Top-Site Adsorption for Potassium on Ni(111)

D. Fisher, S. Chandavarkar,[a] and I. R. Collins
Department of Physics and Surface Science Centre, University of Liverpool, Liverpool, L69 3BX, United Kingdom
R. D. Diehl[b]
Department of Physics, Penn State University, University Park, Pennsylvania 16802
P. Kaukasoina and M. Lindroos
Department of Physics, Tampere Institute of Technology, Tampere, Finland

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We have used dynamical low-energy electron diffraction (LEED) to determine the adsorption site and the geometry of the surface region for the $p(2\times2)$ overlayer of potassium adsorbed on Ni(111). The structure consists of the potassium atoms adsorbed on *top* of the Ni atoms with vertical reconstructions of Ni atoms in the first and second substrate layers combined with a slight horizontal reconstruction of the first substrate layer. The potassium-nickel bond length is found to be 2.82 ± 0.04 Å corresponding to a rather short effective potassium "radius" of about 1.57 Å.

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The nature of the chemical bond between adsorbed alkali-metal atoms and metal substrates has been a matter of some controversy for the past few years. While some experimental and theoretical results have been interpreted as supporting a picture of ionic bonding at low coverages [1-4], others have been interpreted as supporting a picture of covalent bonding at all coverages [5,6]. Although alkali-metal adsorption systems are among the simplest of chemisorption systems and they have been studied extensively [7], there have been only a few complete structural determinations of them [8-13], as shown in Table I. All of these except one, a LEED study of Cs/Cu(111) [9], indicate that alkali-metal atoms occupy high-coordination sites. No explanation has been proposed for the low-coordination site of Cs/Cu(111), possibly due to low confidence in the result since it is both unexpected and uncorroborated. Therefore it has been common to assume that the site of adsorption for alkali metals on low-index, atomically flat metal surfaces is the high-coordination site as a consequence of the nondirectional bonding expected of the alkali *s* orbital [14-17]. The results presented in this paper show that this is not a good assumption in all cases and that our current understanding of the alkali-metal chemisorption bond is not complete.

This experiment was carried out in an ultrahigh vacuum system which was Mumetal shielded and had a base pressure of 6×10^{-11} mbar. The data were obtained using a standard Varian four-grid optics in constant-beam-current mode and a video data acquisition system [18,19]. The crystal was cut to within 0.25° of the (111) surface and was subsequently mechanically polished and chemically etched. It had been used in adsorption studies for at least two years prior to this experiment and so had been through many cycles of 0.5-keV Ar^+ ion bombardment and annealing to 1200 K. After additional cleaning cycles and before running each of these experiments, the crystal was heated to 1200 K and slowly cooled at a rate of about 1 K/s to 120 K in order to minimize the surface defect density [20].

The phase diagram and the procedure for producing the $p(2\times2)$ structure in the potassium overlayer have been determined in previous LEED experiments [21]. The surface was routinely checked for impurities using Auger electron spectroscopy (AES) both before and after adsorption experiments, and after experiments there were no detectable impurities. The detectability limit for carbon is a few percent of a monolayer. The experiments reported here were carried out under the same experimental conditions as were used for previous studies of the incommensurate structures of potassium on Ni(111) [22], which were found to be even more sensitive than AES to surface impurities such as carbon. Therefore we believe that the impurity level in these experiments is less than 1%. Potassium was evaporated onto the crystal from a SAES getters source which had been degassed at essen-

TABLE I. Previous structural determinations for alkali-metal adsorption on unreconstructed metallic surfaces.

System	Structure	Site	Method	Effective alkali radius	r_{ionic}	r_{metallic}	Ref.
Cs/Rh(100)	$c(4\times2)$	Hollow	LEED	2.10 ± 0.06	1.67	2.73	[12]
Cs/Cu(111)	$p(2\times2)$	Top	LEED	1.73 ± 0.05	1.67	2.73	[13]
K/Co(1010)	$c(2\times2)$	Hollow	LEED	1.87 ± 0.05	1.33	2.38	[14]
Na/Ni(100)	$c(2\times2)$	Hollow	LEED	1.59 ± 0.10	0.97	1.91	[15]
Na/Al(100)	$c(2\times2)$	Hollow	LEED	1.43 ± 0.07	0.97	1.91	[16]
Na/Al(111)	$(\sqrt{3}\times\sqrt{3})R30^\circ$	Subst.	SEXAFS	1.88 ± 0.03	0.97	1.91	[17]

