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# Removal of the clock reconstruction of Ni(100)-(2×2) $p4g$-N by coadsorption of K: A spot-profile-analysis low-energy-electron-diffraction and angle-resolved ultraviolet-photoemission-spectroscopy study

P. Finetti,* M. J. Scantlebury, and J. R. Mercer
*IRC in Surface Science, The University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom*

S. D'Addato
*Istituto Nazionale di Fisica della Materia and Dipartimento di Fisica dell' Università di Modena,*
*via G. Campi 213/a, 41100 Modena, Italy*

R. McGrath
*IRC in Surface Science and Physics Department, The University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom*

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Previous work has revealed that the $(2\times2)p4g$structure formed by adsorption of N on Ni(100) is a clock reconstruction. A coverage of 0.5 ML of N atoms located in alternate fourfold hollow sites on the surface results in an expansion of each hollow by means of rotation of the Ni atoms in alternate clockwise and counterclockwise directions. Here we report on the removal of this substrate reconstruction by coadsorption of K. The structural changes induced by the alkali metal on the N precovered Ni(100) surface have been monitored by means of spot-profile-analysis low-energy-electron diffraction. The chemisorption bonding of N on Ni(100) and K on Ni(100) has been investigated by means of angle-resolved ultraviolet-photoemission spectroscopy. The band structure of the adsorbate-induced states is presented. The changes in the dispersive behavior of the N-derived bands upon coadsorption of K have been related to the structural changes. Our data suggest a mechanism for the removal of the reconstruction based on the K-induced restoration of the screening of the repulsive forces between the topmost Ni atoms. [S0163-1829(97)06835-5]

## I. INTRODUCTION

The structure formed by half a monolayer of atomic carbon or nitrogen on Ni(100) is a well-documented example of adsorbate-induced reconstruction.[1–7] The chemisorption of these species is characterized by a penetration into alternate fourfold hollow sites to the extent to which they lie nearly coplanar with the top layer of the Ni substrate. Such an intrusion of the adsorbate causes the adsorption site to expand radially. The expanded hollow sites are accommodated in the available space by means of tangential movements of the Ni atoms which consists of alternate clockwise and counterclockwise rotations. This substrate distortion has the effect of turning the otherwise $c(2\times2)$ overlayer structure into an overall $p(2\times2)$ phase with $p4g$ space-group symmetry [see Fig. 1(a)]. The presence of glide lines, which are characteristic of the $p4g$space group, is revealed by the systematic absence of spots in the $p(2\times2)$ low-energy-electron diffraction (LEED) pattern observed at normal incidence [e.g., the $(0,m+\frac{1}{2})$and $(m+\frac{1}{2},0)$ diffraction spots]. Although the same LEED pattern could be attributed to domains having $p2g$ symmetry,[1] there is now conclusive evidence that the fourfold coordination of the adsorption site is retained in the reconstruction and that the LEED pattern actually corresponds to the clock or $p4g$ type of reconstruction.[1–7]

Structural investigations of the C and N adsorption systems by means of various techniques have provided an estimate of the tangential movement of the Ni atoms to be of the order of 0.35–0.55 Å.[1,5,6] Furthermore, a LEED study of the $p4g$ of C on Ni(100) (Ref. 5) has shown that associated with the reconstruction parallel to the surface there is also restructuring of the substrate in the perpendicular direction, such as rumpling of the second Ni layer (about 0.16 Å), and outward relaxation of the topmost layer (about 10%). While the structure has been determined rather accurately, the driving force of the clock reconstruction has not been fully understood. The fact that in contrast with C and N, half a monolayer of oxygen in the same highly coordinated hollow site leads to the formation of a simple $c(2\times2)$ structure, has stimulated several theoretical and experimental comparative studies.[8–14]

*Ab initio* total-energy calculations by Müller, Wuttig, and Ibach[9] led to the conclusion that the $p4g$ reconstruction is driven by the relief of adsorbate-induced surface stress. According to their model, the chemisorption bond of C or O removes charge from the Ni-Ni topmost layer interstitial region resulting in a repulsive interaction between the incompletely screened Ni nuclei. In the case of C the resulting stress is sufficiently strong to reconstruct the surface. As pointed out by Hayden, Pervan, and Woodruff these calculations should be updated by taking into account the restructuring perpendicular to the surface.[14] Nevertheless, the idea of a surface stress driven reconstruction is supported by direct measurements of this quantity upon C and O adsorption.[12]

