4-15-1993

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Citation/Publisher Attribution
Tang, D., & Heskett, D. (1993). Unoccupied electronic structure of Na/Ni(111). *Physical Review B*, *47*(16), 10695-10699. doi: 10.1103/PhysRevB.47.10695
Available at: http://dx.doi.org/10.1103/PhysRevB.47.10695

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PHYSICAL REVIEW B VOLUME 47, NUMBER 16 15 APRIL 1993-II

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(Received 3 September 1992)

Using the technique of inverse photoemission spectroscopy we have measured the unoccupied electronic states of Na on Ni(111) as a function of Na dose on the Ni(111) surface. An image-potential surface state pinned to the vacuum level shifts towards the Fermi level and disappears for Na coverages greater than 0.07 monolayer (ML). This image state reappears at high coverage, when the Na coverage is larger than 0.6 ML and is detected at 2.4 eV above the Fermi level at 1 ML of Na coverage. A Na-induced state which we assign as the Na $3p$ level appears for Na coverages above 0.02 ML and shifts down towards the Fermi level with increasing coverage. We compare our results with studies of related systems.

I. INTRODUCTION

The adsorption of alkali-metal atoms on metal surfaces has been of great interest to experimentalists and theorists for many years.[1-8] These systems are simple chemisorption systems which can serve as the first step towards investigation of the general properties of metal adsorption on surfaces. In experimental studies of these systems, inverse photoemission spectroscopy (IPES) has recently proven to be a valuable technique. The systems Na/Cu(111),[9] Na/Al(111),[10,11] K/Ag(110),[12] Na/Ni(110),[13] and Li/Be(0001) (Refs. 14–16) have all been investigated using IPES. In this paper we use this technique to investigate Na/Ni(111).

We have recently performed measurements of the Na core levels for the systems Na/Cu(111) and Na/Ni(111).[17] The binding-energy shifts of the Na $2p$ core level versus Na coverage on Ni(111) and Cu(111) are quite similar, though electronically the substrates are quite different (Ni is a transition metal, Cu is a noble metal). However, they have similar lattice constants and we have observed identical overlayer structures. Therefore it is particularly interesting to determine what happens to the unoccupied states. In the following, we compare our results of Na/Ni(111) with a recent study of Na/Cu(111),[9] as well as other alkali-metal systems.

In the next section we briefly describe the experimental apparatus. In Sec. III we present the results of our measurements and a discussion. Conclusions are presented in Sec. IV.

II. EXPERIMENT

The measurements reported here were performed in an ultrahigh-vacuum system equipped with an angle-resolved inverse photoemission spectrometer, Auger electron spectrometer (AES), and low-energy electron-diffraction (LEED) apparatus. The base pressure in the chamber was approximately 1×10^{-10} Torr.

The IPES measurements were performed in the isochromat mode. The electron gun used in the experiment was a Zipf gun[18] with a sample current of ~1.5 μA. The emitted photons were detected with an I_2-He-filled Geiger-Muller tube detector equipped with a SrF_2 entrance window. The overall energy resolution was ~0.4 eV. The detector was positioned at 45° with respect to the normal of the sample surface. The incident angle θ was changed by rotating the electron gun.

The Ni(111) single-crystal surface was cleaned by argon ion sputtering and annealing to 1000 K for 6 min. Its cleanliness was checked by IPES and AES. Sodium was evaporated onto the sample at room temperature from a commercial SAES getter source equipped with a shutter and collimation. The pressure during evaporation stayed in the low 10^{-10} Torr range. The work-function-change measurements reported in this paper were determined previously in a separate investigation using photoemission spectroscopy.[17]

III. RESULTS AND DISCUSSION

In Fig. 1 we present inverse photoemission spectra of Na/Ni(111) for normal incidence of the electron beam as a function of Na coverage. The lowermost curve shows the spectrum of clean Ni(111). The intense peak just above the Fermi level is the Ni d band. We also observed an image potential state (labeled IS) at 4.8 eV above the Fermi level. These two peaks were observed and discussed previously by Yang, Garrison, and Bartynski[19] and Goldmann *et al.*[20] in their studies of the clean Ni(111) surface. The uppermost curve in Fig. 1 corresponds to a coverage of 1 monolayer (ML) of Na. Coverage determination was based on work-function measurements and LEED pattern changes, which are presented in more detail elsewhere,[17,21] and are in good agreement with a previous study of this system by Gerlach and Rhodin.[22] Here 1 ML is equivalent to $\theta=0.44$, the ratio of adsorbate to substrate surface atoms at saturation of the first layer.

