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## K and S coadsorption on Ni(100) surfaces

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**Abstract.** In this contribution we report a study of K and S coadsorption on Ni(100) surfaces by means of Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS) and WF (work-function) measurements in UHV. Adsorption of elemental S on clean Ni(100) increases the binding energy, and the maximum coverage of the subsequently deposited K. The presence of the S underlayer maintains the ionicity of K adatoms close to the ionic state up to the completion of the first layer, at  $\Theta_K = 0.67$  ML. The latter coverage is, thus, greater than the estimated 0.38 ML of K on clean Ni(100). The K overlayer on S-covered Ni(100) weakens the S–Ni bond, and forms a compound with S. The presence of S on Ni(100) lowers the WF minimum,  $\Phi_{\min}$ , of K on Ni(100) to a value of  $\sim 1$  eV, which is attributed to K–S compound formation. Deposited S atoms on K-covered Ni(100) are submerged under the K layer up to 0.5 ML and subsequently they are adsorbed on top of the K layer.

### 1. Introduction

The coadsorption of alkali metals and electronegative elements on metallic and semiconducting surfaces has been the subject of intensive investigation [1–5]. Theoretical interest aside, the above coadsorption systems have considerable scope for technological application in thermionic energy conversion, photocathodes and catalytic reactions [6–8]. It is well known that the deposition of the alkali elements on most metal surfaces lowers the work function of the metal substrate to a minimum value  $\Phi_{\min}$ . An increase of the amount of alkali deposited causes a corresponding increase of the WF until the latter levels off and gives a maximum value  $\Phi_{\max}$  at saturation coverage. The  $\Phi_{\max}$  is close to that of the alkali adsorbate in its metallic state. Furthermore, alkali metals coadsorbed with electronegative oxygen or hydrogen exhibit an even greater decrease of  $\Phi_{\min}$  [1–3]. It is rather unfortunate that coadsorption studies of alkali metals and electronegative elements other than oxygen and hydrogen are almost nonexistent [9–13]. In view of this, we have recently investigated the coadsorption of S with Na and S with Cs on Ni(100) surfaces [11, 12]. The behaviours of these two coadsorption systems are markedly different. Thus, predeposited S of  $\leq 1$  ML further decreases the  $\Phi_{\min}$  of Na on clean Ni(100) while coadsorbed S and Na interact strongly with a tendency to form  $\text{Na}_x\text{S}_y$  compounds. In comparison, the presence of S on Ni(100) increases the  $\Phi_{\min}$  of Cs on clean Ni(100) and there is no indication of any Cs–S compound formation [13]. It is therefore obvious that more scientific effort is necessary to understand the mutual effects of S and alkali coadsorbates on Ni(100) surfaces.

In this contribution we are reporting a study of the coadsorption of K and elemental S on Ni(100) surfaces, at room and elevated temperatures, by Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS) and using work-function (WF) measurements in an ultrahigh vacuum (UHV).

## 2. Experimental procedure

The experiments were performed in a commercial ultrahigh-vacuum chamber (base pressure  $1 \times 10^{-10}$  Torr) equipped with the following: a cylindrical mirror analyser (CMA) for AES measurements, a quadrupole mass spectrometer (QMS) for TDS measurements, in conjunction with a linear temperature controller and power supply, a Kelvin probe for WF measurements and facilities for Ar-ion sputtering. The Ni(100) sample was cleaned by Ar<sup>+</sup> bombardment (2 keV, 4  $\mu$ A) and subsequently annealed at 1000 K. This cycle was repeated several times until the main impurities were brought below the detection limit of the Auger spectra. The sample was heated by passing a current through a 0.05 mm Ta strip, uniformly pressed between the sample and a Ta foil case. The temperature of the sample was measured by a Cr–Al thermocouple calibrated with an infrared pyrometer in the range of 900–1300 K. Potassium was evaporated from a commercial K source (SAES getters). Elemental S was deposited by thermal dissociation of single-crystal MoS<sub>2</sub> flakes mounted on a tungsten filament. The K and S atomic density of 1 ML on Ni(100) is considered to be equal to that of the outermost layer of Ni(100):  $1.6 \times 10^{15}$  atoms cm<sup>-2</sup>.