It has also been found that N on Cu(100) occupies the fourfold hollow site and a nearly coplanar geometry has been suggested by LEED analysis,[15] but in this case the overlayer structure is a $c(2\times2)$.This can be due to the fact that N on Cu(100) forms regular arrays of small square $c(2\times2)$ do-

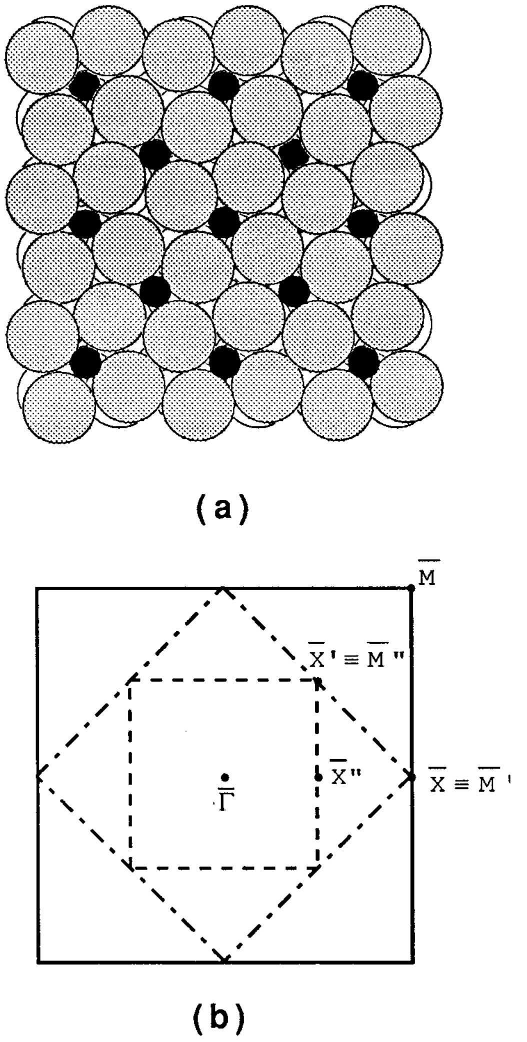

FIG. 1. (a) Schematic diagram of the Ni(100)-$(2\times2)$-N($p4g$) structure. Small black circles represent the N atoms, gray circles represent the Ni topmost layer atoms, white circles represent the positions of these atoms prior to the reconstruction and the substrate atoms. (b) Surface Brillouin zone and symmetry points of the $(1\times1)$, $c(2\times2)$, and $(2\times2)$ unit cells (full line and points with unprimed labels, dashed-dotted line and primed labels, dashed line, and double primed labels, respectively).

mains about 50 Å across,[16] so that the surface stress deriving from the nearly coplanar geometry may be relieved at the boundaries of the domains or in the regions between the domains.[16]

In this paper we present the removal of the clock reconstruction formed by N on Ni(100) via coadsorption of potassium. We find a change in the LEED pattern corresponding to a transition from a $(2\times2)p4g$ to a $c(2\times2)$ structure which occurs at a K coverage of 0.16 ML. We also show the result of an angle-resolved ultraviolet-photoemission spectroscopy (ARUPS) experiment aimed at elucidating the changes in the electronic structure associated with the alkali metal (AM). The two-dimensional adsorbate derived bands are presented for both the N and for the N/K systems. The combination of LEED and ARUPS data can be explained in terms of the reduction of the electrostatic forces between the topmost Ni atoms, due to the charge rearrangement induced by the adsorption of the K atoms.