As the Na is dosed onto the surface of the Ni(111) crystal, the features of the clean spectrum change as shown in Fig. 1. The d band becomes less intense gradually as the Na coverage increases. The clean surface image state is rapidly quenched by Na and has disappeared when the Na coverage is about 0.07 ML. A new Na-induced peak appears at low coverage (labeled 3*p*). This peak grows gradually in intensity and shifts towards the Fermi level with increasing Na coverage. After the Na coverage has increased to 0.6 ML [corresponding to an ordered ($\frac{3}{2}\times\frac{3}{2}$) LEED pattern], another peak (labeled IS′) appears.

In Fig. 2 we plot the energies of the unoccupied states as a function of Na coverage along with the work-function change. From this figure we can see that the IS and IS′ states follow the work-function change for the coverage range over which they are observed. This means that these states are pinned to the vacuum level. For this reason we assign the peak labeled IS′ as an image state, which is in agreement with the assignment of Dudde, Johansson, and Reihl from their IPES study of Na/Cu(111).[9] A similar state was also observed for the Na/Al(111) system.[10] In the present case of Na/Ni(111), this image peak has shifted to 2.4 eV above the Fermi level when the coverage is 1 ML.

We would like to note that this image state (IS′) did not show up when we performed an IPES measurement of 1 ML of Cs on Ni(111) (not shown). Comparing the work-function change of both systems, we found that the work

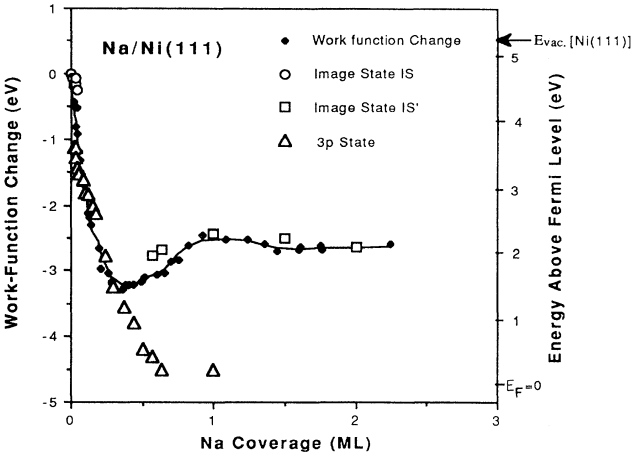

FIG. 2. Plot of the Na/Ni(111) work-function change and the energy of the unoccupied Na-induced peaks as a function of Na coverage. Note the shifted energy scales on the left and right axes.

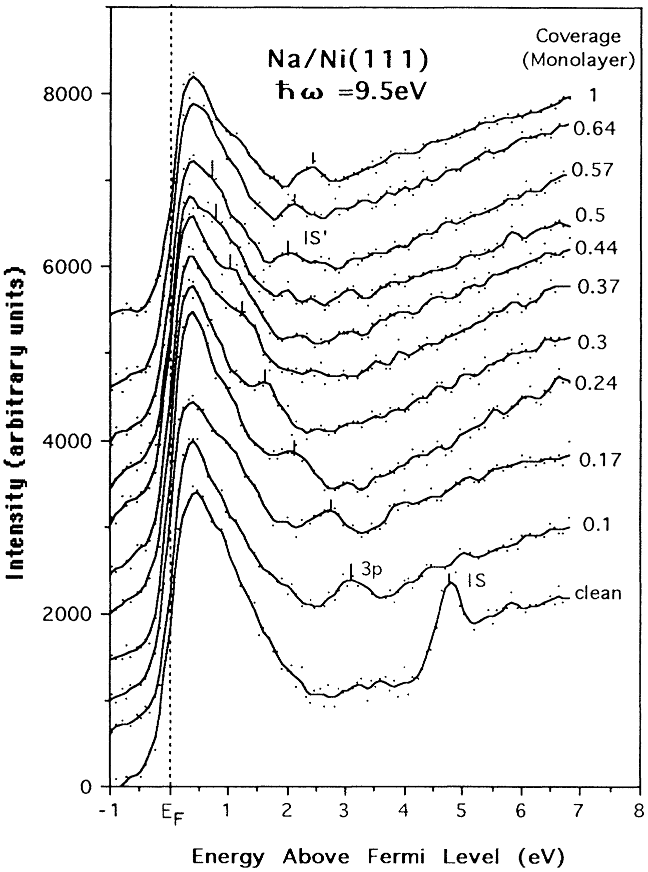

FIG. 1. Inverse photoemission spectra of Na/Ni(111) at $\hbar\omega=9.5$ eV as a function of Na coverage. Spectra were taken at normal incidence of the electron beam. Note that 1 ML corresponds to saturation coverage of the first layer. The tic marks indicate the image states labeled IS, IS′, and the Na 3*p* state.