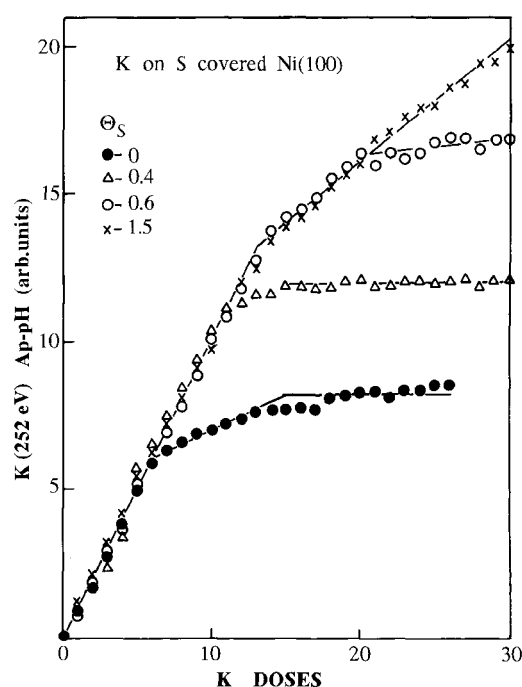
## 3. Results

### 3.1. K on S-covered Ni(100)

To fully understand the results of this study, knowledge of the coverage of each adsorbate on clean Ni(100) is required. From previous results it is known that the maximum coverage of K on clean Ni(100) at RT is 0.38 ML [14] and that the coverage of the first complete physical layer of S is 0.5 ML [15].

Figure 1 shows the K (252 eV) Auger peak-to-peak height (Ap-pH) versus increasing number of doses of K deposition on a Ni(100) surface covered with different amounts of S, at RT. For  $\Theta_S = 0$  (on clean Ni(100)) the K Ap-pH shows a linear increase up to six doses of K deposition. When more K is deposited, the Ap-pH increases at a much slower rate and saturates at the 14th dose ( $\Theta_K = 0.38$ ). The known fact that the initial sticking coefficient for alkali elements on metal surfaces is very close to 1 [16] enables us to estimate the coefficient of sticking of K on clean Ni(100) between its 6th and 14th doses from figure 1. This is about constant and equal to 0.25. The decrease of the sticking coefficient of K upon the saturation of the first physical layer was also observed for Cs during its deposition on clean Mo(100) [17], and attributed to metallization of the Cs layer which involves an increase of the Cs atomic radius.