tially the base pressure of the system for 3 days. To form the $p(2\times2)$ structure, potassium was evaporated onto the crystal to a coverage higher than 0.25, where the structure is incommensurate, and then gently desorbed by warming the crystal until a sharp $p(2\times2)$ LEED pattern was obtained. The crystal was then set to normal incidence by adjusting it until the energy variations of intensity in equivalent beams were identical by eye. This was verified by comparison of equivalent beam intensities during analysis. Frames of the full diffraction pattern were acquired over the energy range $80\leq E\leq450$ eV at 2 eV intervals with appropriate camera lens aperture changes to prevent saturation of the camera. Each run required less than $\frac{1}{2}$ h for setup and data acquisition time.

Spot intensities were extracted from the video frames by integrating the intensity within a 5×5 pixel box, corresponding to an angular acceptance of $0.7°\pm0.1°$ and centered on the diffraction spot. The appropriate corrections for aperture changes were applied when necessary. Spot intensities were extracted for thirteen integral-order beams, resulting in five symmetry-inequivalent beams, and twenty half-order beams, resulting in eight symmetry-inequivalent beams. The intensities for the beams which were symmetry equivalent were averaged in order to reduce the errors due to possible misalignment from normal incidence [23].

Theoretical $I(E)$ spectra were calculated using the program package of Van Hove and Tong [24]. After calculating reflection and transmission matrices for all atomic layers within the self-consistent formalism, interlayer scattering was treated using the layer-doubling technique. For reconstructed nickel layers the combined space method for composite layers by matrix inversion was utilized. The ion-core scattering potentials were of muffin-tin form and we have used the tabulated nickel and potassium potential of Moruzzi, Janak, and Williams [25]. Up to eleven phase shifts were calculated. Phase shifts were temperature corrected using an effective Debye temperature of 440 K for bulk nickel layers and 140 K for the potassium surface layer. Up to 53 symmetry-inequivalent beams in symmetrized programs of Van Hove and Tong were used in the plane-wave expansion of the wave field between atomic layers. The real part of the inner potential was made to be constant over the experimental energy range and was treated as an adjustable parameter; its final value for the optimum geometric structure was 4 eV. The imaginary part of the optical potential was fixed at 4 eV. We made no further attempts to vary nonstructural parameters to further improve the level of agreement between theory and experiment as our main aim was to obtain the geometry of the surface.

Five completely different geometries were tested for the structure of the potassium overlayer: fcc hollow sites, hcp hollow sites, on-top sites, bridge sites, and substitutional sites in the top Ni layer. Agreement between theory and experiment was tested by a conventional Pendry r-factor [26] analysis which included the full set of beams, five integral-order beams and eight half-order beams. The quoted precision of the structural parameters is determined by a sensitivity analysis which is based on the steepness of the r-factor minimum. As the Pendry r factor is highly sensitive to noise in spectra, the experimental spectra were first filtered by a 5 points median filter which removes single spikes. Both experimental and theoretical spectra were smoothed by convolving each data set with a 2 eV wide Lorentzian before carrying out the r-factor analysis. Experimental and theoretical spectra for the optimum structure of each geometry are shown in Fig. 1 for two integer and two half-integer beams. The r factor for the integer-order beams was found to be largely insensitive to the surface geometry, a finding which agrees with visual inspection of the beams. Its value was within the range 0.26 to 0.35 for most geometries whether or not substrate reconstruction was included in the calculation. The half-order beams, however, were extremely sensitive, both by r factor and by eye, to the surface geometry, including both the position of the adatoms and the substrate reconstruction.

The optimum r factors are shown in Table II for the geometries which we studied extensively, and all of these include vertical relaxations of the overlayer and substrate