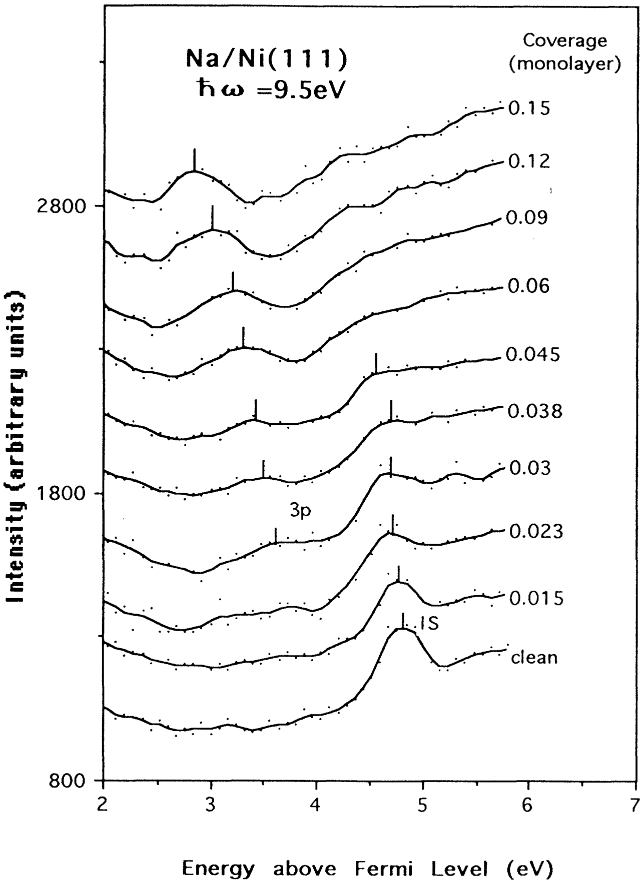

FIG. 3. Normal-incidence inverse photoemission spectra of Na/Ni(111) at $\hbar\omega=9.5$ eV as a function of Na coverage for low Na coverages.

function of Cs/Ni(111) is 0.7 eV lower than Na/Ni(111) at saturation coverage. It is therefore possible in the Cs/Ni(111) case that the image state could not be distinguished from the Ni *d*-band peaks. For Na/Ni(111) we found that this state exists only after an ordered adsorbate $(\frac{3}{2}\times\frac{3}{2})$ hexagonal structure has been formed.

In Fig. 2 we can also observe the shift of the Na-induced peak (labeled 3*p*) with Na coverage. This peak follows the work-function change for a while, but continues shifting towards E_F after the work function passes through a minimum. It has a very similar qualitative behavior to the binding energy of the Na 2*p* core level which we have previously measured with photoemission.[17] We assign this unoccupied peak as a Na 3*p* state though we cannot rule out hybridization with the Na 3*s* level, as suggested by the calculations of Ishida for Na/jellium.[8] A similar peak and assignment was discussed for Na/Cu(111) by Dudde, Johansson, and Reihl.[9] In our case, this state merges into the Ni *d* bands at high coverage near 1 ML. The total shift is about 3 eV, which is significantly larger than for the Na/Al(111) system (~1 eV),[23] and more similar to Na/Cu(111) (~2.4 eV).[9]

The original clean Ni image state is pinned to the vacuum level and shifts down slightly before it disappears at a coverage of ~0.07 ML. The new peak (labeled 3*p*) gradually appears when the Na coverage is above 0.03 ML. In Fig. 3, to better illustrate these changes, we expand the region near the vacuum level for a narrow Na coverage range. This set of spectra in particular demonstrates that these two peaks exist simultaneously over some coverage range (0.023–0.045 ML), proving that these are separate states.