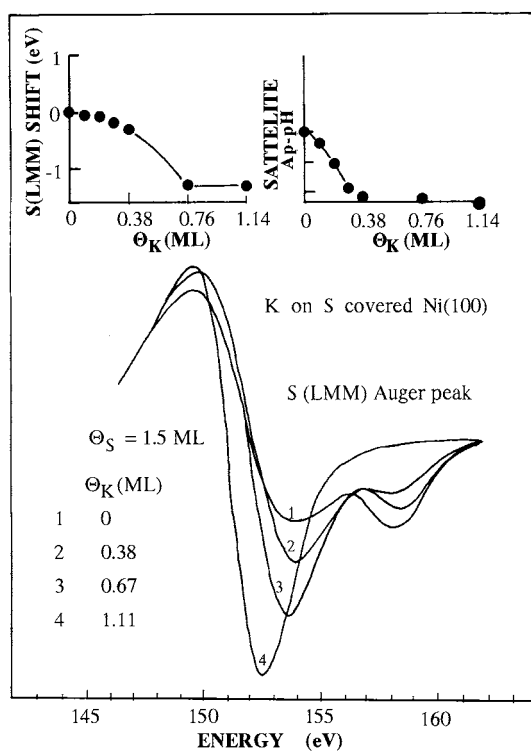
Deposition of K on S-covered Ni(100) initially causes a linear increase of the K Ap-pH. The slope of the initial linear increase of the K Ap-pH versus the number of K doses on S-covered Ni(100) is the same as that of K on clean Ni(100). It remains constant as the amount of predeposited S increases, even when the coverage of K is greater than the maximum K coverage on clean Ni(100) (figure 1). This indicates that the initial sticking coefficient of K on S-covered Ni(100), upon the increase of the amount of S predeposited on Ni(100), is the same as that of K on clean Ni(100) and that it remains unaltered for a longer period of K deposition. At relatively high S coverages ( $\Theta_S \approx 0.5$  ML) the K Ap-pH curves (figure 1) form breaks near the 14th dose (0.67 ML) of K deposition. This is attributed to the completion of the first physical layer of K on the Ni(100) surface and the beginning of the formation of a second layer. The maximum Ap-pH of K increases with a corresponding increase in the quantity of predeposited S. The latter suggests that the maximum amount of K which can be deposited on Ni(100) increases substantially with increased amount of S on the Ni(100) surface.



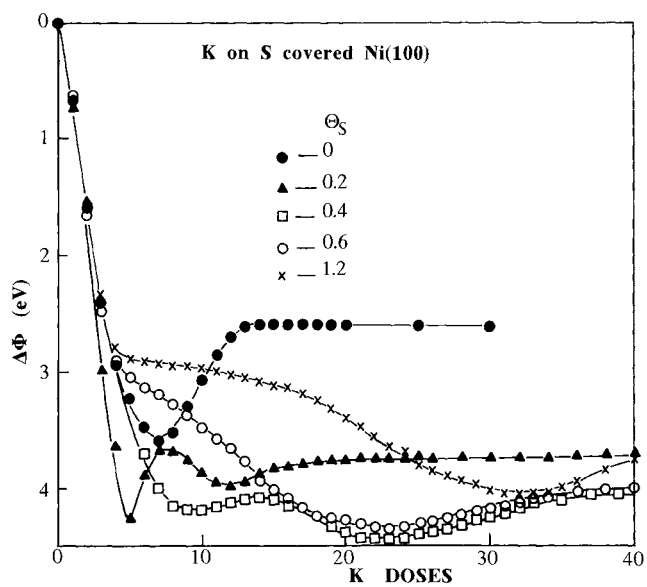
**Figure 1.** Auger peak-to-peak height (Ap-pH) of K (252 eV) versus the number of doses of K deposition on Ni(100) surfaces covered with different amounts of S at RT.

Figure 2 shows changes in the sulphur LMM Auger peak at 150 eV, after different amounts of K were deposited on Ni(100) that was covered with 1.5 ML of S. At zero and low coverages of K, the S LMM peak exhibits a distinct satellite at the high-energy end of the spectrum examined. The amplitude of this satellite peak decreases as more K is deposited and disappears for K coverages above one physical layer, which is equivalent to about 0.67 ML. As indicated by the upper right inset of figure 2, the decrease is not linear up to one physical layer of K which is 0.67 ML on this surface. We can also observe in the upper left inset of figure 2 that the main S LMM peak at 150 eV shifts by about 1 eV to a lower energy as the amount of K deposition increases. The high-energy satellite peak of the S LMM Auger line reappears after the thermal desorption of K, while the main peak of S shifts back to its initial position following the complete desorption of K. Upon heating the sample up to 1300 K, the S desorption from the Ni surface is incomplete, while it should be noted that applying heat at even higher temperatures causes destruction of the sample [15].

