

Sodium Adsorption and Reaction on NiO(111)/Ni(111)[†]

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Sodium adsorption and reaction on a NiO(111)/Ni(111) surface is studied via X-ray photoelectron spectroscopy (XPS) and X-ray Auger electron spectroscopy (XAES). The observed work function decrease is similar to that for metals and semiconductors. However, the processes taking place on the oxide surface are more complex. At low and intermediate coverages Na becomes (partly) ionic and concomitantly reduces the Ni ions in the substrate near the surface to metallic Ni. This occurs at temperatures near 100 K. Eventually, Na₂O is formed. At higher coverage the Na remains metallic. As the substrate is heated to $T = 500$ K, there are indications that a sodium nickelate is formed on the surface.

Introduction

Alkali metal adsorption on metal and typical semiconductor surfaces has been subject to intensive studies in the past decade, and reviews can be found in the literature.¹ In contrast to this, less systematic information about alkali metal adsorbates on oxide surfaces is available.²⁻⁷ Hall et al.,⁶ for example, have investigated the system K/NiO/Ni(100) with respect to its chemical reactivity toward hydrocarbons but did not control the crystallography of the oxide substrate. The structure of the surface, however, could be important if specific, possibly catalytically active, surface compounds are to be formed. For example, along the (111) direction the NiO forms a layered structure, which is advantageous for the formation of layered alkali nickelate compounds.⁸ In this paper, the adsorption of sodium on epitaxially grown NiO(111) formed on a Ni(111) substrate is studied.⁹ The epitaxially grown nickel oxide film has been previously characterized in detail by applying a variety of surface spectroscopic techniques including X-ray photoelectron spectroscopy (XPS),¹⁰ angle-resolved photoelectron spectroscopy (ARUPS),¹¹ and electron energy loss spectroscopy (ELS, HREELS)¹⁰⁻¹² as well as low-energy electron diffraction (LEED).¹³ The original motivation for the

present study has come from reports in the literature that alkali additives to NiO promote methane coupling reactions¹⁴ and lead to very high selectivities in the yields.¹⁵ However, even though it now seems that the selectivities are somewhat less than expected,¹⁶ there are several other interesting aspects of alkali-oxide interaction. The question of the change in the electronic structure of NiO upon doping or reaction with alkali is still not settled and remains interesting,^{3,17,18} but equally important is the question of metal insulator transitions in alkali overlayers on an oxide substrate like NiO. While the latter problem has been addressed recently in some detail for alkali and alkali earth overlayers on metal surfaces,^{19,20} there are only a few reports for alkali overlayers on oxide surfaces.³⁻⁷ We will show in this paper that at low temperature ($90 \text{ K} < T < 140 \text{ K}$) sodium on NiO(111) behaves similar to metals and semiconductors with respect to work function changes. However, reactions occur in the process, including the initial reduction of Ni ions in NiO to metallic Ni, and the formation of Na₂O concomitantly, and at higher temperatures ($450 \text{ K} < T < 500 \text{ K}$), probably, the formation of a new compound. The XPS measurements indicate that the sodium ions are incorporated into the NiO bulk locally, forming a sodium nickelate with a Ni2p spectrum similar to that for alkali nickelate in the literature.²¹

Experimental Section

The experiments were performed in a UHV-chamber equipped with an Omikron LEED-System, a VSW XP/XAE-Spectrometer, and a Leybold-Heraeus Iongun. The complete system has been described elsewhere.²² As a source for the sodium, an outgassed tantalum-caged SAES-getter was used. The heating current was held at about 6.5 A. Base pressure was 2×10^{-10} Torr. During the short-time deposition, the pressure rose to 2×10^{-9} Torr due to thermal desorption of residual gas from inside the tantalum