## II. EXPERIMENT

The structure formed by the coadsorption system has been characterized by means of an Omicron spot-profile-analysis LEED (SPA-LEED).[17] The ARUPS experiment has been carried out separately on the vacuum ultraviolet beamline 4.1 at Daresbury Laboratory,[18,19] in an experimental chamber equipped with a VSW HA54 angle-resolved spectrometer (analyzer angular acceptance 0.5°) mounted on a two-axis goniometer. The base pressure in both the UHV stations was typically $<10^{-10}$ mbar. The sample was cleaned by cycles of $Ar^+$ ion sputtering followed by anneal in oxygen (oxygen partial pressure equal to $5\times10^{-8}$ mbar) and in vacuum. The $(2\times2)p4g$ surface was prepared by means of sputtering in nitrogen followed by a short annealing at about 600 K. The quality of the surface thus obtained has been previously verified with several techniques including scanning tunneling microscopy (STM).[7] K was coadsorbed onto the N precovered surface with an SAES getter source. Sample cleanliness, purity of the N and K overlayers and coverages were ascertained by means of Auger electron spectroscopy in the SPA-LEED experiment and by means of photoemission and LEED in the ARUPS experiment. All the measurements were carried out at room temperature.

## III. SPA-LEED RESULTS AND DISCUSSION

The $(2\times2)p4g$ LEED pattern of the saturated N/Ni(100) system changes as K is incrementally dosed onto the surface until only a $c(2\times2)$ pattern is observed. Figure 2(a) shows a plot of the average intensities of all the equivalent half-integer diffraction spots appearing in the first $(2\times2)p4g$ surface Brillouin zone as a function of K coverage. These intensities were measured from the area of the spot profiles previously fitted with a Gaussian curve superimposed on a flat background. All the spot profiles were recorded with an electron-beam energy of 130 eV, since at this energy the initial (zero K coverage) intensities of the $(\frac{1}{2},\frac{1}{2})$ and $(\frac{1}{2},1)$-$(1,\frac{1}{2})$ diffraction spots are very similar. It can be seen that the intensity of all the half-integer spots is constant up to a coverage of about 0.08 ML. At higher AM coverages there is a decrease in the intensity of the $(1,\frac{1}{2})$ spots associated with the $p(2\times2)$ periodicity together with an increase in the intensity of the $(\frac{1}{2},\frac{1}{2})$ spots. These would appear both in a $p(2\times2)$ or $c(2\times2)$ overlayer structure [as mentioned earlier the $(0,\frac{1}{2})$ spots are suppressed by the glide lines of the $p4g$ reconstruction]. At a K coverage of 0.16 ML the intensity of the $(1,\frac{1}{2})$ spots drops below the limit of detection leaving a pure $c(2\times2)$ type of pattern. No sign of a $p(2\times2)$ periodicity could be determined throughout a wide range of beam energies. Further increasing of the AM coverage results in a gradually degraded LEED pattern due to a growing background level. This indicates the development of a disordered phase which is clearly associated with the K coverage [see also Fig. 2(b)]. On the other hand, the size of the domains of the ordered layer, as measured from the full

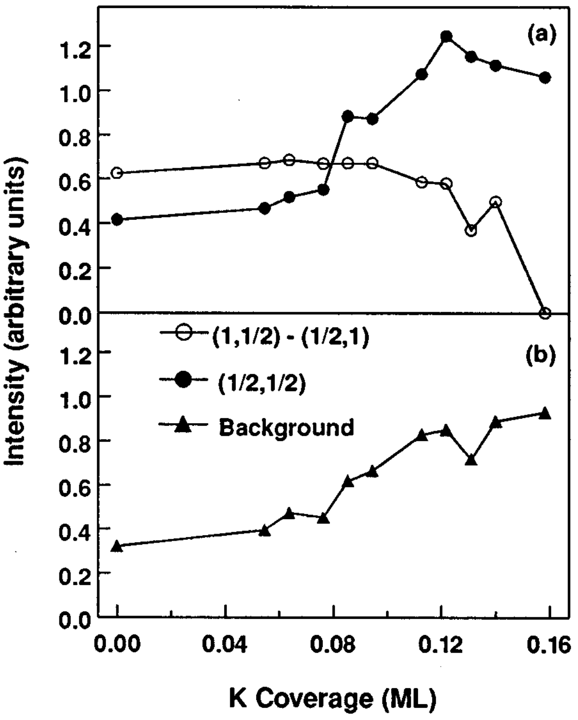

FIG. 2. (a) Average LEED intensity of the $(\frac{1}{2},\frac{1}{2})$ and $(\frac{1}{2},0)$-$(0,\frac{1}{2})$ beams measured from the profiles of the spots as function of K coverage. (b) Average background intensity. The electron-beam energy was $E_p = 130$ eV.

width half maximum of the spot profiles, is not affected by the AM. They are of the order of 200×200 unit cells, both in the $(2\times2)p4g$ and in the $c(2\times2)$ structures. This size of the domain is consistent with the STM findings.

