quite low values. As an example the work function of Cu(111)-Cs $p(2\times2)$ attains a minimum value of 1.3 eV after 0.4-L O_2 exposure. Between 0.4 and 1.0 L the work function increases rapidly with increasing oxygen exposure but remains nearly constant for still further higher exposures. At around 0.5-L O_2 exposure the same LEED pattern is obtained as for Cu(111)-Cs $p(2\times2)$. Between zero and 0.5-L O_2 exposure additional diffraction spots inside the half-order beams indicate that there is at least one ordered phase. The appearance of ordered phases at low oxygen coverage indicates that the oxygen tends to spread evenly over the surface. A similar observation has been made for Fe(110) covered by K and exposed to oxygen.[19]

The minimum work-function value measured for Cu(111)/Na is about 2.2 eV (Fig. 3). At $\Theta = 0.25$, Na forms a $p(2\times2)$ structure which becomes compressed on further Na evaporation. The work-function changes obtained upon oxygen exposure of Na-covered Cu(111) are qualitatively the same as for Cu(111)/Cs, though the minimum obtained for one full monolayer is not as deep (Fig. 4).

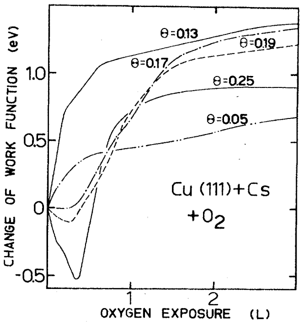

FIG. 2. Work-function change upon oxygen exposure of Cu(111) covered by different amounts of Cs ($1 \text{L} = 10^{-6}$ Torr sec).

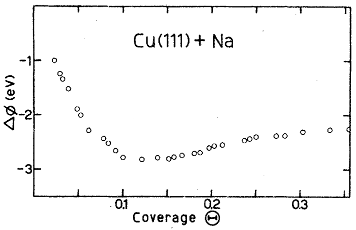

FIG. 3. Work-function change of a Cu(111) substrate versus Na coverage. The monolayer is close packed at around $\Theta = 0.5$.

B. Low-energy excitations

The EEL spectrum of Cu is characterized by a low flat signal level for energy losses below 2 eV [Fig. 5(a)]. The edge at 2-eV energy loss corresponds to the onset of interband transitions due to the excitation of electrons in the uppermost $3d$ band. The present spectra, which are recorded at low incident energies (20–50 eV), show structure similar to that of the loss function calculated from optical constants,[20] or EELS at much higher incident electron energies.[21] The similarity is consistent with the view that the loss spectrum measured in back reflection at low primary energies is the result of two-step processes involving elastic reflections and inelastic scattering processes dominated by small momentum-transfer losses.[22]

As Cs or Na is adsorbed on Cu(111) the EEL spectra show a peak at an energy loss which depends on the coverage (Fig. 5). For Cs a minimum energy loss of 1.2 eV is obtained at around $\Theta = 0.16$ (Fig. 6). Extrapolation of the measured values to zero coverage indicates an energy loss of 3.2 eV. These spectra are obtained using the CMA analyzer. In earlier measurements using the LEED optics as an energy analyzer we did not resolve this peak at low coverage.[10] With further coverage the loss peak strengthens and the energy

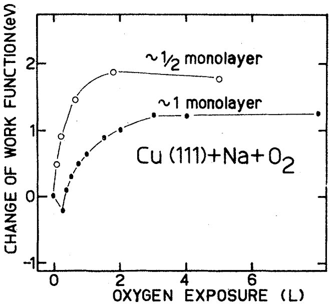

FIG. 4. Work-function change upon oxygen exposure of Cu(111) covered by a full and half-full Na monolayer.

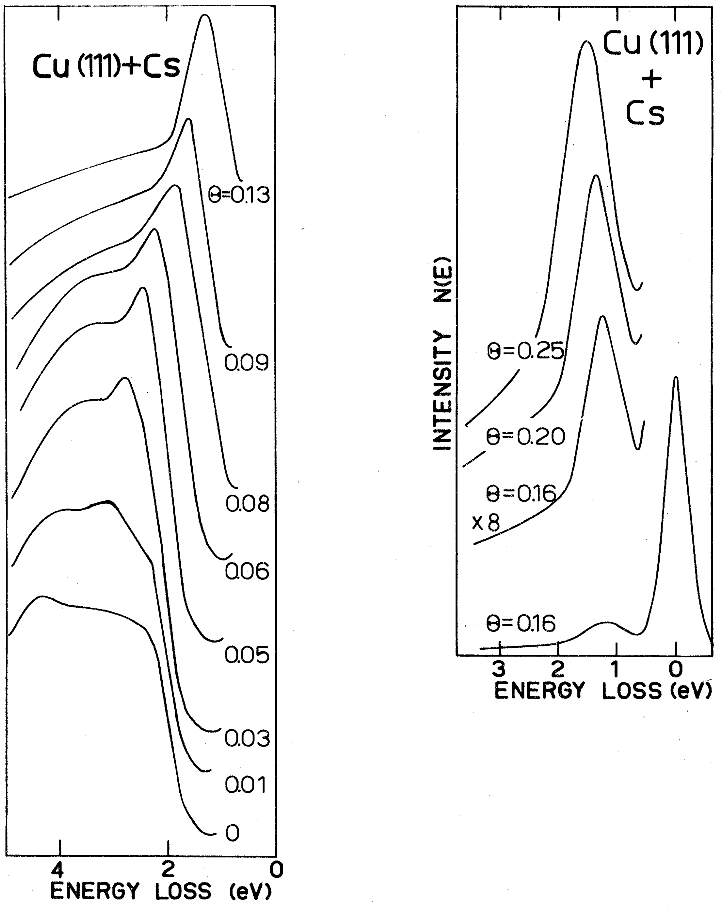

FIG. 5. Electron-energy-loss spectra of Cu(111) covered by different monolayer amounts of Cs.