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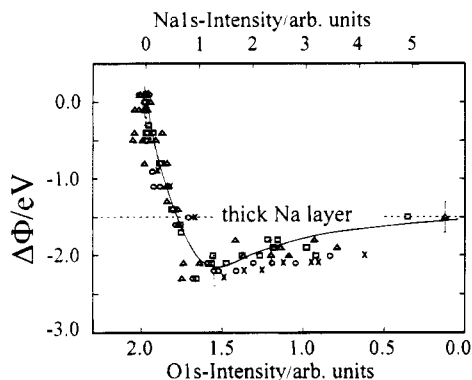


Figure 1. Work function changes of the system NiO(111)/Ni(111) as a function of XPS intensities. Data taken at 90–100 K: (Δ) O_{1s} intensity; (\square) Na_{1s} intensity. Data taken at 280–300 K: (\circ) O_{1s} intensity; (\times) Na_{1s} intensity.

cage. From C1s and O1s XPS spectra, surface contamination by carbon species could be excluded. Before long-time deposition (20–30 min), the cage was heated out by electron bombardment. The pressure thereafter never exceeded 1×10^{-9} Torr.

The preparation of the epitaxially grown NiO(111)/Ni(111) is described elsewhere.¹¹ Two methods for preparing alkali metal layers have been used. Either the alkali metal is deposited at a given crystal temperature to form a desired coverage or a thick, bulklike layer of the alkali metal is deposited and subsequently heated until the desired coverage has been reached. As a measure of the sodium coverage, we show the increase of the Na_{1s}-XPS intensity and the concomitant attenuation of the O_{1s}-XPS intensity with increasing exposure. In the XPS spectra the background has been removed.²³ The layer thickness could be estimated from XPS measurements²⁴ by assuming homogeneous films and taking penetration depths of the photoelectrons from ref 25. But as the processes at the metal-insulator interface seem to involve transport of oxygen from the NiO phase into the Na phase, this analysis is not beyond any doubt. Therefore it has not been possible to determine absolute coverages.

The change in work function (WF) was monitored by measuring the low-energy cutoff of the electron spectra.

Results and Discussion

Work function versus sodium coverage has been determined at two substrate temperature ranges, namely at 90–100 K and at 280–300 K as shown in Figure 1. The experiments have been performed by depositing the desired amount of alkali metal from the getter at the given temperature. The dependences are not significantly different. We observe a more or less linear decrease of the work function toward a minimum, after which we observe a slight increase converging to the value of solid sodium.²⁶ At this point we have no reason to believe that the interpretation of the present work function changes is any different from the one canonically applied to metal surfaces.^{27–29} Briefly, at low coverages well below a monolayer, the alkali is thought to release its electron, transferring it to the substrate. This leads to a dipolar layer at the surface directed in such a way as to decrease the work function. As the coverage increases, it becomes energetically favorable, due to the strong repulsion of the created dipoles, to form a metallic overlayer which, with

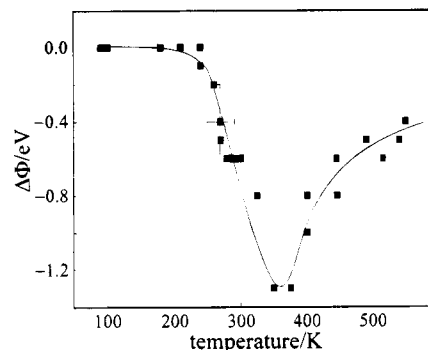


Figure 2. Work function changes after deposition of a thick layer of Na onto a NiO(111)/Ni(111) surface at 90–100 K as a function of surface temperature.

further increasing coverage, approaches the properties of the alkali metal itself. Within the present study we have not observed any ordered alkali overlayer on the oxide surface by LEED. Therefore we have no experimental clue as to the local site of the alkali atoms on the surface. However, the following results show that the situation as compared to the case for a metal is much more complex at an oxide surface.