We believe that the most straightforward interpretation of the phenomena discussed above is that the coadsorption of K on the Ni(100)-$(2\times2)p4g$-N removes the substrate reconstruction without altering the basic N overlayer structure (i.e., N atoms situated in the fourfold hollow site), while the AM forms a disordered phase. This last assumption is not only supported by the observed trend in the background of the LEED pattern but also by the known behavior of the room-temperature adsorption of K on the clean and O-covered Ni(100) surface.[20,21]

As for the possible mechanism for the removal of the reconstruction induced by the AM we note first of all that the bonding of alkali metals with a clean or adsorbate-covered metal surface has the effect of lowering the system work function, that is, because of the high polarization of the AM–transition-metal bonding,[22] charge is drawn toward the surface to form a dipole layer which has the opposite sign to the one of clean metal. According to the model of Müller, Wuttig, and Ibach[9] the N-induced substrate reconstruction does not originate from a direct adsorbate-adsorbate interaction but by an adsorbate-induced increase of the Ni-Ni repulsion. It is then possible that the AM-induced charge rearrangement acts to restore the screening between the Ni topmost layer atoms. The observed structural phase transition is completed at a K coverage corresponding to the minimum of the work function for the K/Ni(100) system.[23,24] Due to the nearly coplanar geometry of the N atoms, any dipole moment carried by this species should not interact strongly with the AM dipole moment, which extends outward with respect to the clean metal surfaces.[25–28] Therefore, it is reasonable to assume that the behavior of the work function for K on the N precovered Ni(100) surface would be very similar to that observed on the clean metal.

Alternatively, a mechanism involving a more direct adsorbate-adsorbate interaction may not be ruled out. In a highly simplified picture, charge donation to the N atoms could account for an oxygenlike behavior.

## IV. ARUPS EXPERIMENT

### A. Background

The critical dependence of the occurrence of the Ni substrate reconstruction upon the occupation number of the adsorbate $2p$ states, which is underlined by the behavior of C and N on one side and O on the other, has stimulated comparative studies of the electronic properties of these chemisorption bonds.[13,14,29–31] Experimental work has been carried out by means of ARUPS (Ref. 13) and soft x-ray emission[29,31] (SXE) for the occupied states, and with near-edge-x-ray absorption fine structure[30] and $k$-resolved inverse photoemission spectroscopy[14] (KRIPES) for the unoccupied ones. Although the interpretation of these results is somehow hampered by the lack of theoretical calculations for C and N, the combined experimental effort and theoretical work carried out on the O/Ni(100) system[32,33] allows the following description of the chemisorption bond between C, N, or O and Ni(100). The chemisorption bond occurs mainly via hybridization of the adsorbate $2p$ states with the Ni $sp$ band. The occupied part of these hybridized states has strictly bonding character and gives rise to structures observed with ARUPS (Ref. 13) and SXE (Refs. 29 and 31) in the range between 4 and 7 eV below the Fermi level, with an increasing binding energy going from C to O. More controversial is the role played by the Ni $3d$ states. The ARUPS data[13] show that adsorption of C or N leads to the formation of adsorbate-derived states in the region of the Ni $d$ band. No similar states have been observed with this technique upon chemisorption of O. The unoccupied states, which have been recently investigated by means of KRIPES (Ref. 14) show nearly dispersionless bands due to C or N (at about 1 and 4 eV above the Fermi level, respectively) and a rather strongly dispersing O derived band (around 2–5 eV above the Fermi level). These results, which identify common features for C and N, have been interpreted in terms of hybridization of these species with metal $d$ states stronger than in the case of O adsorption. It has also been suggested that this interaction could be responsible for the shift in the energetic balance toward the substrate reconstruction. The existence of adsorbate derived features (with mainly $p$ character) in the region of the Ni $d$ band has been recently confirmed by an SXE study of N on Ni(100).[31] On the other hand, SXE data taken on the O/Ni(100) system show that O adsorption also gives rise to $2p$-derived states spreading throughout the Ni $d$ band region.[29]

So far, the adsorbate $2p$ states have been discussed as a single set but it is clear that the nondegenerate components parallel (here denoted $p_x$ and $p_y$)and perpendicular to the surface ($p_z$) are expected to play quite a different role in the bonding of C and N on one side and O on the other. It is in fact the $2p_z$ orbital which should interact more strongly with the second Ni layer in the nearly coplanar geometry. In the case of oxygen the $p_z$ orbital is filled and thus should give a minor contribution to the O-Ni bonding.

