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Adsorption of alkali metals on W(100) : an EELS study

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Résumé. — Nous avons étudié l'adsorption de Na et de K sur la face (100) du W à la température ambiante par variation du travail de sortie, diffraction d'électrons lents et spectroscopie de perte d'énergie d'électrons résolue angulairement. Pour ces deux alcalins, des diagrammes de diffraction $C(2 \times 2)$ sont observés jusqu'à la monocouche. Nous interprétons ces diagrammes à bas taux de couverture par une reconstruction du substrat provoquée par l'alcalin adsorbé. La variation de l'énergie de la perte principale en fonction du taux de couverture présente un minimum marqué (peu accentué) pour Na(K). Au-delà de ce minimum, la perte est due à l'excitation d'oscillations collectives. Ce comportement est comparé à celui observé pour une couche de Cs adsorbée sur le même substrat : les liaisons entre les atomes de Na, K et Cs et la face (100) du W sont de même nature.

Abstract. — Room temperature adsorption of Na and K on the W(100) face is studied by work function changes, LEED and angular resolved electron energy loss spectroscopy (EELS). $C(2 \times 2)$ patterns are observed up to the monolayer for both alkalis. At low coverage, this pattern is interpreted as the result of a reconstruction of the W(100) face induced by alkali adsorption. The changes of the energy loss *versus* alkali coverage exhibit a deep (shallow) minimum for Na(K). Collective oscillations are assumed for coverage beyond the minima. This behaviour is discussed in regard to previous studies, particularly that of Cs on W(100). We conclude that the bonds between Na, K and Cs atoms and the W(100) face have the same nature.

1. Introduction.

Adsorption of alkali metals on materials has been intensively studied for its technical applications and for its fundamental interest because it provides one of the simplest example of chemisorption. The alkali adsorption is generally described by a model [1] in which the alkali atoms are ionized at low coverage. A strong decrease of the work function (WF) occurs as the result of the induced dipoles and is followed by a minimum due to their interaction when the coverage increases. Beyond this minimum neutralization is achieved and the alkali overlayer becomes metallic as suggested by the plasmons observed on Na, K, and Rb on Ni(100) [2] and Na, and Cs on Cu(111) [3]. From electron energy loss spectroscopy (EELS) experiments on Cs on W(100), Mac Rae *et al.* [4] interpreted their results similarly for coverage beyond the WF minimum, while Soukiassian *et al.* [5] considered that interband transitions occur for coverage up to the monolayer. This latter interpretation is consistent with

theoretical calculations performed independently by Wimmer *et al.* [6] on a Cs monolayer on W(100). These authors, who took into account the true electronic structure of the system, showed that the adsorption of a Cs monolayer is dominated by the hybridization of the Cs 6s electron with the W surface state situated just below the Fermi level, and that a covalent polarized bond is formed. These calculations predict that the surface state shifts by one eV to higher binding energy and keeps an appreciable intensity. These predictions agree with Angular Resolved Ultraviolet Photoemission Spectroscopy (ARUPS) results obtained on this system [7]. A similar behaviour of the surface state of Mo(100) and Ta(100) upon cesiation was observed using ARUPS [8]. In EELS experiments of Cs deposited on W(100) and Mo(100), the main loss was interpreted as being due to an interband transition between the Cs 6s electron hybridized with the surface state of W or Mo(100) and the Cs 6p [8].

Does this description, which provides a good picture of the electronic properties of Cs on a (100) face of W or Mo, apply for other alkali metals adsorbed on the same substrates? In the present study, we examine the adsorption of Na and K on the W(100)

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face at room temperature. We show that the EEL spectra obtained for these overlayers are different from those of Cs on W(100).

2. Experimental

The experiments were performed in an ultra-high vacuum chamber with a base pressure of 5×10^{-9} P. The experimental setup was described previously [9] but was modified in order to fit a resonance UV lamp without a monochromator. In these ARUPS experiments, the neon I radiation (16.85 eV) was used. The incident angle of the light was set at 60° . Work function changes were deduced from the secondary electron cutoff in ARUPS spectra.

For EELS, the angular resolved spectra were obtained in the specular direction with an incident angle of 45° . The resolution was better than 150 meV. Various primary energies (30 to 50 eV) were used.

The W(100) surface was cleaned in the usual way : by cycles of oxidation and flash heating at 2 200 K. The cleanliness was checked using ARUPS at $\bar{\Gamma}$ since the amplitude of the high-lying surface state of W(100) is very sensitive to contamination.