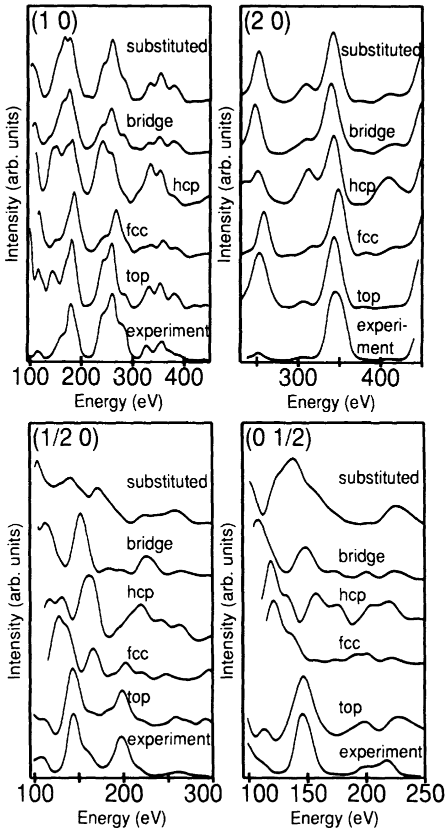

FIG. 1. Experimental spectra and optimum calculated spectra for five geometries for two integer and two half-integer beams.

TABLE II. Minimum Pendry r factors for various model structures.

Adsorption site geometry	r integer	r half-integer	r total
hcp hollow	0.47	0.86	0.69
fcc hollow	0.34	0.82	0.63
Bridge site	0.32	0.82	0.59
K substitutes Ni	0.28	0.76	0.49
K on top of Ni	0.26	0.39	0.32

atoms. For each of these geometries, the relaxations of the first and second layers were independently varied by approximately ±50% and ±10%, respectively, of the values expected for a simple overlayer on the truncated bulk substrate. The fcc hollow, hcp hollow, and bridge site geometries gave half-order r factors which were very poor and minima which were ill-defined. The remaining two geometries, adsorption in a top site and substitutional adsorption, are in fact quite similar structures if one allows the vertical distance of the overlayer atom to vary with respect to the top layer of substrate atoms. The essential difference between these structures is whether or not a substrate atom is present directly below the adatom. Within these basic structures, vertical reconstructions of the first and second Ni layers and horizontal reconstruction of the first layer were tested. This involved independently moving the substrate atoms by as much as 30% of their bulk spacings in directions which are consistent with the overall $p(2\times2)$ symmetry of the system. The reconstructions improved the half-integer r factor for the top-site structure from 0.48 to 0.39 and for the substitution structure from 0.76 to 0.60. The optimized substitutional structure has a K-Ni distance of only 2.50 Å; we believe this is unphysically small for a substitutional K atom. Because the K-Ni distance found for the top-site case (2.82 Å) is also somewhat smaller than those observed for other potassium adsorption systems, we made extensive searches (including reconstructions) to check other (local) r-factor minima at larger K-Ni distances. The result of these searches was total r factors of 0.46 for a K-Ni bond length of 3.09 Å and 0.56 for a K-Ni bond length of 3.49 Å. Our conclusion from these searches is that the structure of this surface has the K atoms on top of Ni atoms at a bond length of 2.82 Å, with a small reconstruction of the top two substrate layers.

This optimum structure for the $p(2\times2)$ structure of K/Ni(111) is shown schematically in Fig. 2. The top-layer Ni atoms which are occupied by a K atom have relaxed inward (toward the bulk) slightly (0.12 Å) relative to those which are not occupied. The atoms in the second substrate layer show smaller vertical relaxations which are complementary to those of the first layer. The vertical relaxations slightly increase the coordination of the adsorbed atoms, although it is nowhere near the coordination which would be experienced by an adatom in a threefold hollow site. The structural parameters in the vertical direction are summarized in Fig. 2(b). The unoccupied Ni atoms in the top layer have a small (0.06±0.06 Å) horizontal reconstruction which causes the unoccupied Ni atoms to draw together in groups of three, as shown in Fig. 2(a). The precision of this parameter is poor compared to those of the vertical parameters because of the lower sensitivity of this LEED technique to lateral displacements. However, these lateral shifts are consistent with those which one would expect to occur as the relatively large adatom is drawn into the top layer —i.e., as the K atom is drawn inward, it pushes the surrounding Ni atoms away. The Ni atoms move toward the positions of the nearer second-layer Ni atoms, effectively producing a density modulation involving the top two Ni layers. This modulation has the period of the $p(2\times2)$ superlattice within which the Ni-Ni distances vary from 2.39 to 2.59 Å, compared to a bulk Ni-Ni spacing of 2.49 Å.