loss increases to 1.5 eV at full monolayer coverage [Fig. 5(b)]. For Na the energy loss at low coverage is 3.2 eV (Fig. 7) and the minimum energy loss is 2.3 eV. The energy loss then increases to a value of 3.8 eV, which is the Na surface plasmon energy,[20] when few atomic layers have been deposited. At this stage several peaks due to multiple losses are observed (Fig. 8).

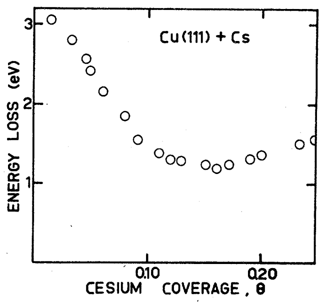

FIG. 6. Energy loss versus Cs coverage for the low-energy-loss structure shown in Fig. 5.

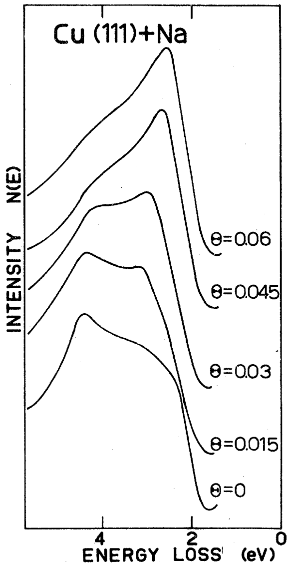

FIG. 7. Electron-energy-loss spectra of Cu(111) covered by different amounts of Na.

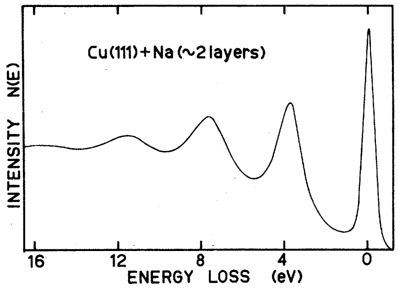

FIG. 8. Electron-energy-loss spectrum for Cu(111) covered by around two full layers of Na.

When oxygen is adsorbed on Cs-covered Cu(111) the changes of the loss spectrum are qualitatively different at high and low Cs coverage. At low Cs coverage the Cs-induced loss peak remains constant but becomes weaker as more oxygen is adsorbed (Fig. 9). At full Cs monolayer coverage there is a gradual decrease of the energy loss as the amount of adsorbed oxygen is increased (Fig. 10). An initial decrease of the energy loss on oxygen exposure is observed for Cs coverages above $\Theta = 0.16$. After the initial decrease the energy loss remains constant and the loss peak becomes weaker on further O_2 exposure (Fig. 11). The maximum oxygen adsorption-induced shift of energy loss is larger for a higher Cs coverage. A plot of the square of the energy loss, E_L^2, against oxygen exposure, Q, for samples with different Cs coverages, Θ, shows a linear relationship between E_L^2 and Q (Fig. 12). Oxygen adsorption on Na-covered Cu(111) produces a damping of the plasmon loss structure at high monolayer coverages, but only a small change of loss energy.

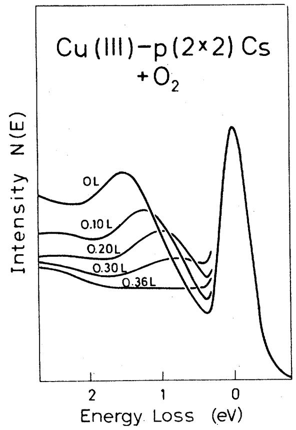

FIG. 10. Electron-energy-loss spectra at different oxygen exposures of a Cu(111) crystal covered by a full Cs monolayer.

Above, we have discussed loss structure induced by the alkali adsorbate and as modified by oxygen adsorption. The oxygen exposure also induces a new loss structure at relatively low energies. Thus a peak at $E_L \approx 5$ eV is resolved at O_2 exposures larger than 0.5 L for a high coverage of Cs on Cu(111) (Fig. 13).

We associate this loss peak with the perturbed O 2*p* level of oxygen when the latter is bound to the substrate. The interpretation in terms of oxygen bound to Cu is based primarily on the expo-

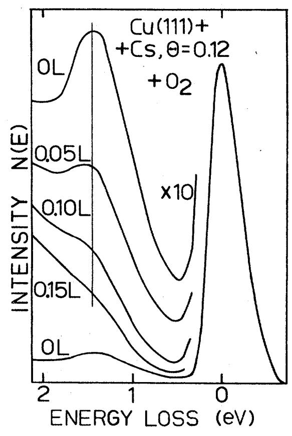

FIG. 9. Electron-energy-loss spectra at different oxygen exposures for a Cu(111) crystal at a Cs coverage of 0.12.