Pure Na and K layers were deposited onto the surface from a couple of resistively heated chromate sources which had been carefully out-gassed. The growth of the K layers was monitored by both AES measurements using LEED optics and by work function changes. The calibration of the Na coverage could only be obtained by this last method.

3. Results.

For both alkali metals, $C(2 \times 2)$ patterns were observed in the whole coverage range investigated in agreement with previous RHEED results on these systems [10, 11].

Figure 1 shows the WF changes *versus* alkali coverage (θ). For convenience, the alkali coverage is taken to be equal to 1 at the complete monolayer (ML). For K adsorption, the intense LMM Auger transition (252 eV) was used for calibration. As the Na sticking coefficient on W(100) remains constant up to the monolayer [10], its calibration is deduced by considering that the WF minimum arises at 0.6 ML, as it does for K and Cs layers on this substrate. The minimum values of WF (1.5 for K and 1.6 for Na) are lower than those given by Blaszczyzyn *et al.* [12].

EEL spectra for various Na coverages are shown in figure 2. The main result is the variation of the P_3 energy loss with the Na coverage. After a decrease in the energy loss to 2.8 eV for 0.6 ML, P_3 suffers a continuous shift up to 3.8 eV for coverages beyond the monolayer. At $\theta = 1$, the energy loss is equal to 3.7 eV. The energy loss variation against Na coverage is reported in figure 3. Note that losses P_1 and P_4 disappear at low coverage, while P_2 grows for a coverage near the monolayer.

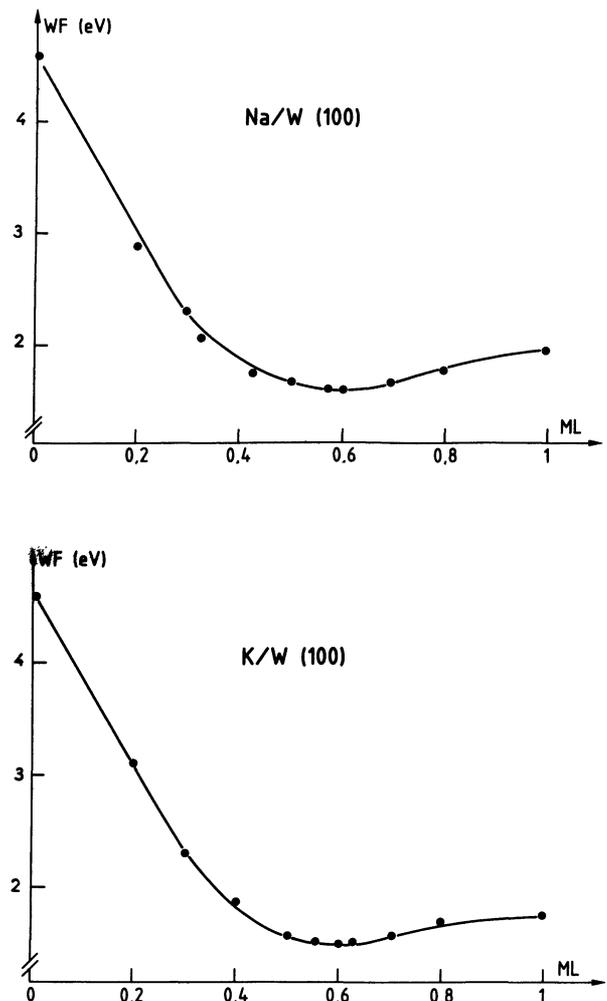


Fig. 1. — Variation of the work function *versus* alkali coverage. a) Na; b) K.

For K adsorption, the EEL spectra are very similar to those obtained with Na except for the energy variation of P_3 . The change in the main energy loss *versus* K coverage is shown in figure 3, in which a shallow minimum can be seen. The Cs results are also reported [7] in this figure, the Cs population at the monolayer being 4.3×10^{14} atoms.cm² [13].

The ARUPS results obtained on Na and K overlayers will be reported and discussed elsewhere [14]. For the following discussion, we need only to consider the behaviour of the surface state of the W(100) face situated at 0.4 eV below the Fermi level on a clean face. This state shifts continuously by 2 eV to higher binding energy for increasing alkali coverage up to 1 ML.

4. Discussion.

Before discussing the electronic properties of alkali overlayers on W(100), we have to determine the population of the adsorbed alkalis.