In order to determine the extent to which the features displayed in photoemission by C and N can be considered peculiar to the substrate reconstruction, we have performed an ARUPS experiment on the unreconstructed $c(2\times2)$ surface of K/N-Ni(100). We focus our attention on the adsorbate-derived states, in particular N states, having even parity with respect to the bulk symmetry planes. These are the states that display the greatest difference in dispersive behavior in comparison with O. In order to distinguish between the N- and K-derived states and between these and the substrate ones, we have also acquired data on the clean Ni(100) surface and on the Ni(100)-$(2\times2)p4g$-N surfaces. Mapping of states with strictly even parity with respect to mirror symmetry planes is achieved by making use of linearly polarized radiation with the electrical vector lying in the plane of incidence (which is set to be coincident with the plane of symmetry) and by moving the electron analyzer in the same plane. Data were collected along the two main azimuthal directions [$\langle 011\rangle=\bar{\Gamma}\bar{X}$ and $\langle 001\rangle=\bar{\Gamma}\bar{M}$; see also Fig. 1(b)] by moving the analyzer in the range $-5°$ to 70° measured from the direction normal to the surface. The angle of incidence of the light was 45° and the photon energy was 37 eV.

### B. ARUPS results and discussion

Figure 3 shows an overview of the angle-resolved spectra taken on the two adsorption systems. Labels $a-d$ refer to the states which have been identified as adsorbate induced and have been subsequently mapped. It can be seen that the adsorption of K on the N precovered surface does not modify the emission near the Fermi level. This is the region where K $4s$ derived states are expected to appear.[34,35] The broadening induced by hybridization with the substrate makes these states difficult to observe in photoemission, even when the alkali adsorption occurs on metals with a small background emission. Also the intensity of the N derived states (feature labeled $a$ at about 1 eV binding energy) appearing in the region of the Ni $d$ band is unmodified by K. This result would suggest that hybridization between N $2p$ and Ni $3d$ states is not generally affected by the AM adsorption or by the structural changes occurring at the substrate. K adsorption results in the appearance of new states in the binding energy region around 6 eV (feature labeled $d$; see also Fig. 4). This K-induced feature is very close to the Ni $3d$ photoemission satellite[37] but a careful examination of the spectra taken on the clean and N dosed surface confirms its K-induced origin. K-induced features appearing well below the $d$ band have been previously reported for adsorption on several transition metals.[34,36] The binding energy of these states suggests they have a strong substrate metal character. Features labeled $b$ and $c$ are N-derived states.

Figure 5 shows the band structure of the adsorbate-derived states plotted in the reduced zone scheme of a $c(2\times2)$ overlayer structure [see Fig. 1(b)]. The use of a $c(2\times2)$ Brillouin zone in the case of the N-$(2\times2)p4g$ emphasizes the overlayer structure with respect to the bulk rather than the topmost layer. A $(2\times2)$ periodicity should imply an additional band folding along $\bar{\Gamma}\bar{X}'$ and the presence of two atoms per unit cell, such as in the $p4g$ structure, should lead to the splitting of each adsorbate-derived band in two nondegenerate branches (except at $\bar{X}''$, where symmetry constraints impose degeneracy).[38] It was pointed out by Prince *et al.*[38] that the observation of the additional back folding (and of the resulting additional states) in photoemission is generally forbidden by the glide line symmetry of the $p4g$ space group (with the exception of special experimental geometries). As a result, the experimentally determined bands of a $(2\times2)p4g$ structure display the same periodicity of the $c(2\times2)$ overlayers.[13,38–40] As an alternative to the symmetry based considerations of Ref. 38, it has been pro-