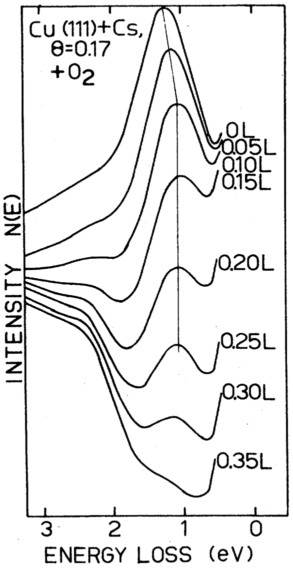

FIG. 11. Electron-energy-loss spectra at different oxygen exposures of a Cu(111) crystal at a Cs coverage of 0.17.

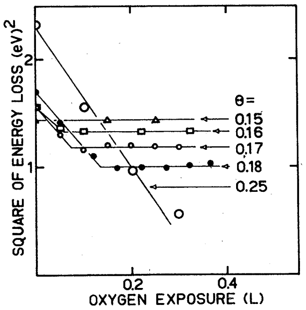

FIG. 12. The square of the energy loss versus oxygen exposure for a Cu(111) crystal covered by different monolayer amounts of Cs.

sure dependence of the peak strength. The peak intensity grows on further oxygen exposure even at exposures much higher than the ~0.5 L needed to ionize all the Cs atoms on the fully alkali-covered surface. It is probably difficult to distinguish between oxygen bound to Cs and that bound to Cu by recording the characteristic energy loss. EEL measurements on thicker Cs films than ours show that oxygen adsorption introduces peaks at characteristic energy losses of 4.8 and 7.2 eV (Ref. 23); the former value is close to the energy loss observed here. The exposure dependence of the peak shows that the oxygen uptake proceeds at an enhanced rate due to the Cs coverage. For clean Cu(111) little change of the loss spectra is observed for exposures around 10^4 L. The assignment of the loss peak to the excitation of oxygen bound to the substrate is also consistent with the observation of an oxygen-adsorption-induced peak in photoemission spectra of Cu at an initial energy of about 5 eV below the Fermi energy.[24] Enhanced oxygen-uptake rates as a result of alkali adsorption have been reported previously for Ni.[25]

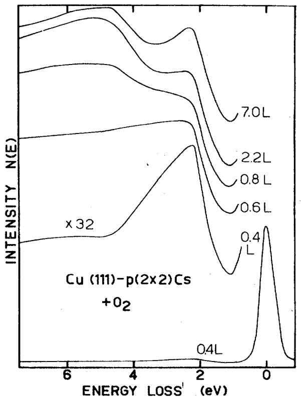

FIG. 13. Electron-energy-loss spectra at different oxygen exposures of Cu(111) covered by a full Cs monolayer.

C. Core-level excitations

We have recorded the loss structure produced by excitation of the Cs 5*p* electrons at different Cs coverages (Fig. 14). These spectra are derivatives of the energy distributions and are obtained by using the LEED optics as a retarding field energy analyzer. Our present interest is the dependence of the characteristic energy loss on coverage. This energy marks the threshold for Cs 5*p* excitations and reflects the charge transfer between adsorbate and substrate. The threshold decreases from 13.2 eV for the more ionic Cs adsorbate at low coverage to 11.6 eV for the nearly neutral adsorbate at high coverage. The values have been obtained by measuring the energy separation between the primary peak and the middle of the step at the low-energy-loss side of the Cs 5*p* loss structure. We note that especially at intermediate coverages the loss spectrum is more complicated than expected from a simple folding of the spin-orbit split 5*p* level with the Fermi edge.

The Cs 5*p* binding energy can be measured by UPS. Figure 15 shows angle-resolved photoelectron energy spectra of Cu(111)/Cs at different Cs coverages recorded for a 21.2-eV photon energy, a polar exit angle of 20°, and an azimuth 45° away from [$\bar{2}$11]. The dashed part of the spectrum is influenced by hydrogen impurity lines which make it difficult to resolve the Cs 5*p* derived emission peak at low Cs coverages. The Cs 5*p* initial-state energy relative to E_F is plotted (open circles) in Fig. 16, together with the threshold energies (filled circles) determined by EEL measurements. Observations of binding-energy changes due to a coverage change have recently been reported for two other chemisorption systems, K on Fe(110) (Ref. 14) and Xe on Pd(110) (Ref. 15). Since the filled and open circles in Fig. 16 fall close to a common curve there is little need in the present

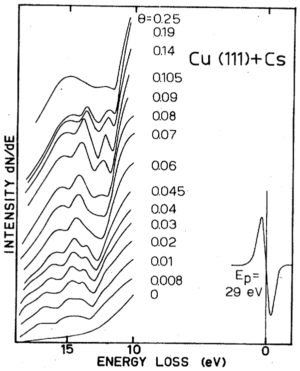

FIG. 14. Derivatives of the electron-energy-loss spectra of Cu(111) at different Cs coverages.

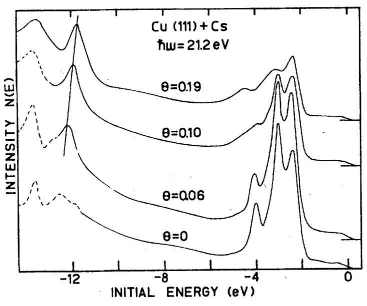

FIG. 15. Angle-resolved photoelectron energy spectra obtained at $\hbar\omega = 21.2$ eV, 20° polar angle, and an azimuth 45° away from $[\bar{2}11]$ from Cu(111) at different Cs coverage. Hydrogen impurity lines affect the spectra in the dashed region.

case to make a distinction between binding energy and excitation threshold.