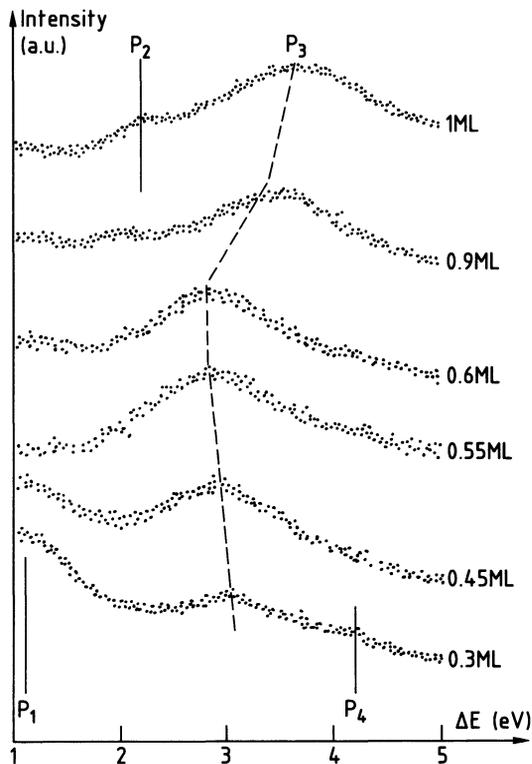


Fig. 2. — EELS spectra for various Na coverages on W(100). The elastic peak was omitted ($E_p = 50$ eV). The intensity of these spectra is not normalized.

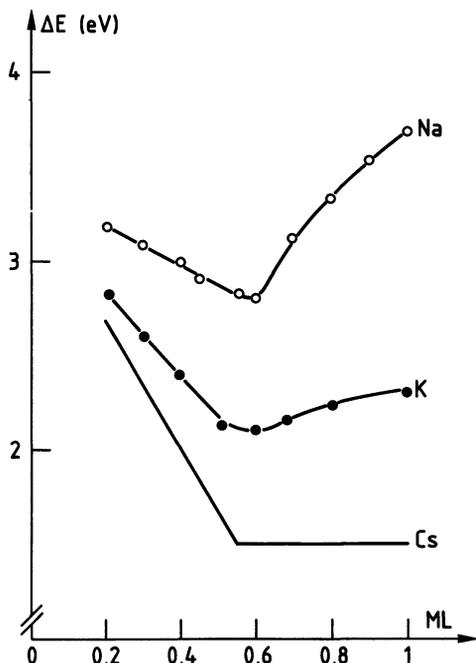


Fig. 3. — Variation of the main energy loss *versus* alkali coverage. Note that the atomic population of Na, K and Cs monolayers amounts to 5×10^{14} atoms.cm⁻², 5×10^{14} atoms.cm⁻² and 4.3×10^{14} atoms.cm⁻² respectively.

4.1 ALKALI COVERAGE. — For both alkali metals, C(2 × 2) patterns are observed for the whole coverage range investigated. Below the monolayer, as will be discussed below (section 4.3), the C(2 × 2) pattern observed corresponds to a change in the substrate structure. At the monolayer, however, the arrangement of the Na overlayer corresponds to a C(2 × 2) lattice which is maintained through several layers, as has been shown by RHEED [10]. The atomic population is half that of the W(100) and amounts to 5×10^{14} atoms.cm⁻². As pointed out previously [10], the nearest neighbour distance 4.47 Å in the Na monolayer is larger by 4% than that of a Na(100) bulk plane.

On the other hand, the C(2 × 2) K monolayer corresponds to a compact arrangement along [110] since the bulk interatomic distance is equal to 4.70 Å. The population of the K overlayer at the WF minimum and at the monolayer are respectively the same as that of the Na overlayer (3×10^{14} and 5×10^{14} atoms.cm⁻²). Blaszczyzyn *et al.* reported higher values [11] than ours but in the same ratio. At the monolayer, our result agrees with those of Mlynczak and Niedermayer [10].

4.2 EELS INTERPRETATION. — These spectra were obtained in the specular direction where « vertical » ($\Delta K_{\parallel} = 0$) one-electron transitions and $q_{\parallel} = 0$ collective modes are observed.

First we will discuss the behaviour of the main loss *versus* Na coverage. The curve of the energy loss P_3 *versus* Na coverage (Fig. 3) is very similar to that reported for Na and Cs on Cu(111) [3] and Na, K, and Rb on Ni(100) [2]. Two regions in these curves can be observed : the decreasing part at low coverage, and the area beyond the minimum.