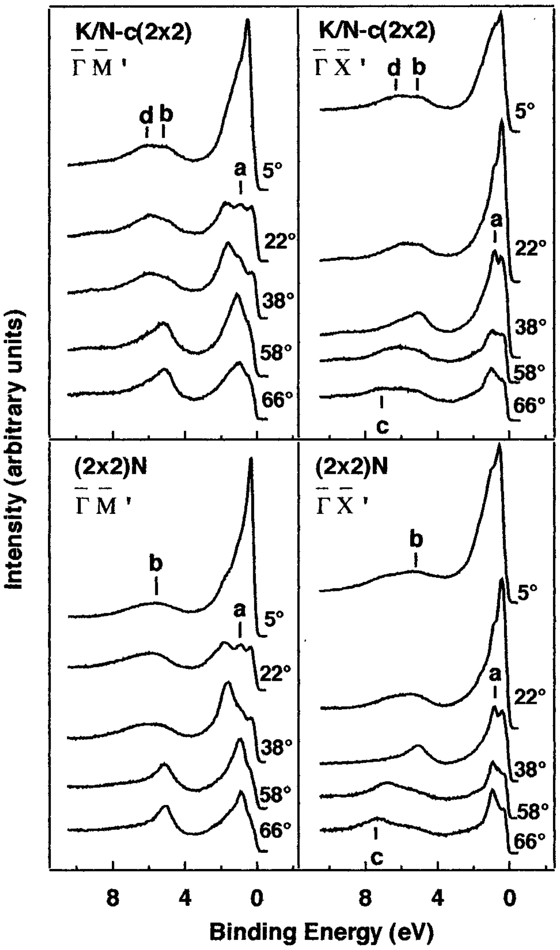

FIG. 3. Overview of the ARUPS spectra taken along the main azimuthal directions [see Fig. 1(b)] on the N-Ni(100) and N/K-Ni(100) coadsorption systems. The full set of data has been acquired by changing the angle of emission in steps of 1° in the first half of the first $c(2\times2)$surface Brillouin zone of electrons with 26 eV kinetic energy, 2° in the second half, and in steps of 4° in the second and third zone. The spectra have been normalized to the high-binding-energy background. The photon energy was $h\nu=37$ eV, the angle of incidence of the light 45°. Labels $a-d$ refer to the adsorbate-derived states which have been mapped (see text for the assignment).

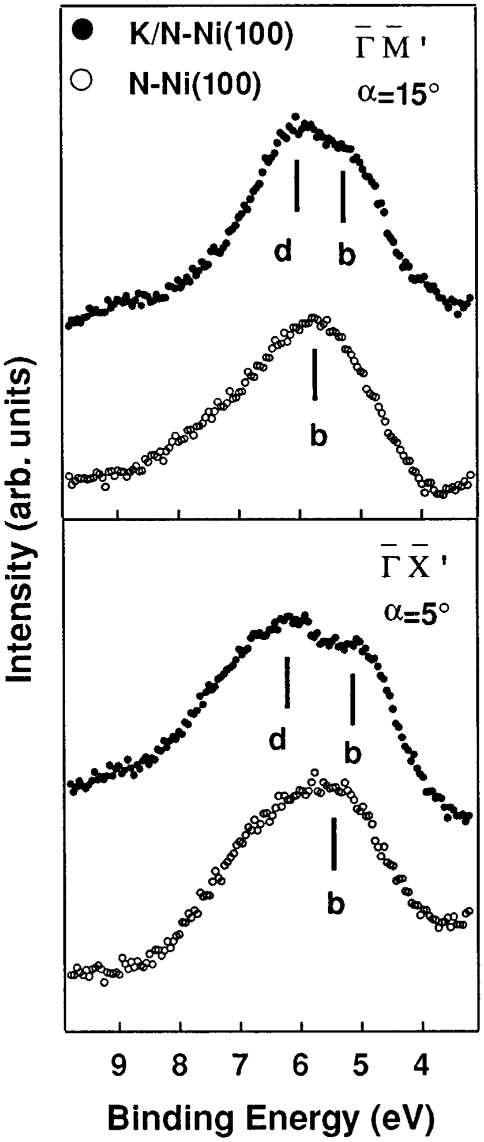

FIG. 4. Comparison of spectra taken on the N-Ni(100) and K/N-Ni(100) system in the binding-energy region between 3 and 9 eV ($\alpha$ is the emission angle). These data show in more detail the K-induced feature labeled *d* in Fig. 3.

posed that the $c(2\times2)$ periodicity of the $(2\times2)p4g$ bands may not be apparent but it may reflect the fact that the surface distortion is just a small perturbation of an overlayer displaying (if isolated) a $c(2\times2)$ periodicity and interacting not only with the topmost layer but also with the unreconstructed underlying bulk type of structure.[13,39] Finally, the use of the same $c(2\times2)$ surface Brillouin zone facilitates the comparison of data taken for different overlayer structures.