The trough at around 11 eV in Fig. 17 is due to Auger emission of valence electrons following the excitation of Cs $5p$ electrons. A rapid increase of peak height between $\Theta = 0$ and $\Theta = 0.10$ is followed by a slower increase between $\Theta = 0.10$ and 0.25. Compared to the Cs $5p$ binding-energy shifts the coverage dependence for the Auger peak position is small. At low coverage the peak appears at 11.0 eV above the Fermi level, while at full monolayer coverage this energy is 10.7 eV. If a Cu(111)-Cs $p(2\times2)$ sample is exposed to oxygen the Auger peak (labeled *A* in Fig. 18) becomes weaker. An extrapolation to zero intensity of the measured exposure dependence of the peak height gives an exposure value of around 0.4 L (Fig. 19). The Auger peak shifts from 10.7 eV to 10.4 eV above the Fermi energy between zero and 0.3-L oxygen exposure. A larger shift is observed for the Cs $5p$ excitation threshold, which for Cu(111)-Cs $p(2\times2)$ changes from 11.6 eV to about 10.8 eV upon 0.4-L oxygen exposure (peak *C*, Fig. 18). We have previously made UPS measurements of the Cs $5p$ binding-energy shift produced by oxygen exposure of Cs-covered Cu(111).[26] Within the limits of experimental error the shift is the same as for the excitation threshold obtained from the present measurements. Apart from the energy-loss shift of peak *C* and the decrease of the Auger emission peak *A*, the oxygen adsorption can be monitored by the appearance of a peak (labeled *B* in Fig. 18) at ca. 21-eV energy loss. We associate this peak, which grows as the exposure increases, with the excitation threshold of the oxygen $2s$ electrons.

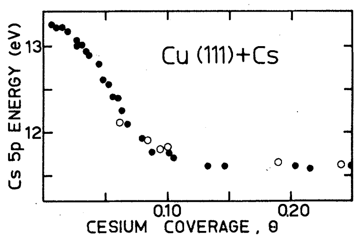

FIG. 16. The Cs $5p$ excitation threshold measured via EELS (filled circles) and the Cs $5p_{3/2}$ binding energy measured by UPS (open circles) plotted against Cs coverage on Cu(111).

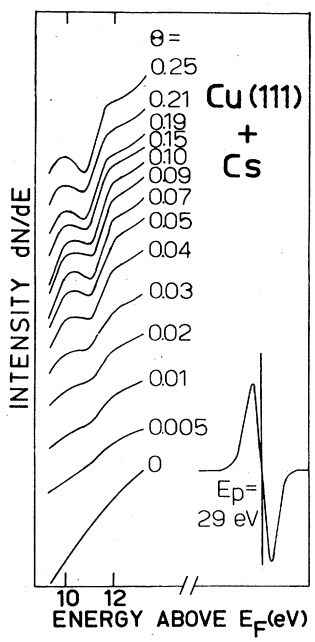

FIG. 17. Auger emission involving Cs $5p$ and valence electrons at different Cs coverages on Cu(111).

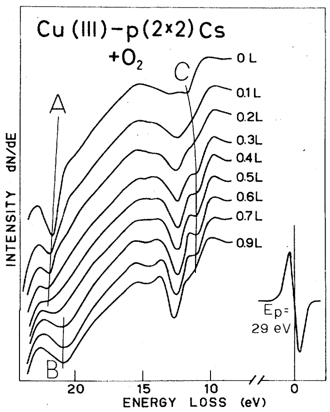

FIG. 18. Cs Auger emission peak (*A*), oxygen $2s$ loss structure (*B*), and Cs $5p$ loss structure (*C*) at different oxygen exposures of Cu(111) covered by a full Cs monolayer.

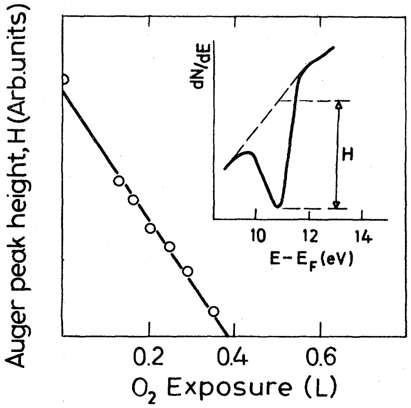

FIG. 19. The intensity of peak *A* in Fig. 18 plotted versus oxygen exposure.

IV. DISCUSSION

A. Work function and Cs 5*p* binding energy

The observations presented above are concerned mainly with the electronic structure of the alkali adsorbate. Complementary information about the chemisorption systems may be obtained by recording the adsorption-induced changes of the substrate electronic structure[4] or the level structure of the adsorbed oxygen.[19,27] A characteristic feature of the alkali monolayers is the large difference in the effect of the adsorbate at low and high coverage. At low coverages the adsorbate can be regarded as an array of ions, whereas at high coverage its behavior is that of a metal. Of considerable interest also is that the electronic structure appears to change in a gradual manner, a small change of coverage producing a small change of excitation energy. A reason for this is the uniform distribution of adatoms, which is also observed for other alkali adsorption systems.[7,28] This means that a relatively well-defined adatom-adatom separation can be varied in a continuous fashion and over a wide range by changing the coverage.