At low coverage, interband transitions were assumed. For Lindgren and Wallden [3], the initial and final states were respectively identified with the *ns* and *np* levels of the alkali atom or ion ($n = 3$ or 4 for Na and K respectively). The drop in the energy loss with increasing coverage was thought to be correlated with depolarization effects. But for Cs on W(100) or Mo(100), the initial state was identified with the W(d) surface state hybridized with Cs 6s electron, the final state being the Cs 6p [8]. The decrease in the energy loss is due to a simultaneous shift of the two levels upon cesiation.

A similar mechanism is proposed for the present Na adsorption, for which a continuous shift of the W(d) surface state is observed in ARUPS [14].

For alkali coverage beyond the minimum of the energy loss (ΔE), Jostell [2] and Lindgren and Wallden [3] reported the following variation of ΔE :

$$\Delta E \propto n^{\alpha}$$

with α nearly equal to 0.5 and n the atomic alkali density. These authors consider that the energy loss is due to collective oscillations in the alkali layer. This

interpretation was generally supported by the observation of a second harmonic peak for alkali coverage in the monolayer range.

In our case, this relation applies for $0.6 < \theta \leq 1$ ML. Furthermore, a peak which appears at 7.4 eV for Na coverage in the monolayer range corresponds to the second harmonic of P_3 . As the loss value at the monolayer is close to that of the surface plasmon (3.85 eV) observed for the bulk [15] which is reached above the monolayer coverage, we consider that collective oscillation (surface plasmon excitation) is the most probable mechanism for the P_3 loss above 0.6 ML.

The other weak peaks observed in figure 2 are attributed to interband transitions. In the energy loss range of interest ($\Delta E \leq 8$ eV), the peaks P_1 and P_4 observed on a clean W(100) surface have been discussed by Avery [16] and Meister *et al.* [17]. The bulk loss P_1 (1.2 eV) is attenuated by the Na deposition. P_4 situated at 4.2 eV is very sensitive to adsorption and is attributed to a transition from a surface state, which may be the low-lying surface state situated at 4.2 eV below the Fermi level on a clean W(100) face. The loss P_2 which grows at high coverage and shifts slightly with coverage may be attributed to a transition from the high lying W surface state shifted by Na to the Fermi level.

For K adsorption, the interpretation of the EEL spectra is less straightforward. At low coverage, the decreases in figure 3 are due to interband transition as it is for Na. But for the K overlayer beyond the minimum, the relationship $\Delta E \propto n^\alpha$ gives $\alpha \sim 0.2$, which is far from the theoretical value ($\alpha = 0.5$). However, we remark that the energy loss for $\theta > 1$ ML (2.4 eV) is close to that measured by Jostell (2.3 eV) [3] for his « dense » monolayer on Ni(100). Furthermore, the peak situated at 4.9 eV, which appears in the monolayer range, may be interpreted as the second harmonic of a plasmon loss. Therefore, the main loss in K EEL spectra has the same origin as in Na. Plasmon excitation in K layers on W(100) was previously assumed [18]. We notice a weak peak at 2 eV appearing as a shoulder in the main peak, and this is attributed to an interband transition.

4.3 CORRELATION BETWEEN EEL SPECTRA AND ELECTRONIC PROPERTIES. — Figure 3 shows that each alkali metal adsorbed on W(100) exhibits a particular shape of the energy loss curve *versus* alkali coverage. Beyond the minimum, the Na overlayer illustrates the $n^{1/2}$ dependence almost perfectly while the plateau obtained for Cs may be considered as the other limit. The K layer appears as an intermediate case.

The key question is to determine whether these different behaviours are related to particular electronic structures.

From the Na monolayer structure, it is clear that the adsorbate substrate interaction must be the dominant term of the energy of the system. This is also true for K since the C(2 × 2) is observed in contrast to other substrates such as Ni(100), in which a compact

hexagonal structure is reported [2]. The adatom interaction term is increased for the Cs, where the compact hexagonal layer is mainly adsorbed incoherently, as on Mo(100) [19]. But as Wimmer *et al.* [6] successfully described the electronic properties of a hexagonal monolayer of Cs on W(100) by considering a C(2 × 2) overlayer structure, these two arrangements are equivalent for these properties at least at $\bar{\Gamma}$. Thus, we believe that the model describing the Cs adsorption on W(100) may be extended to the K and Na overlayers on this substrate. This assumption results mainly from the similarity of the behaviours of the ARUPS peaks at $\bar{\Gamma}$ upon increasing alkali coverage. For the three alkali metals, we observe a continuous energy shift of the W(100) — d like surface state during alkali deposition. This shift was one of the dominant features predicted by the calculations for the Cs monolayer on W(100) [6].