Our experimentally determined band map of N-derived states for N in the $(2\times2)p4g$ phase is in agreement with that of Ref. 13 in the binding-energy region between 5 and 7 eV. In addition we could map, throughout the surface Brillouin zone, the state at a binding energy of about 1 eV (feature labeled *a* in Fig. 3). This state has been recognized not only as a characteristic of the substrate reconstruction, but it has also been suggested that it could provide the key to the driving force of the reconstruction.[13] According to a model originally proposed for the reconstruction of the clean W(100) surface,[41] if a surface state of the unreconstructed system crosses the Fermi level at the midpoint of the surface Brillouin zone, the additional back folding due to the higher periodicity of the reconstructed surface may result in the opening of a gap. The opening of such a gap, in turn, could lead to a reduction of the total energy of the system. Assuming that the dispersion of this N-induced state is not affected by the AM, our data taken on the unreconstructed coadsorption system rule out this type of model, at least for the N on Ni(100) system.

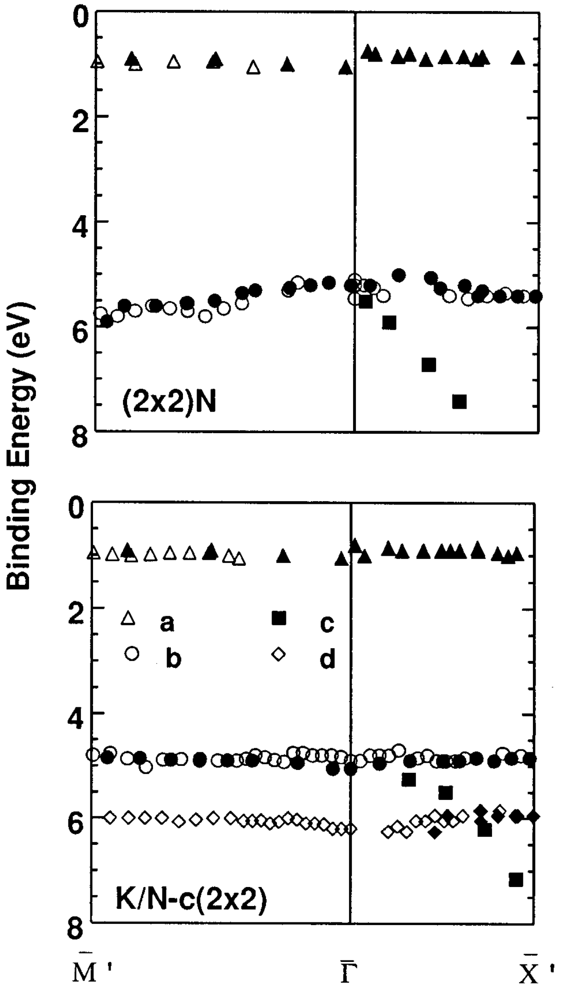

FIG. 5. Band structure of the adsorbate-derived states with even parity of the Ni(100)-$c(2\times2)$-N/K and Ni(100)-$(2\times2)p4g$-N structures. Empty symbols refer to states in the first Brillouin zone, full symbols are states folded back from higher zones.