The variation of the work function and of the Cs 5*p* binding energy with alkali coverage both reflect the charge transfer between adsorbate and substrate. The ionic character of the adsorbate produces the rapid initial drop of the work function. If the work-function change at low coverage is equated with the potential drop across a dipole layer at the surface created by the charged adatoms and their images, then this indicates a dipole moment of 2.0 ± 0.2 e Å for Cs and 1.2 ± 0.2 e Å for Na. (The ionic radii are 1.7 Å and 0.95 Å for Cs^+ and Na^+, respectively.) The potential drop is calculated as for a parallel-plate capacitor.

Assuming that the work function of Cu(111) is 4.9 eV (Ref. 18), then work-function values of 1.9 and 2.7 eV are obtained at full monolayer coverages of Cs and Na, respectively. According to Lang,[29] who considered a model system consisting of an adsorbed jellium monolayer on top of a substrate jellium having a higher electron density, a full monolayer has nearly the same electron density and work function as a bulk sample of the overlayer jellium. For Cs and Na work-function values of 2.0 eV (Ref. 30) and 2.75 eV (Ref. 31) have been reported. The results thus suggest that the alkali is essentially neutral at full monolayer coverage.

Although one would expect the jellium picture to be applicable only at high coverages, Lang's model predicts well the main features of the coverage dependence of the work function over the entire monolayer range. The variation of the work function at low coverage is also reproduced in the calculations by Newns and Muscat,[32] who consider a model system of alkali adatoms which interact with each other and with the substrate. Within both models the charge on the alkali atom decreases rapidly with increasing coverage for coverages below that producing the work-function minimum.

The prediction by the model calculations that the adsorbate changes from a nearly ionic to a nearly neutral entity at relatively low coverages is also consistent with the observed variation of the threshold energy for exciting Cs 5*p* electrons. A nearly constant excitation energy between $\Theta = 0.12$ and 0.25 suggests that, in this coverage range, the charge on the alkali is nearly constant. For lower coverages the gradual increase of the number of valence electrons on the adsorbate as more alkali is adsorbed produces a coverage-dependent chemical shift. The total shift of threshold energy, 1.6 eV, is somewhat bigger than the 1.2-eV difference in excitation energy between the Cs ion (13.5 eV) and the Cs atom (12.3 eV).[33]

At low coverage the Cs 5*p* related loss structure is a doublet split by about 2.5 eV, a value larger than the 1.9-eV spin-orbit splitting of the ion.[33] At intermediate coverages the loss structure is more complex. We are unable to explain this structure, but we note that similar observations have been made for Cs adsorbed on W(110) (Ref. 34) and Rb on Ni(100) (Ref. 35). We also note that the spin-orbit splitting alone cannot explain the photoelectron energy spectrum associated with the 5*p* electrons of adsorbed Xe. If Xe is adsorbed on W(100) (Ref. 36) or Pd(110) (Ref. 15), the $5p_{3/2}$ derived emission peak is broader than for gaseous Xe, and when Xe is adsorbed on Pd(100), the peak is split.[37]

According to Waclawski and Herbst[36] the broadening is produced by the crystal field of the metal substrate, while Scheffler *et al.*[37] ascribe the splitting observed by them to the lateral overlap of adatom orbitals. The present UPS data reveal no splitting of the Cs $5p_{3/2}$ level. At the relatively high coverages used, one reason for this may be that there is enough valence charge on the alkali atom to screen the $5p$ electrons from the field created by the neighboring atoms.

The Cs $5p_{3/2}$ binding energy as measured by UPS is close to the Cs $5p$ excitation threshold determined by EELS over the studied coverage range (Fig. 16). This suggests that the two probes create nearly the same final state. For the ionic adsorbate at low coverage, the final state at the excitation threshold is expected to be a $5p^5 6s$ state, which is the lowest excited state of the free ion. In photoemission this state must be reached via a relaxation around the core hole. The relaxation can then be described as a downward energy shift of the $6s$ resonance, such that half of it becomes filled. This excited-atom picture of the screening was discussed by Lang and Williams, who found it to be a good approximation for alkali adsorbates.[38] It is less evident, however, that the approximation is equally justified for the almost neutral adsorbate at intermediate coverages. A neutral adsorbate means that the $6s$ resonance is half filled. A downward shift to accomodate one more electron means that the high-energy part of the resonance also becomes filled. On the high-energy side of the resonance one would expect that mixing with $6p$ states is more important than for the low-energy half of the resonance. If the $6p$ states are involved in the screening this may be one reason why the measured shift of 1.6 eV differs from 1.2-eV excitation threshold shift between ion and atom. A theoretical estimate of the screening charge at intermediate coverage could be obtained from a Lang and Williams method of calculation for an alkali adsorbate with two core holes.

B. Alkali valence electron excitations

In our view the previous EELS work on alkali monolayers provides solid evidence for the interpretation of the low-energy-loss peaks observed at high alkali monolayer coverages in terms of collective oscillations of the valence electrons in the alkali layer. This view is based primarily on the observed gradual change of the loss spectrum into the alkali-metal surface-plasmon-loss structure as the thickness of the overlayer increases. For a further discussion of the monolayer plasmons the reader is referred to the relevant papers.[5,9,39-41] The low-energy-loss peak observed at small alkali coverage is more difficult to explain. For the systems studied the measured energy losses, when plotted against coverage, fall along a curve which joins smoothly to the plasmon energy losses obtained at higher alkali coverage. This might be accidental and due to nearly equal excitation energies for two different processes. Alternatively, the excitation process changes character gradually as the coverage is changed. In a previous work on alkali-covered Ni(100) (Ref. 8), it was suggested that the observed loss structure is due to the alkali valence-electron $ns \rightarrow np$ excitation, which is a strong transition for the free atom. For the adsorbed alkali the transition involves a resonance-broadened and fractionally occupied ns level and a broadened np level. Due to somewhat better resolution the present spectra demonstrate more clearly than the previous work the peak-shaped character of the loss structure at low and intermediate coverage. The peak is only marginally wider than the limit of about 0.5 eV set by the experimental resolution.