Figure 2 shows the work function changes with increasing temperature, starting from a thick alkali overlayer. Just before the surface reaches a temperature of 300 K, the work function starts to decrease. A plateau value about 0.6 eV below the initial value, i.e. close to the value for which the work function minimum is observed during direct deposition (Figure 1), cannot always be identified and depends somewhat on preparation. The work function decreases further on toward a minimum, about 1.3 eV below the value of the pure Na metal.²⁶ After the minimum in the temperature range $350 \text{ K} < T < 400 \text{ K}$, the work function increases again just above the plateau value if we do not increase the temperature above 600 K. Above that temperature the complete system becomes unstable. This is also true for the clean NiO(111)/Ni(111) system.¹¹

From the work function measurements alone it is not possible to draw any conclusions, but together with the following XPS data we have strong indications that the observed effects are due to at least two reaction channels.

Let us first consider the sodium data. We recorded the Na1s and Na2p core levels as well as the KL₂₃L₂₃ Na Auger decay. We only show the Na1s and Auger data. Figure 3a,b collects these data for the surface temperatures 90–100 and 280–300 K, respectively. The core level signals only slightly shift in a range of 0.2–0.5 eV as a function of coverage. This is surprising, considering the possibility of forming ionic sodium versus metallic sodium. In contrast to this the Auger spectrum shows large shifts as we increase the sodium coverage. There is an important feature in the XPS and Auger spectra, independent of the chemical shift, that allows us to directly deduce information about the metallic character of the alkali overlayer, i.e. the appearance of plasmon losses.³⁰ The plasmon loss features appear at maximum or postmaximum work function change, which indicates the metallic character in the surface layer. In other words, around the maximum work function change the sodium overlayer gains its metallic character. In contrast to the small chemical shifts in the XPS data, the large chemical shifts in the Auger spectra allow us to identify four features which change their relative intensity as a function of coverage. There

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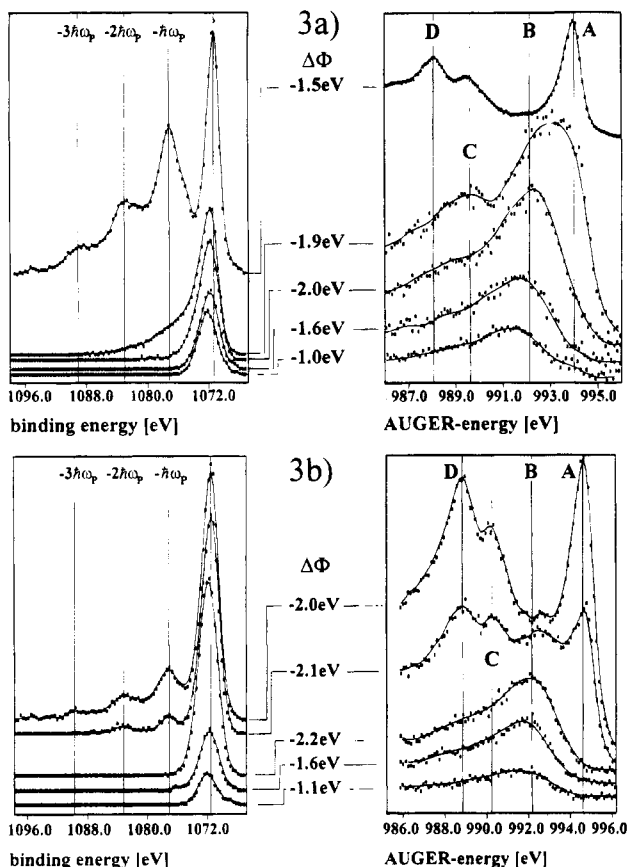


Figure 3. Na 1s XPS spectra (left panel) and Na $KL_{23}L_{23}$ Auger spectra (right panel) of various increasing Na coverages. Work function changes are given for (a) surface temperature in the range 90–100 K and (b) surface temperature in the range 280–300 K.

is a preliminary indication that this chemical shift is dominated by final state effects in this case. The metallic Na $KL_{23}L_{23}$ ($1D$) state (A) is found at higher kinetic energy. The same state for the Na species initially at the surface, i.e. B, is shifted by about 2.5 eV to lower kinetic energy. Feature C corresponds to a species that grows as an increasing amount of sodium is present on the surface. In the metallic sample this feature is superposed by a signal (dashed line in Figure 3) which is assigned to the surface plasmon of Na.³⁰ Feature D at last represents the bulk plasmon loss associated with signal A.