Figure 3 depicts the work-function (WF) changes as a function of the number of K doses deposited at RT on the Ni(100) surface that has been covered with different amounts of S. The WF decreases rapidly with K deposition on clean Ni(100), then passes through a minimum ( $\Phi_{\min} = 1.3$  eV) and subsequently increases, near saturation ( $\Theta_K = 0.38$  ML), to a final value of 2.3 eV. This final WF value is close to that of the metallic K [18]. The aforementioned WF minimum appears after 6–7 doses corresponding to 0.29 ML of K deposition. The deposition of K on Ni(100) covered with a small amount of S ( $\Theta_S \leq 0.2$  ML) gives a sharp WF minimum at low K coverages while a second broader WF minimum appears at higher K coverages. These two minima broaden and shift to regions of greater K coverage as the amount of predeposited S increases. As the precovering S on Ni(100) amounts to values above 0.5 ML, the first



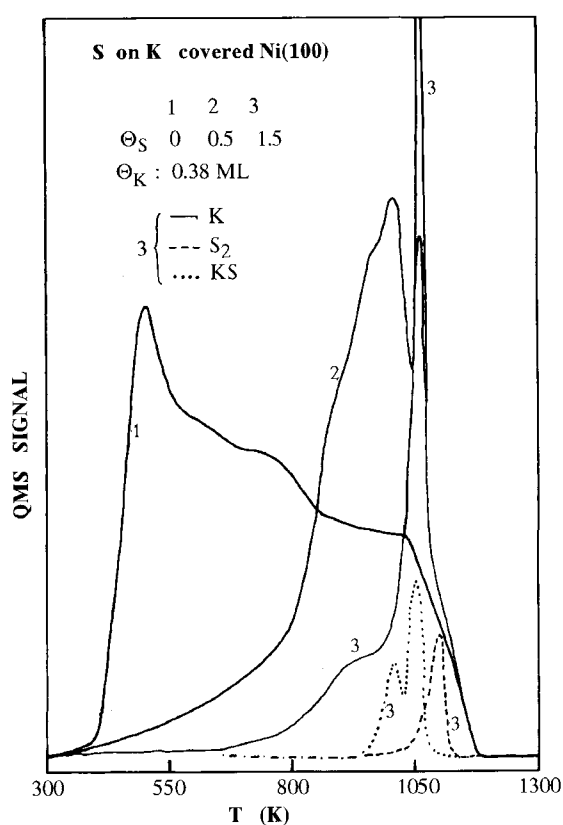
**Figure 2.** The S LMM Auger peak after deposition of different amounts of K on Ni(100) covered with 1.5 ML of S. The insets show (left) the chemical shift of the S LMM peak and (right) the decrease of the satellite Ap-pH as a function of the K coverage on Ni(100).



**Figure 3.** Work-function changes as a function of number of K doses at RT on Ni(100) surfaces covered with different amounts of S.

WF minimum changes to a plateau while the second minimum shifts even further to higher K coverages. When K is deposited on a Ni(100) surface already covered with 0.6 ML of S, the WF minimum value is about 1.0 eV. Such a low WF minimum value was also observed during the oxidation of Cs multilayers [19–21], and during Na deposition on S-covered Ni(100) surfaces [11]. The former was attributed to the formation of caesium suboxides and the latter to that of a  $\text{Na}_x\text{S}_y$  compound [19–21]. We may, thus, also expect the formation of K–S compounds in our present study.

Figure 4 shows the K (39 amu) thermal desorption spectra after deposition of 0.38 ML of K on a Ni(100) surface which was covered with different amounts of S. Also indicated here are the  $\text{S}_2$  (64 amu) and KS (71 amu) desorption spectra after deposition of 0.38 ML of K on Ni(100), covered with 1.5 ML of sulphur. The heating rate was  $15 \text{ K s}^{-1}$ . According to the aforementioned data, the binding energy of K increases drastically with the presence of S. The  $\text{S}_2$  peak appears before the complete desorption of K at a temperature of about 1100 K.