The $6s \rightarrow 6p$ excitation energy of the Cs adsorbate may be expected to decrease as the coverage increases. For the nearly ionic adsorbate at low coverage we compare the observed 3.2-eV energy loss with the difference between the $5p^6 \rightarrow 5p^5 6s$ (13.3 eV) and the $5p^6 \rightarrow 5p^5 6p$ (15.7 eV) excitation energies of the Cs ion.[33] At around $\Theta = 0.15$, when the adsorbate is close to neutral, the energy loss is 1.2 eV, while the $6s \rightarrow 6p$ transition requires an energy of 1.4 eV for the Cs atom. A more detailed comparison should also take into account the widths of the levels and fractional filling of the initial state for the adsorbate. Since only part of the $6s$ resonance is occupied one expects that the observed excitation energies are somewhat higher than the estimates from tabulated excitation energies of the free atom or ion. For Na, the energy loss is about 3.2 eV at low coverage, while the minimum energy loss is 2.3 eV. For an ion the $2p^6 \rightarrow 2p^5 3s$ (32.9 eV) and $2p^6 \rightarrow 2p^5 3p$ (36.4 eV) transition energy difference is 3.5 eV, while the $3s \rightarrow 3p$ excitation energy is 2.1 eV for a Na atom. The present results and those reported for Na, K, and Rb on Ni(100) (Ref. 35) all show that the minimum energy loss is close to the $ns \rightarrow np$ excitation energy of the atom. The agreement at low coverage with the ionic excitation energy differences is less convincing. The main observation is that at low coverage the excitation energies are remarkably equal (3.4 ± 0.2 eV) for the different alkalies and substrates.

Muscat and Newns[42,43] have calculated the valence electronic structure of alkalies adsorbed on jellium. For a reasonable distance between the center of the alkali atom and the jellium boundary the authors find that, in the case of Cs on a jellium representative of Cu, the full widths at half maximum are 0.6 eV for the 6s level, 0.4 eV for 6p_z, and 1.0 eV for 6p_{xy}. If these width estimates are correct then one would expect the excitation energies to be sufficiently well defined to allow observations via EELS at least for intermediate coverages when the ns resonance level is nearly half filled. At low coverage, with only the tail of the resonance filled, it is more difficult to explain the observed peak-shaped character of the loss structure. Other theoretical calculations find that the alkali ns and np levels are strongly hybridized.[44] Here we note that the relevance of treating the substrate as a jellium is uncertain for Cu(111). In the energy range of the ns and np resonances the electronic structure is strongly anisotropic because of the approximately 5-eV wide $L_2' - L_1$ conduction-band gap. In summary an interpretation of the low-coverage loss in terms of $ns \rightarrow np$ transitions is based mainly on the fact that the excitation energies at intermediate coverage are nearly equal to the values for the free Na and Cs atoms. Such a comparison is justified at these coverages because the adsorbate is nearly neutral and yet not sufficiently close packed for the valence electronic structure to have lost its atomic character. At still higher coverage, and because of adatom-adatom interaction, the layer can be regarded as a slab of alkali metal.

In the above discussion of single-particle transitions it has been assumed that the loss peak observed at low coverage is associated with electronic excitations involving levels characteristic of the alkali atom. Another possibility is that the structure is associated with transitions between states characteristic of the substrate. It has been observed for Cu(111) and Ni(111), and so far for only these crystals, that surface states can shift in energy as a result of adsorption. For Cu(111) such a shift has been observed on adsorption of Cs (Ref. 4) and Na (Ref. 45) and for Ni(111) on adsorption of hydrogen.[46] The observed peak-shaped loss spectrum demands, however, that there also exist a well-defined final state, but no surface resonances have been reported in the energy range of interest for Cu(111) and Ni(111).

C. Alkali/oxygen coadsorption

The small oxygen exposures required to bring about the observed changes of EEL spectra, work function, and Auger emission show that the oxygen sticking coefficient must be close to unity for the alkali-covered surface. For example, after about a 0.5-L exposure of Cu(111)-Cs $p(2\times2)$ a $p(2\times2)$ pattern appears indicating equal numbers of Cs and O atoms on the surface. The observation of diffraction patterns, indicating one or maybe two ordered phases in the exposure range between zero and 0.5 L, means that the adsorbed oxygen atoms tend to keep apart. Independent evidence for this is provided by the gradual decrease of the energy loss E_L upon an increase of oxygen exposure. If there had been a tendency toward clustering one would expect E_L to remain nearly constant, as observed for Na monolayers, and the intensity of the loss peak to decrease as more oxygen is adsorbed. The formation of ordered alkali/oxygen monolayers having a large unit mesh has been reported previously for Fe(110) (Ref. 19) and W(100) (Ref. 47) substrates. The same type of exposure dependence of the work function as found for Cu(111)-Cs $p(2\times2)$ has been reported for Cs-covered W(100) and W(112) crystals.[47] To explain the reduction of the work function observed at low oxygen exposures, the authors assume that the oxygen ions adsorbed during this initial stage are located somewhat beneath the Cs layer. Upon oxygen adsorption the Cs becomes ionized. The dipoles thereby created in the surface layer lower the work function until, at around 0.4-L oxygen exposure, a minimum value is obtained when the first oxygen layer is completed. The rapid increase of the work function for exposures above 0.4 L then corresponds to the formation of a second oxygen layer.