However, more can be learned from the spectra after a thick Na overlayer deposited on the NiO substrate is heated. In this case we start from Auger spectra that indicate metallic behavior, as shown in Figure 4. The plasmon loss features begin to disappear at temperatures above $T = 250$ K, which again indicates the breakdown of the metallic character in the surface layer. At temperatures above $T = 280$ K, a single peak is observed. Its position is near peak C in Figure 3. We shall show that this peak is connected with the reaction of the Na with the NiO.

In Figure 5 binding energies of the Na 1s level are plotted versus Auger energies of the Na $KL_{23}L_{23}$ decay for the present measurements as well as literature data for several sodium species. This figure represents a so-called Wagner plot.^{31,32} Wagner³¹ has proposed to use the Auger

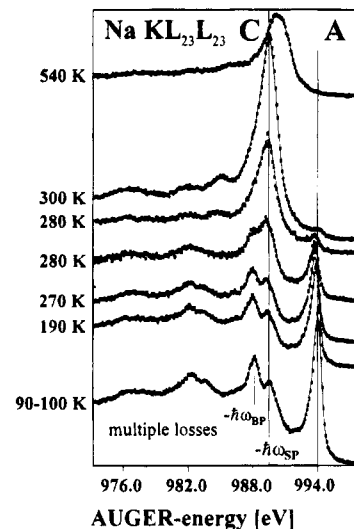


Figure 4. Na $KL_{23}L_{23}$ Auger spectra after deposition of a thick layer of Na onto a NiO(111)/Ni(111) surface at 90–100 K as a function of surface temperature. Bulk and surface plasmon losses are indicated by BP and SP, respectively.

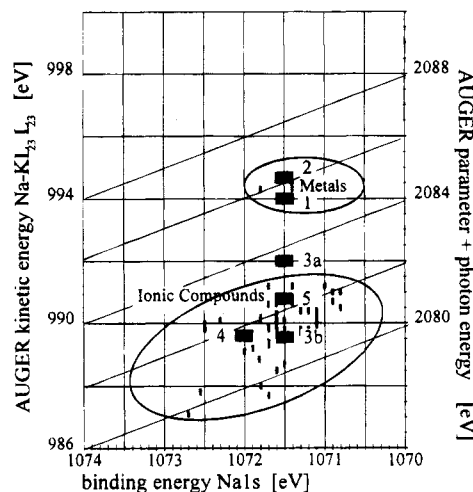


Figure 5. Na 1s binding energies versus Na $KL_{23}L_{23}$ Auger kinetic energies for a variety of Na-containing compounds (small symbols) from the literature.³⁰ The data from Figure 3 and Figure 4 are included (large symbols): (1 and 2) thick sodium layer deposited at 90–100 and 280–300 K, respectively; (3) sodium coverage below multilayer (3a) Figure 3 feature B, (3b) Figure 3 feature C; (4) thick layer heated to 300 K Figure 4 feature C; (5) thick layer heated to 540 K.

parameter as a basis for the chemical shift analysis because it is independent of sample charging. In addition, the Auger parameter range for a given element is often larger than the binding energy range. This is also true for the present case. For a wide variety of different chemical environments, the Na 1s binding energy varies by about 2 eV. As is seen in Figure 5, the chemical shift of Na in a metallic environment is not clearly differentiable from an ionic environment. The larger variation of the Auger parameter, i.e. by about 5 eV, is due to the sensitivity of the Auger signal to the chemical environment. As has been shown previously,^{31,32} this is an indication that final state effects are important to interpret chemical shifts. The data from the present study are shown as large symbols. The data from the thick Na layers in Figure 3 (features A) are given as 1 and 2, and they coincide very well with typical values for a metallic environment, in