**Figure 4.** Thermal desorption spectra of K (39 amu),  $\text{S}_2$  (64 amu) and KS (71 amu) after deposition of 0.38 ML of K on a Ni(100) surface covered with different amounts of S.

Figure 5 shows thermal desorption spectra of the KS (71 amu) compound after different amounts of S and K were deposited on the Ni(100) surface. The KS peak appears for S coverages higher than 0.5 ML. At high K and S coverages the KS spectrum gives three distinct peaks at 950 K, 970 K and 1020 K. We did not observe any  $\text{K}_x\text{S}_y$  compound other than KS for  $\leq 300$  amu.

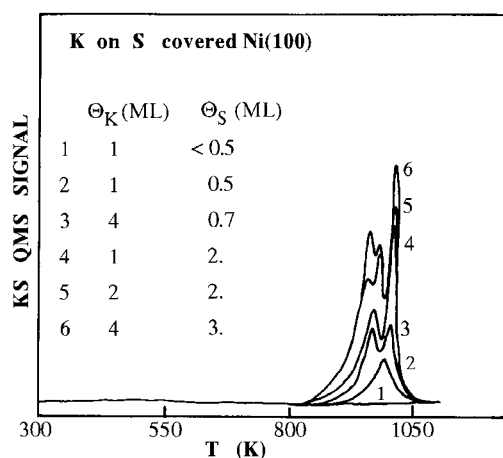


Figure 5. Thermal desorption spectra of the KS (71 amu) compound after deposition of different amounts of S and K on Ni(100) surfaces.

### 3.2. S on K-covered Ni(100)

Figure 6 shows the Ap-pH for S (150 eV), K (252 eV) and Ni (61 eV) as functions of S deposition on the K-covered (0.38 ML) Ni(100) surface. The S Auger curve for K-covered Ni(100) is linear up to 0.5 ML of S deposition, whereas its slope decreases continuously with further increase in the amount of S. The Ni (61 eV) peak decreases analogously. The K (252 eV) peak remains constant up to 0.5 ML of S deposition where it starts to decrease as the amount of S deposited increases. The initial stability of this peak is attributed to the submergence of S under the K layer.

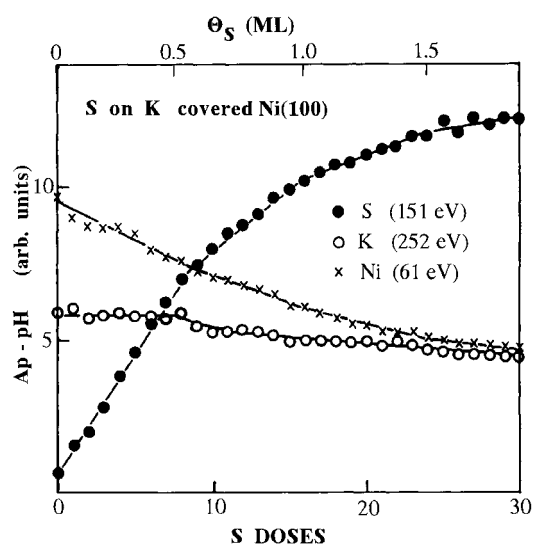
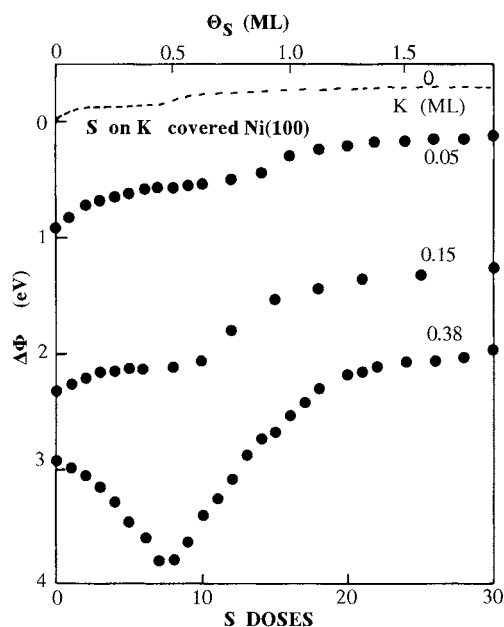


Figure 6. Ap-pH for S (151 eV), K (252 eV) and Ni (61 eV) as functions of S deposition on K-covered (0.38 ML) Ni(100) surfaces.