We assume that the usual relationship between plasma frequency and electron density, $\omega_p \sim n^{1/2}$, is valid for monolayer films and associate the linear decrease of E_L^2, when plotted against oxygen exposure, with a decrease of the free-electron density in the adsorbed layer. For close-packed monolayers, support for the assumption of a $\omega_p \sim n^{1/2}$ dependence is obtained from the values reported for the different alkalies. For Cs the energy loss is about 1.5 eV when it is adsorbed both on W(100) (Ref. 5) and on Cu(111), whereas for Na, K, and Rb on Ni(100), the values are 3.1, 2.3, and 1.7 eV, respectively.[8,9] The energy losses for close-packed alkali layers are close to half the bulk plasmon energies and thus appear to reflect the electron density in the alkali layer. Further support for the assumption of a $\omega_p \sim n^{1/2}$ dependence is provided by the increase of the energy loss from 1.2 to 1.55 eV observed when the Cs coverage is increased from $\Theta = 0.16$ to 0.25. Assuming the Cs fills a given monolayer volume, one would expect an increase of around 30%. Within our simple picture the density of electrons in the Cs-O layer then decreases as $n = n_0(1 - Q/Q_0)$, where n_0 is the density of free electrons in the close-packed Cs monolayer and Q_0 the exposure value obtained by extrapolating the observed E_L^2

vs Q dependence to zero energy loss (Fig. 12). We note that the Q_0 values obtained for different experimental runs are between 0.3 and 0.5 L; this is somewhat lower than the exposure values of 0.5–0.6 L, which give the most distinct $p(2\times2)$ diffraction pattern.

An independent measure of the amount of Cs valence charge in the adsorbed layer is obtained from the strength of the Auger peak shown in Fig. 18. The Auger peak decreases at approximately the same rate as the E_L^2 values when plotted against oxygen exposure (Fig. 19). As far as plasmon excitations are concerned our experimental results suggest that for exposures below around 0.4 L, the Cs-O layer acts as a free-electron-like metal. Some of the Cs valence charge has been transferred to the oxygen ions, but the remaining Cs electrons are able to form an electron gas even when a large fraction of the Cs valence charge is bound to the oxygen. The Cs-O mixture in the surface layer thus shows a behavior typical for binary solid solutions of simple metals. The difference in the present case is that one of the constituents, the oxygen, traps electrons. Because the oxygen tends to be distributed evenly over the surface, the atomic arrangement is similar to that of a disordered binary solid solution. Since bulk metals do not form solid solutions with oxygen over large concentration intervals, situations similar to that of the present surface layer are not encountered for fully three-dimensional cases. There are, however, examples of bulk oxides which show some similarity to the monolayer films, namely, the metal-rich oxides Cs_7O and $Cs_{11}O_3$. These oxides are metallic and have plasma frequencies which have been measured via energy-loss satellites to peaks in UV photoemission spectra.[48] The frequencies obtained are close to the values predicted from free-electron theory if one first transfers enough Cs valence charge to the oxygen to create O^{2-} ions and then allows the remaining Cs valence electrons to form a homogeneous electron gas in the crystal. As a first step toward theoretical justification of the simple model used here to explain the EEL spectra, it would be valuable to obtain electronic structure calculations of the metal-rich Cs oxides.

Considering the results obtained for the bulk oxides it should not be very surprising that some reduction of the electron-gas density of the Cs layer may be obtained via oxygen adsorption. It is remarkable, however, that the density of the electron gas can be reduced over such a wide range as required to explain the energy shift of the loss peak from 1.5 eV to ca. 0.5 eV, which is the lowest energy loss measured. If the $\omega_p^2 \sim n$ relationship is correct, then this implies that the electrons in the layer are able to form a gas having a density of only 10% of that for the Cs $p(2\times2)$ layer. With only Cs on the surface we found a lowest energy loss of 1.2 eV. This difference between the Cs and the Cs-O layers might be explained partly by the dipoles present in the Cs-O layer helping the valence electrons to stay in the layer. Furthermore, the atomic configuration is different. For the Cs layer the nearest-neighbor distance increases upon decreasing the amount of Cs adsorbed. For the Cs-O layer those Cs atoms which have not reacted with the oxygen still have nearest neighbors at close-packed distance even when some of the Cs has reacted with oxygen, although the number of such neighbors decreases as the oxygen exposure increases.