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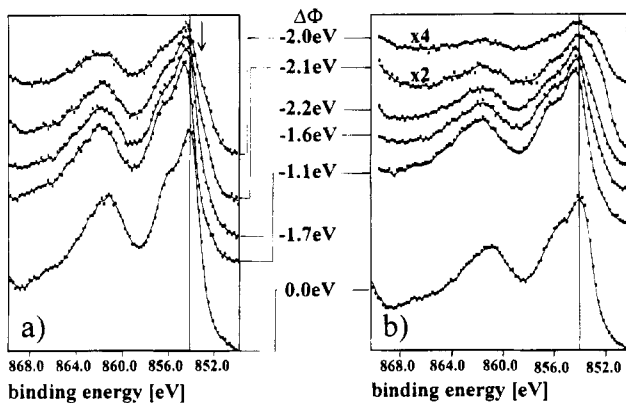


Figure 6. Ni $2p_{3/2}$ spectra of the NiO(111)/Ni(111) substrate as a function of Na coverage at near-normal take off angles: (a) at 90–100 K surface temperature and (b) at 280–300 K surface temperature.

line with the arguments based on plasmon loss features given above. The data (3b) corresponding to feature C (Figure 3) fall in the range of the ionic compounds close to the value deduced for feature C (4) from Figure 4. This is indicative of the formation of Na₂O. The data point (3a) for feature B in Figure 3 is situated intermediate between the ionic and the metallic compounds. It is not possible to deduce the ionicity directly because there are several effects contributing to the Auger parameter value. The analysis for the species formed after being heated to $T > 450$ K also yields a value in the range of ionic compounds (5). Thus, the sodium data are not conclusive with respect to a definite assignment of the species formed. More conclusive with respect to the nature of the species are the changes in the Ni $2p$ spectra of the oxide substrate upon alkali adsorption, which we shall discuss in the following.

The Ni $2p$ spectra as a function of increasing coverage are shown in Figure 6 for both low temperature (Figure 6a) and room temperature (Figure 6b). The spectra are typical for NiO. The NiO Ni $2p$ spectrum has been widely discussed, and it has been recognized that the spectrum exhibits intense satellite structure. Its assignment is still a matter of debate.^{17,33–37} At this point we only take the spectrum as a fingerprint of Ni²⁺ in a NiO-like environment. Note that we always only show the Ni $2p_{3/2}$ band. Clearly, the intensity of the Ni signal is attenuated as expected due to increasing sodium coverage. However, the habit of the spectrum does not change dramatically, indicating at first glance that the character of the substrate does not change. One might observe, however, some intensity filling in at the low binding energy side of the Ni $2p$ spectrum (arrow). In Figure 7 difference spectra between the Ni $2p$ spectra of the sodium-covered NiO surface near the work function minimum and the clean NiO surface, respectively, are shown for $T = 90$ –100 K as well as for $T = 280$ –300 K. Comparing them to the spectrum of nickel metal indicates that this intensity is due to the appearance of metallic Ni on the surface of the NiO film. It is therefore obvious that already at low

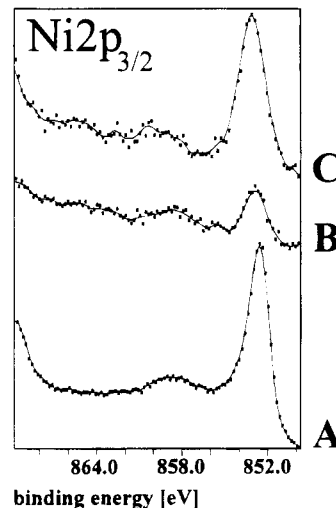


Figure 7. Ni $2p_{3/2}$ spectrum of bulk nickel metal (A) in comparison with Ni $2p_{3/2}$ difference spectra of Na/NiO(111)/Ni(111) and pure NiO(111)/Ni(111): (B) at 90–100 K ($\Delta\Phi = -2.0$ eV); (C) at 280–300 K ($\Delta\Phi = -2.2$ eV).