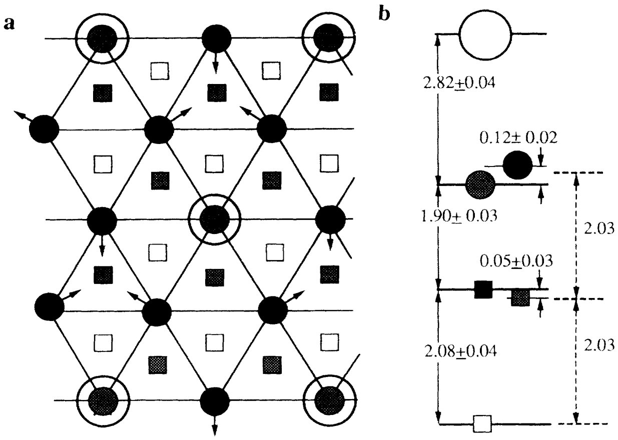

FIG. 2. Schematic drawings showing the positions of atoms in the equilibrium structure. The large open circles denote potassium atoms, the filled and shaded smaller circles denote top-layer Ni atoms, the filled and shaded squares denote second-layer Ni atoms, and the open squares denote third-layer Ni atoms. (a) Positions of atoms as viewed from above the adlayer. The intersections of the lines indicate the bulk positions of the top-layer Ni atoms; the direction of the horizontal shifts is shown by arrows (the actual value of the shift is 0.06 Å). There are no horizontal shifts of second- and third-layer atoms. (b) Vertical positions of atoms; dimensions are in Å. The bulk interlayer spacing of 2.03 Å is shown on the right for comparison.

In Table I we have listed the ionic and metallic radii of the alkali metals. We have calculated an "effective radius" of the alkali metal for the adsorption systems by subtracting the metallic radius of the substrate atom from the adsorbate-substrate bond length. We have no theoretical justification for using the metallic radius of the substrate atom and it would be particularly dubious in the event of true ionic bonding between the alkali-metal atom and the substrate atom. Also, we do not imply that the adatom charge distribution is spherical. However, the effective radius obtained is useful as a means of compensating for different atomic sizes of the substrate atoms when making bond-length comparisons. In comparing the results of Table I to the data presented here which give an effective K radius of 1.57 Å, and the recent results from two additional studies [27,28] there are two results which are common to all of these results. First, top sites have been observed only on hexagonal substrates, and second, the effective radius of the alkali-metal adatoms when they are in top sites is less (relative to ionic and metallic radii) than when they are in higher-coordination sites.

There have been no extensive calculations that we know of for simple alkali-metal adsorption systems which consider in detail the possibility of on-top adsorption sites and so our attempts to account for it can only be speculative. A likely reason for the occurrence of top sites only on close-packed surfaces is that the potential-energy corrugation due to the repulsive part of the adatom-substrate potential in these systems must be very small or it will dominate the site preference. It is intriguing that a recent calculation showed that the attractive interaction between a point charge outside an Al(111) surface and its image is significantly stronger when the point charge is located on top of the surface atoms [29]. However, a cluster calculation for K/Pt(111) indicates that for one adatom the hollow site is preferred to the top site by an energy exceeding 0.1 eV [30]. This raises the interesting question of whether the adsorption site of the first adatom is different from that in a commensurate layer. In order to resolve the exact nature of the bonding of alkali metals to metal substrates it will ultimately be necessary to carry out some extensive and systematic electronic structure calculations for these systems as a function of overlayer density.

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[a] Present address: FOM Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands.

[b] To whom correspondence should be addressed.

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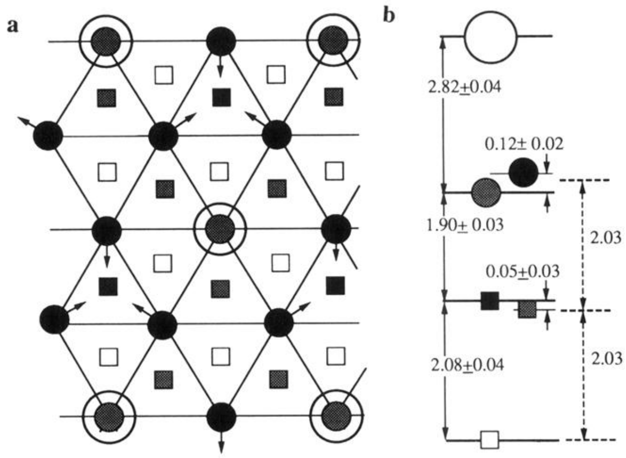

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