Considering the coadsorption system we note first of all that the K-induced state is basically dispersionless. This result is in agreement with previous findings.[34,36] Also, the dispersion of the N-derived states and in particular that of the lower band around 5 eV (feature labeled *b* in Fig. 3) is greatly reduced. In contrast with the pure N system (where this band shows a downward dispersion from $\bar{\Gamma}$) in the coadsorption system it is rather flat, with only a slight upward trend of about 0.2 eV. As mentioned earlier, the analysis of the width of the LEED pattern spot profiles indicates that the size of the domains of the ordered phase (due to the nitrogen) is not affected by the AM and is quite large. Thus, the reduced dispersion cannot be attributed to an increased disorder of the N overlayer but must be an effect of the K-N interaction and/or removal of the substrate reconstruction. Also O adsorption in the $c(2\times2)$ structure leads to the observation of two bands in the binding-energy region between 5 and 7 eV. However, while both the N-derived bands disperse downward from $\Gamma$, O displays also an upward dispersing band. By comparing the experimental O-derived bands with the theoretical calculations of Liebsch,[32] this upward dispersing band was attributed to O $2p_z$ states.[13,42] In the case of N (for which theoretically calculated bands are not available), both bands were attributed, on the basis of their dispersive behavior, to $p_x$ and $p_y$ states.[13] Given the potassium-induced change in the dispersion observed in the N-derived band labeled $b$, we suggest that it could be assigned to $p_z$ states. Indeed these are the states that are expected to undergo a major change upon a phase transition from a $(2\times2)p4g$ to a $c(2\times2)$ due to the previously mentioned strong interaction with the Ni second layer. We are reminded that the main effect of the substrate reconstruction is the expansion in the hollow site to accommodate the adsorbate in a nearly coplanar geometry. If the substrate distortion is removed and if the substrate-adsorbate bond length is not severely affected by this process, then the adsorbate must be squeezed out of the hollow site and sit higher above the surface. We can estimate the height of the N atoms in the unreconstructed system from the N-Ni bond length measured by Wentzel *et al.*[4] (average N-Ni bond length of 1.88 Å) and from the bulk Ni structural parameters (Ni-Ni nearest-neighbor distance of 2.49 Å). These data lead to an estimated N-Ni topmost layer distance $d_\perp \cong 0.66$ Å, which is substantially larger than the value of 0.1 Å measured in the reconstructed system[4] and similar to the value found by means of LEED analysis for Ni(100)-$c(2\times2)$-O ($d_\perp = 0.77$ Å).[43] With these structural assumptions the similarity between the dispersion of the N in the N/K system and O-derived states is not too surprising and perhaps reinforces the assignment of the feature labeled $b$ to N $2p_z$ states. Nevertheless, the experimentally determined upward dispersion of the O $2p_z$ states is much stronger (about 1.5 eV).[13] Apart from possible differences in the dispersive behavior that may originate from the different electronic structure of the N and O atomic species, we suggest that a reduced dispersion of the N $2p_z$ states may be due to a high sensitivity of these states to the disorder introduced in the electronic environment by the coadsorbed K layer. K atoms that do not occupy a well-defined site in the N-N interstitial region may, for instance, disrupt the lateral interactions between the $p_z$ orbitals in a not systematic way.

As a final remark, we note that apart from the reduced dispersion of the feature $b$, which we think can be explained in terms of the geometrical changes occurring at the surface, the photoemission data do not suggest a strong K-N interaction. Therefore, we believe that they are in better agreement with a model for the removal of the reconstruction which is based on the restoration of the screening of the repulsive forces between the topmost Ni atoms.

## V. CONCLUSIONS

We have observed a change in the LEED pattern formed by N on Ni(100) induced by the coadsorption of K. This change can be attributed to a phase transition of the N-Ni layer from a $(2\times2)p4g$ with substrate reconstruction to an unreconstructed $c(2\times2)$ phase.

ARUPS data taken on the N/Ni(100) give a more detailed description of the N-derived states located in the region of the Ni $3d$ band. Data taken on the Ni(100)-K/N coadsorption system show how the structural changes observed in the LEED pattern are coupled with changes in the dispersion of the N-derived energy bands located in the region of the Ni $4sp$ band. The dispersive trend displayed by one of these bands suggests that it could be attributed to N $2p_z$ states. We have proposed a simple qualitative model to explain the dispersive trend of this N-derived band based on the structural changes occurring at the Ni surface, namely, the increase of the N-Ni topmost layer distance. Our ARUPS data do not give evidence of N-K direct interaction. This result is consistent with a mechanism where the electronic charge rearrangement induced by the AM acts to restore the electrostatic forces between the Ni topmost layer atoms prior to the N-induced $4pg$ reconstruction.

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*Present address: CLRC Daresbury Laboratory, Warrington WA4 4AD, U.K. Also at: Department of Physics & Astronomy, University of Leicester, Leicester LE1 7RH, U.K.

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