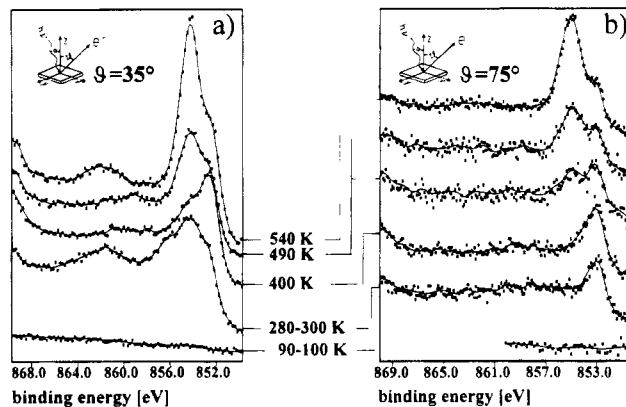


Figure 8. Ni $2p_{3/2}$ spectra of the NiO(111)/Ni(111) substrate after a thick layer has been deposited and heated subsequently to various surface temperatures: (a) at near-normal take off angle; (b) at grazing take off angle.

temperature NiO is reduced to Ni metal, and Na is oxidized concomitantly as was shown above.

The situation appears to be similar to an experiment where a thick layer is heated (Figure 8). As long as a thick layer of sodium is present (90–100 K), the NiO signal is fully attenuated. Between 280 K $< T < 300$ K, Ni $2p$ spectra (Figure 8) may be recorded at both near-normal emission (Figure 8a) and the grazing take off angle (Figure 8b). By comparison to the spectrum of bulk Ni and bulk NiO, the signal in near-normal emission indicates both NiO and metallic Ni on the surface. In the grazing take off detection, however, the metallic part strongly dominates, showing that metallic Ni is indeed formed preferentially on the surface. An angular scan is explicitly shown in Figure 9 for a surface temperature of 280 $< T < 300$ K. This result of the heating experiment is quite in line with the analysis presented by Rogelet et al.³ Clearly, we have demonstrated above that the reaction does happen already at low temperature.

The situation changes as we increase the substrate temperature to higher values. At $T = 490$ K an additional peak is found in the spectra shown in Figure 8. To analyze the results at 280 $< T < 300$ K and at 540 K, we compare spectra and difference spectra in Figure 10. Figure 10a shows the spectrum of the system at 280 $< T < 300$ K as trace B. If we subtract the part due to metallic Ni (A), we

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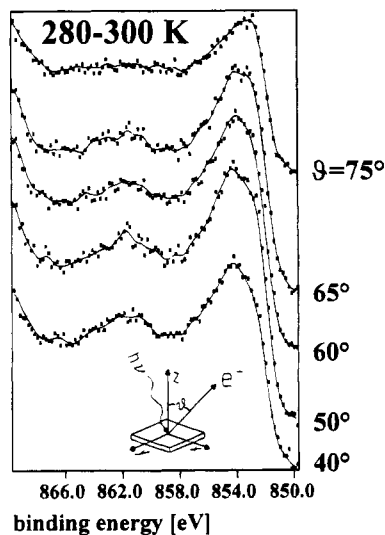


Figure 9. Angular dependence of $\text{Ni}2p_{3/2}$ spectra after a thick sodium layer is heated to 280–300 K. (This corresponds to a preparation different from the one used for Figure 8.)