Figure 7 shows the WF change versus the number of doses of S deposited on Ni(100) surfaces which were covered with different amounts of K. For a small number of K doses on the Ni(100) surface, the WF increases continuously as the adsorption of S also increases. Sulphur deposition on Ni(100) covered with greater amounts of K initially causes a decrease of the WF which passes through a minimum at  $\Theta_S = 0.5$  ML, and subsequently increases to a final value. The initial decrease of the WF is attributed to the submergence of S under the K layer, which is in agreement with Auger measurements.



**Figure 7.** Work-function changes versus S deposition dosage on Ni(100) surfaces covered with different amounts of K.

The thermal desorption spectra of S on K-covered Ni(100) are similar to those of K on S-covered Ni(100) (figures 4, 5) and are not shown here.

#### 4. Discussion

The experimental results indicate, according to reference [16], that the initial sticking coefficient  $S_0$  of K on clean Ni(100) is constant and equal to 1 until  $\Theta_K = 0.29$  ML (six doses). Then it subsequently changes to  $S_K = 0.25S_0$  and remains constant, up to its saturation point at  $\Theta_K = 0.38$  ML. This change of  $S_0$  occurs near the work-function minimum (figure 3) where the transition from the ionic to the metallic state of the K overlayer takes place. The metallization of the K overlayer is accompanied by a weakening of its bond to the substrate [2]. It is also characterized by an increase in the radii of the K adatoms from ionic 151 pm to nearly covalent 203 pm proportions.

When K is deposited on S-covered Ni(100) surfaces, however, the initial sticking coefficient of K is constant and independent of the S coverage, up to 0.29 ML. This is in agreement with earlier studies of alkali on S-covered metallic and semiconducting surfaces [10, 11, 13]. For  $\Theta_K > 0.29$  ML, the sticking coefficient of K on S-covered Ni(100) continues to remain equal to one. The greater the amount of S on the surface, the more K can be deposited



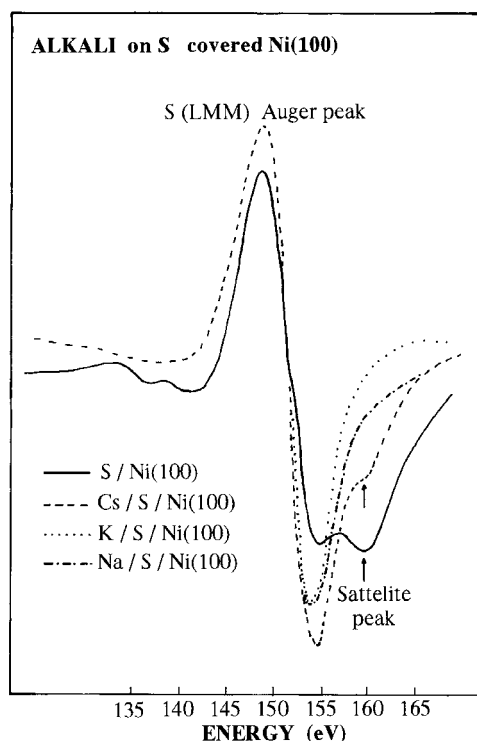
with  $S_K$  remaining at 1. For  $\Theta_S > 0.5$  ML, as is seen in figure 1, the first break of the K Auger curve occurs near  $\Theta_K \cong 0.67$  ML. This means that the saturation coverage of K within the first layer on S/Ni(100) is greater than that on clean Ni(100). The latter behaviour is attributed to the S conserving the ionicity of K, which remains close to the ionic state up to the completion of the first layer. The repulsion between K ions is screened by the S atoms between them, and/or by the formation of a K–S compound. More K ions, therefore, are needed to complete a physical layer. It must be noted here that the ratio of the above K coverages on clean and S-covered Ni(100), respectively, is 0.57, while the ratio of the areas occupied by K in its covalent and ionic forms, also respectively, is 0.55. The fact that these two ratios are approximately equal further points to the ionicity of K on S-covered Ni(100).