We have considered several possible origins for the coverage-dependent shift of the peak we assign to the Na 3*p* level. As noted above, this peak does not track the work function over the entire coverage range, ruling out an interpretation as an image or barrier-type state. We have also considered a comparison to our previous photoemission investigation of the (occupied) Na 2*p* core level of Na/Ni(111).[17] In this case, we obtained an overall coverage-dependent shift in the binding energy of the core level of ~1.0 eV *in the other direction* (towards the Fermi level from the occupied side). In addition, a comparable shift in the initial-state energy of the core, as derived from the electrostatic potential change, was obtained for this system from a first-principles calculation of Na/jellium.[17] Therefore a strictly initial-state shift is also an unlikely explanation for these results. Finally, we

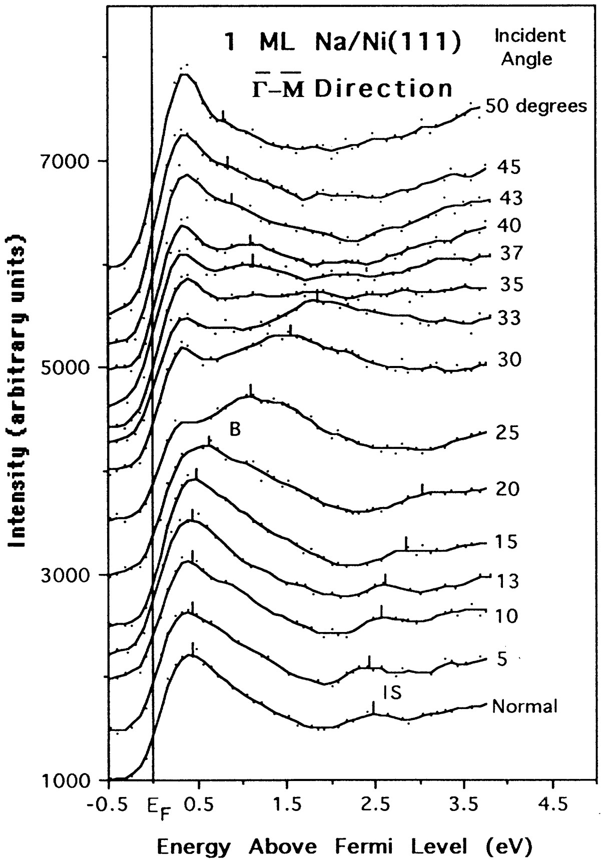

FIG. 4. A set of spectra taken for different incident-beam angles with respect to the normal direction along the $\bar{\Gamma}$-$\bar{M}$ direction in reciprocal space. The Na coverage is 1 ML $(\frac{3}{2}\times\frac{3}{2})$.

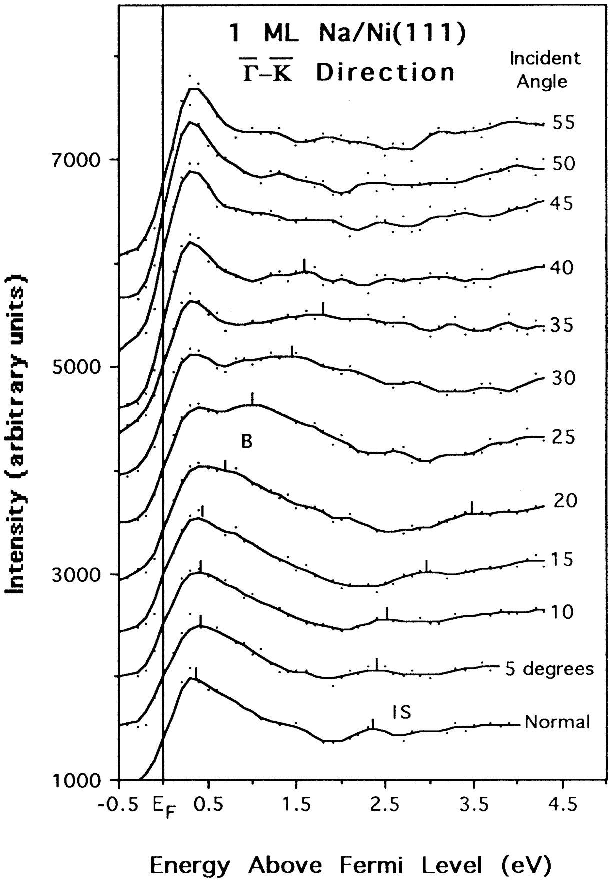

FIG. 5. A set of spectra taken for different incident-beam angles with respect to the normal direction along the $\bar{\Gamma}$-$\bar{K}$ direction in reciprocal space. The Na coverage is 1 ML $(\frac{3}{2}\times\frac{3}{2})$.

have calculated the depolarization shift using the simple model of Persson and Ishida, which considers only dipole-dipole interactions in the alkali overlayer.[24] Using their model, to obtain good agreement with our data, we found it necessary to assume an unphysically large value of 3.6 Å for the Na/jellium edge spacing. We can only suggest that at this point final-state effects also need to be considered in accounting for these results. We hope that future work will clarify this issue.