Therefore, we have to consider the origin of the different shapes observed in figure 3.

It is known that the excitation frequency of a thin layer depends on three parameters :

- the density of free electrons. For different alkali metals adsorbed on the same substrate, the number of alkali valence electrons involved in the bond with the substrate may vary with the nature of the alkali. Then, the density of the free electron depends on the nature of the alkali metal ;

- the presence of interband transition, which modifies both the strength and the frequency of the oscillation [19, 3] ;

- the microgeometry of the overlayer, which determines the true local density of charges. The growth mode has to be considered. For example, the growth by island formation was assumed in order to explain the constant value of the loss energy when Na is deposited on a Ni(100) C(2 × 2) S structure [21]. Island formation was also demonstrated for K on a reconstructed Si(100) (2 × 1) [22].

As for Na adsorption on W(100), the $n^{1/2}$ relation is satisfied for $0.6 < \theta \leq 1$: it requires that the local charge density increases linearly with coverage in this range. We deduce that the Na atoms are uniformly spread over the surface despite the absence of rings in the LEED pattern at low coverage. Such an absence was noted previously at room temperature for several systems [23-25]. As island formation is excluded, it follows that the C(2 × 2) pattern observed at low coverage is due to a substrate reconstruction induced by Na adsorption. In the monolayer range, the observed LEED pattern may result not only from the reconstruction of the substrate but also from an ordered Na arrangement [10]. Such an induced reconstruction was demonstrated for Cs on Mo(100) [19] and has been suggested for Cs on W(100) [8].

Considering the similarity between the LEED results obtained with Na and K, the same mechanism of growth is assumed for both the alkali overlayers.

Therefore, an island formation is excluded for K. This means that a substrate reconstruction occurs with K, and that the low increase of the energy loss beyond the minimum (Fig. 3) may be explained by both a competition and an interaction between the collective modes (plasmons) and interband transitions. It is worthwhile remarking that the measured minimum of the energy loss corresponds to that of the sp transition calculated at $\bar{\Gamma}$ by Wimmer [26] for an unsupported K layer.

For Cs, it was shown that the plateau which appears in figure 3 cannot fully be explained by island formation. An interband transition was therefore postulated for $0.6 < \theta < 1$ [7]. At the monolayer, the collective mode may appear since, the energy loss increases slowly for increasing Cs coverage and reaches the surface plasmon of bulk for 10 layers [4].

Therefore, the differences observed in the EELS curves *versus* Na, K and Cs coverages do not reflect a qualitative change in the alkali-substrate bond. Rather they are related to both competition and interaction between the collective mode and the individual transition.

On the other hand, a comparison of the values of the main loss reported for overlayers of a given alkali metal on several substrates as Ni(100) [2, 20], Cu(111) [3], Pt(111) [27] and W(100) indicates a substrate effect. The minimum energy loss for adsorbed Na, K and Cs is higher on W(100) than on other substrates. These low values are attributed by Jostell [2] to the influence of interband transitions on collective oscillations. The energy of these transitions is lower with a Ni substrate (2.2 eV and 1.5 eV for Na and K respectively) than on W(100), where these values are 2.8 eV and 2.1 eV respectively.

5. Conclusion.

The adsorption of K and Na on the W(100) face is studied at room temperature using LEED, EELS and WF measurements. $C(2 \times 2)$ patterns are observed in the whole range of investigated alkali coverage. At low coverage, this LEED pattern is interpreted as being due to a reconstruction of the W(100) face induced by the alkali overlayers. In the monolayer range, the $C(2 \times 2)$ may result not only from an ordered alkali arrangement but also from the reconstructed substrate.

The curves showing the energy loss *versus* alkali coverage exhibit a minimum for both Na and K. Collective oscillations are assumed for coverage beyond the minimum for both the alkalis; the Na layer behaves as a free electron gas, while the plasmon frequency for K is strongly modified by the presence of interband transitions.

This behaviour contrasts with that of Cs adsorbed on the same substrate and for which interband transitions had been previously postulated. Arguing from the similarity of the ARUPS data obtained for the three alkali metals on W(100), we consider that the differences between EELS spectra for each alkali do not reflect a qualitative change in the alkali-substrate bond. Competition and interaction between interband transition and collective oscillation may explain these differences.

A more detailed understanding of the alkali adsorption on W(100) requires further experimental and theoretical investigations of the electronic properties of these systems.

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