The presence of S on the Ni(100) surface, moreover, drastically increases the bond energy of K (figure 4). This means that K strongly interacts with S. Similar results have also been observed during alkali deposition on metallic surfaces covered with electronegative elements [22–24]. In addition, we measured a KS compound desorption peak for S coverages higher than 0.5 ML. Alkali–sulphur compounds such as this have also been identified during Na deposition on S-covered Ni(100) [11]. During Cs deposition on S-covered Ni(100), however, we did not obtain any Cs–S compound desorption peaks [13]. The differences between Cs and K or Na on S-covered Ni(100) surfaces, which are indicated by thermal desorption spectra (figure 4), are accompanied by an evident difference between the corresponding WF measurements. The presence of S on Ni(100) increased the  $\Phi_{\min}$  and the final value of (the WF maximum)  $\Phi_{\max}$  during Cs deposition [13]. We did not observe any other substantial changes in the shape of the WF curve during Cs deposition on S-covered Ni(100). During K or Na deposition, on the other hand, the presence of S on Ni(100) causes a dramatic change in the shape of the WF curve, as shown in figure 3 and reference [11]. Sulphur shifts the  $\Phi_{\min}$  and creates a second minimum with a lower WF value ( $\sim 1$  eV). Such very low WF values have also been measured during the oxidation of Cs multilayers, and were then attributed to caesium suboxide formation [19–21]. In the present case, on the basis of the TDS measurements (figure 5), we attribute the low WF value of the K–S/Ni(100) system to the formation of a K–S compound. Similar behaviour has also been observed during the deposition of Na on S-covered Ni(100) and has been attributed to the formation of a Na–S compound [11]. This is opposite to the case for Cs deposition on S-covered Ni(100), where the Cs–S compound desorption peak was absent [13].

The K–S interaction on the Ni(100) becomes more apparent when we examine the high-energy satellite of the sulphur LMM Auger peak observed for S-covered Ni(100) which decreases and disappears as the amount of K on the surface increases (figure 2).

It is known that the three p orbitals ( $p_x$ ,  $p_y$ ,  $p_z$ ) of a single S atom are energetically degenerate [25]. Upon adsorption of S on the Ni(100) and other substrates, the degeneracy is partly lifted [25, 28, 29]. The S LMM satellite peak is attributed to the lifting of the degeneracy of the 3p S orbitals due to the S–Ni interaction. Using the most elementary description, the S Auger electron peak (figure 2) may be considered to be the self-convolution of the local density of states of the S atoms (neglecting the effect of inelastic scattering which is believed to be small). Self-convolution leads roughly to a doubling of the energy width of the density of states, and smears out its structure [30, 31]. The 7 eV separation of the high-energy satellite from the main feature in figure 2, therefore, suggests an average splitting between the  $p_z$ - and ( $p_x$ ,  $p_y$ )-derived levels of about 3.5 eV in agreement with the UPS results [25–27]. The disappearance of the satellite peak during K deposition is attributed to a change of the S bonding structure from S–Ni to S–K in agreement with previous interpretation [29]. This is supported by the detection of S–K compounds in TDS measurements (figure 5). Heating of the K/S/Ni(100) system leads to a desorption of K and some of the S, whereas the S LMM satellite Auger peak reappears, and remains even after heating to 1300 K.