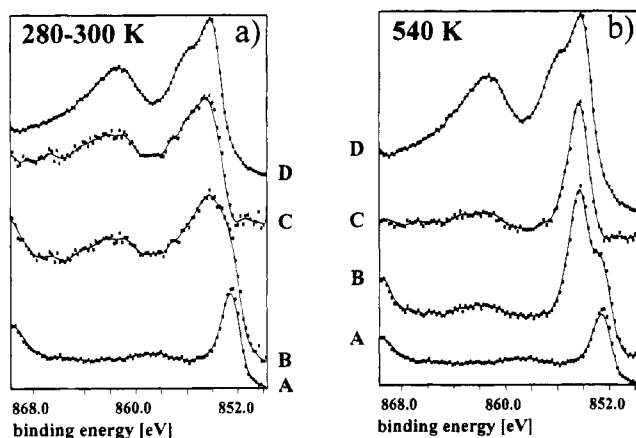


Figure 10. Comparison of the $\text{Ni}2p_{3/2}$ spectra **B** taken from Figure 8 (a) at $T = 280\text{--}300\text{ K}$ and (b) at $T = 540\text{ K}$ with the spectra of clean metallic Ni (**A**) and $\text{NiO}(111)/\text{Ni}(111)$ (**D**). The difference spectra between **A** and **B** are also shown as **C**.

are left with a spectrum (**C**) which favorably compares with clean $\text{NiO}(111)/\text{Ni}(111)$, shown as trace **D**.

Upon proceeding in the same manner for a surface temperature $T = 540\text{ K}$, we obtain Figure 10b. The difference spectrum (**C**) is very different from the spectrum of $\text{NiO}(111)/\text{Ni}(111)$ (**D**). We note that not only does the main line shift but also the relative positions of the satellite are different for Ni and NiO. This observation is not in line with interpretations based on band bending. At present we are not in a position to assign the spectrum definitely. However, in order to preliminarily interpret the spectrum, we show in Figure 11 a comparison with a lithium nickelate LiNiO_2 spectrum recently recorded by Kemp and Cox.²¹ Our spectrum is very similar to the nickelate spectrum and not at all reminiscent of NiO. Kemp and Cox²¹ argue on the basis of ELS spectra in the d–d transition range, in comparison to transition metal complexes, that, for example in LiCoO_2 , the Co is in an oxidation state of +3. However, the oxidation state of Ni in the compound formed after the reaction at $T = 500\text{ K}$ remains unclear, but the present analysis suggests that

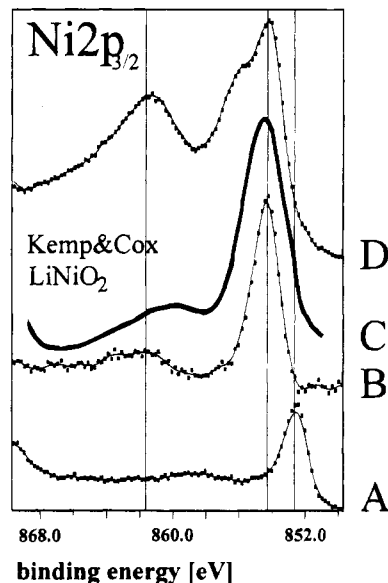


Figure 11. Comparison between the difference spectrum **C** in Figure 10b with the $\text{Ni}2p_{3/2}$ spectra of metallic Ni and $\text{NiO}(111)/\text{Ni}(111)$ substrate as well as the spectrum of LiNiO_2 reported by Kemp and Cox.²⁰

the formation of a nickelate is not unlikely to take place on the surface.

Conclusion

We have studied the adsorption of sodium on a $\text{NiO}(111)/\text{Ni}(111)$ substrate by applying predominantly X-ray photoelectron spectroscopy and X-ray induced Auger spectroscopy. It is found that at low and intermediate coverages the alkali loses its electron, (partly) forming Na^+ and concomitantly reducing NiO to metallic Ni. We observe the formation of Na_2O . Above a certain coverage the alkali has the tendency to keep its electrons and form a metallic alkali overlayer. Thus the alkali adsorption on oxides is more complex as compared to the one observed on metal and semiconductor surfaces. In the presence of alkali on the oxide surface a chemical reaction takes place in the sense that the cations on the surface are reduced to metal and the alkali forms the corresponding oxide. It is possible to trigger further reactions at the oxide surface by elevating the surface temperature above 500 K. The appearance of a new XPS spectrum and comparison with literature spectra of alkali metalates suggest the formation of a sodium nickelate. It will be particularly interesting in the future to explore the chemical reactivity of such a surface toward small molecules and particularly hydrocarbons.

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