The present interpretation provides support for the basic hypothesis of a model by Clark for the electronic structure of the activating layer in III-V: Cs-O negative electron affinity photoemitters.[49] Clark explores the consequences of assuming that the activating layer is a single amorphous phase of composition CsO_y, where y can have a range of values. The assumptions made, i.e., that each O traps two electrons and that there exists a range of y values for which the layer is metallic with an electron density given by $n = n_{cs}(1-2y)$, in fact coincides with our interpretation of the energy-loss shifts on oxygen exposure of Cu(111)/Cs at high alkali coverage. It may even be the case that the model is more appropriate for the present substrate than for the III-V compounds. For semiconductor substrates, complications may be expected because for several systems there is no abrupt boundary separating the substrate and the adsorbate. For the present system we have found no evidence for any mixing of the substrate and the adsorbed species. Clark also uses the expression $n^{1/3}a_H \sim 0.25$ derived by Mott and Davis[50] to estimate the composition limit for a metallic Cs-O layer. As pointed out by the author the estimate must be regarded as uncertain. The dielectric constant ϵ and effective electron mass m^x necessary for a determination of $a_H = \hbar^2\epsilon/m^x e^2$ are not well known. The obtained density limit $n = 1.0 \times 10^{21}$ cm^{-3} is about 10% of the density for Cs metal. There is evidently no contradiction with the present results since the lowest recorded energy loss according to our interpretation corresponds to a density which is also ca. 10% of the density for a close-packed Cs layer. Since the lowest observed energy losses are close to the limit set by the present experimental resolution, we have not been able to determine the low-energy limit of energy losses for a fully Cs-covered Cu(111) surface.

To explain the observed shift of energy loss on oxygen adsorption it has not been necessary to invoke any role for the substrate. This does not necessarily mean that the substrate plays a passive role in the binding of the oxygen to the surface. Our interpretation assumes that the energy loss reflects the change in the density of free electrons in the overlayer. This change could be produced by a transfer of Cs valence electrons to the substrate with the ionization of the oxygen achieved by a transfer of electrons from the substrate. The net effect could then be the same as for a direct transfer between Cs and O, although the local charge distribution would differ. To explain the binding energies observed for the potassium and oxygen coadsorbed on Fe(110), Pirug *et al.*[19] have recently proposed that the oxygen is bound mainly to the substrate. This interpretation would favor the more complicated picture of charge transfer. The situation is expected, however, to differ between the various adsorption systems depending on the binding energies of the oxygen to the substrate and alkali adsorbate. For the present system support for a direct charge transfer between Cs and O is obtained from the decreasing Cs $5p$ binding energy on oxygen adsorption and from the observation that a Cu(111) surface state, which is removed by oxygen adsorption on clean Cu(111), is not markedly damped when Cs-covered Cu(111), is exposed to oxygen.[26] We also note that the observation of a gradual energy-loss shift on oxygen adsorption supports the view that the overlayer can be regarded as a cesium oxide, since the formation of metal-rich metallic oxides is typical for Cs.

As discussed above, the Cs adsorption-induced loss peak shifts to gradually lower energies as more oxygen is adsorbed if the Cs layer is close packed. At low Cs coverage the peak remains in constant position and becomes weaker upon oxygen adsorption (Fig. 9). This means that at low coverage the layer can be regarded as a collection of separate particles. Locally, around an adsorbed oxygen ion, there will be a Cu – Cs – O chemisorption complex having a level structure different from that of the Cs adsorbate, and therefore the intensity of the loss peak decreases upon oxygen adsorption. The change from low- to high-coverage behavior occurs at around $\Theta = 0.16$. For coverages higher than this critical value the energy loss shifts upon oxygen adsorption in the manner already discussed for the full Cs monolayer. The maximum shift increases as the Cs coverage increases above the critical value (Fig. 12). As far as its response to oxygen adsorption is concerned the electron-gas picture of the Cs overlayer is thus justified for coverages higher than around 0.16. We note that it is also above this coverage that the energy loss shows the $\omega_p^2 \sim n$ dependence expected for plasma oscillations (Fig. 6). Also, the changes of work function upon oxygen exposure are markedly different for Cs coverages above and below 0.16. The exposure dependence for coverages higher than this value is characterized by an initial drop to a minimum followed by an increase to an almost constant value. At coverages below 0.16 there is a monotonic increase of the work function to a nearly constant value (Fig. 2).

Since we find the results obtained for the sodium-oxygen coadsorption system less interesting, we have not investigated this system as thoroughly as the cesium-oxygen system. For high alkali monolayer coverages there is a small initial drop of work function (Fig. 4) and a marginal shift to lower energy of plasmon-energy loss. Our interpretation is that one cannot regard the Na overlayer as a free electron gas, the density of which can be diluted by oxygen adsorption. The reason for this may be that the oxygen in this case prefers to form islands with the remainder of the surface relatively unaffected by the adsorption. In this connection we again note that alkali-rich oxides are known only for Rb and Cs.[46] The present results suggest that this ability of the heavier alkalies in bulk form to share relatively few oxygen atoms on an equal basis is retained by adsorbed monolayers of these elements.

V. SUMMARY

The present results for Na and Cs monolayers on Cu(111) are consistent with the picture of a nearly ionic adsorbate at low coverage and an almost neutral metallic overlayer at high coverage. Combined with previous similar observations of alkalies on Ni(100) (Refs. 8, 9), the present EEL spectra suggest that there exists a well defined low-energy excitation which is common to all alkali adsorbates at low coverage and which gradually changes into the surface plasmon excitation when the adsorbed amount of alkali is gradually increased. Another interesting observation is the progressive decrease of the monolayer plasmon-energy loss when increasing amounts of oxygen are adsorbed on Cu(111) at high monolayer Cs coverage. Supported by work function and Auger emission data, as well as by UPS results for Cs-rich bulk oxides, we associate the changing energy loss with a thinning of the electron gas in the overlayer due to oxygen adsorption.

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