Another noteworthy change is in the main S LMM Auger peak at 150 eV. During K deposition it shifts to a lower binding energy by 1 eV, and comes back to its initial position after the complete desorption of K upon heating to 1300 K. This is a chemical shift due to a strong S–K interaction and indicative of S–K compound formation. Similar Auger peak changes have also been observed during Na deposition on S-covered Ni(100) [11]. Such changes have not been observed, however, during Cs deposition on S-covered Ni(100) surfaces [13] (figure 8).



**Figure 8.** The S LMM Auger peak during deposition of Cs, K and Na on S-covered Ni(100) surfaces.

For S on K-covered Ni(100), Auger measurements show that the presence of K on Ni(100) does not substantially change the sticking coefficient or the maximum amount of the subsequently deposited S (figure 6). The K (252 eV) Auger peak height remains constant (figure 6) for S deposition up to 0.5 ML. This is attributed to the submergence of S atoms under the K overlayer, up to 0.5 ML of sulphur coverage. This coverage completes one physical S layer under the K layer [15]. More S deposition causes a decrease of the K (252 eV) Auger peak height due to the S adsorption on top of the K layer. The aforementioned arrangement is supported by the WF measurements (figure 7) as follows: sulphur on 0.38 ML (one physical layer) of K on Ni(100) initially causes a decrease of the WF to a minimum value near 0.5 ML of S deposition. This value of the WF at the minimum is near 1.0 eV. More S deposition leads to an increase of the WF. The initial decrease of the WF is consistent with the proposed submergence of S under the K overlayer up to the completion of one physical S layer ( $\Theta_S = 0.5$  ML) [1, 3]. Above 0.5 ML of S deposition, S atoms occupy sites above the K layer leading to an increase of the WF (figure 7). The minimum WF value reached during deposition of S on K-covered (0.38 ML) Ni(100) (figure 7) is the same as that reached during deposition of K on S-covered

Ni(100) (figure 3). Our observations have also indicated that the thermal desorption spectra of S on K/Ni(100) and K on S/Ni(100) are similar. These observations indicate that the sequence of deposition affects neither the composition nor the properties of the S–K overlayer.

## 5. Conclusions

From the experimental results and discussion we conclude that the initial sticking coefficient of K on clean Ni(100) is  $S_0 = \text{constant} = 1$  until  $\Theta_K = 0.29$  ML, and that it subsequently changes to  $S_K = 0.25S_0$  up to  $\Theta_K = 0.38$  ML at saturation. This change occurs when the transition of the ionic to the metallic state of the K overlayer takes place. When K is deposited on S-covered Ni(100) surfaces, the initial sticking coefficient of K continues to remain equal to 1 for  $\Theta_K > 0.29$  ML, up to the completion of the first K layer on S/Ni(100) at  $\Theta_K = 0.67$  ML. This coverage is greater than that of a K layer on clean Ni(100). This is attributed to the S maintaining the ionicity of K close to the ionic state up to the completion of the first layer. The presence of S increases the quantity of K deposited on Ni(100).

Predeposited S on the Ni(100) surface drastically increases the binding energy of K. The K adatoms weaken the Ni–S bonds, and interact strongly with S and form a KS compound for S coverages higher than 0.5 ML. The presence of S on Ni(100) further lowers the  $\Phi_{\text{min}}$  of K on Ni(100) to a value of  $\sim 1$  eV, which is attributed to K–S compound formation. The sulphur LMM Auger peak for a clean Ni(100) substrate shows a satellite at a higher energy which decreases and disappears as the amount of K on the surface increases. This is explained by changes of the bonding configuration of S as the amount of K on the S-covered Ni(100) increases.

When 0.38 ML K is adsorbed on clean Ni(100), the subsequently deposited S atoms submerge under the K overlayer up to 0.5 ML, where they complete one physical layer of S. With increasing coverage, S is adsorbed on top of the K layer. In general, the sequence of deposition does not affect the composition and the properties of the S–K overlayer.

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