In Figs. 4 and 5 we plot spectra of Na/Ni(111) taken as a function of incident angle along the Γ-*M* and Γ-*K* directions in reciprocal space for a coverage of 1 ML [corresponding to an ordered $(\frac{3}{2}\times\frac{3}{2})$ hexagonal overlayer]. The bottommost spectrum in both figures is the normal direction (Γ). The indicated angles are incident-electron-beam angles produced by rotating the electron gun from the normal direction. In both sets of spectra, the image state disperses away from the Fermi level and disappears. In addition, peaks (labeled *B*) disperse away from the Ni *d* band at an angle of ~20°. Similar dispersion was reported for the system of Na/Cu(111).[9] On Na/Cu(111), since there is no *d* band just above the Fermi level, this dispersion was easier to detect at small angles.

In Fig. 6 we plot the Na-induced peak dispersion at 1 ML of Na coverage as well as the dispersion of clean Ni(111). Comparing to a calculation of the clean Ni(111) band structure,[20] we find that the Na-induced image state disappears at the edge of the band gap at least along $\overline{\Gamma}$-$\overline{M}$, as does that of the clean surface.[19] For Na/Ni(111), we found an effective mass for this state of $1.3m_e$ along the $\overline{\Gamma}$-$\overline{M}$ direction, the same result that Fischer *et al.*[25] obtained for the system of Na/Cu(111) along this direction using two-photon photoemission. Along the $\overline{\Gamma}$-$\overline{K}$ direction we obtained an effective mass for Na/Ni(111) of $0.78m_e$. For clean Ni(111), we obtained values of $1.1m_e$ and $0.82m_e$ along the $\overline{\Gamma}$-$\overline{M}$ and $\overline{\Gamma}$-$\overline{K}$ directions, respectively. Yang recently reported $(1.05\pm0.05)m_e$ for the effective mass of the clean Ni(111) image state along $\overline{\Gamma}$-$\overline{M}$,[19] in good agreement with our results. Regarding the dispersion of peak *B*, it is clear from the figure that the peak *B* dispersion very closely follows the dispersion of the clean substrate *d* bands. Though we cannot be too definitive about our assignment, we tend to assign this peak to a Na-induced peak, partially because this peak is very similar to the results of Na/Cu(111).[9] In addition, we have investigated a coverage of 1 ML of Cs on Ni(111) and a similar dispersion was not observed.

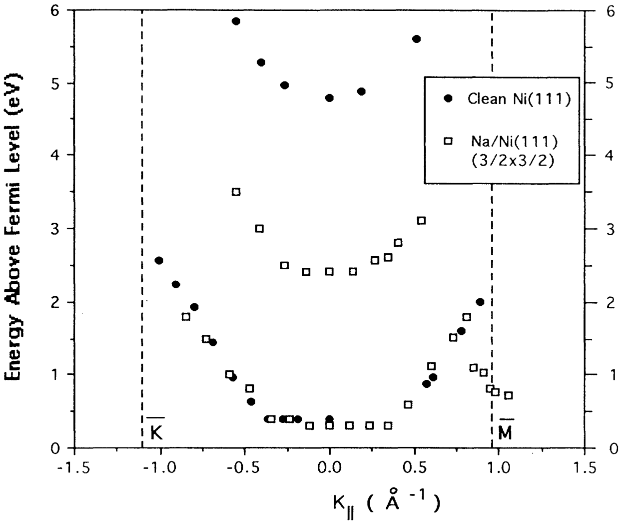

FIG. 6. The dispersion of unoccupied electron states of Na/Ni(111) for 1 ML of Na coverage and for clean Ni(111). The two dashed lines correspond to the reciprocal-space zone boundaries of the Na $(\frac{3}{2}\times\frac{3}{2})$ overlayer.

IV. CONCLUSIONS

We have measured the unoccupied electronic states of Na/Ni(111). The clean surface image state shifts towards the Fermi level with increasing sodium coverage and disappears for Na coverages above 0.07 ML. This image state reappears at completion of an ordered overlayer structure, at which point the Na coverage is 0.6 ML. We also observed an additional Na-induced state and assign this as the Na 3*p* state. The dispersion of the 3*p* state and image state were measured along both $\overline{\Gamma}$-$\overline{M}$ and $\overline{\Gamma}$-$\overline{K}$ for 1 ML of Na. The effective mass of the image state is $1.3m_e$ and $0.78m_e$ in the two directions, respectively. The dispersion of the 3*p* state closely follows the dispersion of the Ni *d* bands of the clean Ni(111) surface.

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