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Density functional study of the adsorption of K on the Cu(111) surface

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Abstract. The adsorption of potassium on the Cu(111) surface in a (2 × 2) pattern has been simulated with all-electron full-potential density functional calculations. The top site is found to be the preferred adsorption site, with the other highly symmetric adsorption sites being nearly degenerate. The bond length from potassium to the nearest copper atom is computed to be 2.83 Å. Population analysis and density of states indicate that there is no evidence for covalent bonding so that the binding mechanism appears to be a metallic bond.

PACS. 68.43.Bc *Ab initio* calculations of adsorbate structure and reactions

1 Introduction

The study of adsorbates on metal surfaces is of high importance for scientists as well as for industry with potential applications, for example in catalysis. Alkali metals are relatively simple systems to consider as adsorbates. Initially, it was assumed that they would always occupy high-coordination sites. It was therefore a big surprise when a first system was discovered where Cs, adsorbed on the Cu(111) surface, occupied the top site and not the threefold hollow site [1]. Meanwhile, further systems of alkali metals with top adsorption have been found – typically heavier alkali atoms (from K on) on closed packed surfaces (for a review, see references [2,3]). The situation is thus more complex than in the case of halogens where the adsorption site on closed-packed surfaces is usually the threefold hollow site.

Due to the increase in computational power, the theoretical study with methods based on density functional theory (DFT) of these adsorbate systems has become feasible in the last few years. For example, systems such as Na and K on the Al(111) surface [4] or Na on the Cu(111) surface [5] have been studied recently.

In this article, we study the adsorption of potassium on the Cu(111) surface as a model system for alkali adsorption on metal surfaces. This is an extension of earlier work of halogens on metallic surfaces (Cl on Cu(111) [6] and Cl on Ag(111) [7]). For the system Cu(111) (2×2)-K, adsorption on the top site was observed experimentally [8]. The addressed questions are therefore whether first principles simulation is able to reproduce the preferred adsorption site, the magnitude of the energy splitting of different highly symmetric adsorption sites, the geometry, the charge of the adsorbate, and the mechanism of the bond.

The applied methods are all-electron full-potential calculations with a local Gaussian basis set. Mainly gradient corrected density functional calculations were performed, the energetically most favorable structure was additionally optimized with the local density approximation, for comparison.

2 Computational parameters

A local basis set formalism was used where the basis functions are Gaussian type orbitals centered at the atoms as implemented in the code CRYSTAL [9]. For Cu, a $[6s5p2d]$ all-electron basis set as used in previous studies on copper metal and chlorine adsorption on copper metal was employed [10,6]. The K all-electron basis set from work on alkali halides was chosen [11], with the two outermost sp-exponents replaced by two sp-exponents optimized for the free K atom (0.29 and 0.08 a.u.) and an additional d-exponent (0.50 a.u.), resulting in a $[5s4p1d]$ basis set. Compared to the calculations on alkali halides, more diffuse basis functions are necessary because the potassium atom is not fully ionized and a description of its $4s$ and $4p$ states is required. A further enlargement of the potassium basis set is achieved indirectly because basis functions from neighboring centers are used to describe the charge distribution [12]. The bulk of the calculations was done with the gradient corrected exchange and correlation functional of Perdew and Wang (GGA) [13]. For the energetically most favorable site, the geometry was reoptimized at the level of the local density approximation

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(LDA) with Dirac-Slater exchange [14] and the Perdew-Zunger correlation functional [15], for comparison.

An auxiliary basis set was used to fit the exchange-correlation potential. For copper, it consisted of 12 even tempered (*i.e.* the ratio from one to the next higher exponent was kept fixed) s-exponents and 12 p-exponents in the range from 0.1 to 2000, 8 d-exponents and 8 f-exponents in the range from 0.1 to 100. For potassium, the same s- and p-exponents were chosen, and 5 d-exponents in the range from 0.8 to 100.

The adsorption was modeled by using a three-layer copper slab with the copper atoms arranged as in the face-centered cubic (fcc) lattice, at the GGA-optimized bulk Cu lattice constant [6] of 3.63 Å. Potassium was adsorbed on one side of this slab. This is presently the computational limit for desktop workstations with this approach. This is similar to earlier studies [6,7] where three layers of metal and a single-sided adsorbate layer were found to be sufficient for a theoretical description. A supercell approach with a (2×2) adsorption pattern as in the experiment was used [8]. This slab was not repeated in the third dimension so that the model is truly two-dimensional. The copper atoms in the top layer were allowed to relax vertically, an additional horizontal shift as observed in the adsorption of K on Ni(111) [16] would, however, require too much numerical effort to be simulated. For comparison, the vertical relaxation of the copper atoms was simulated in two different ways: simulations were performed where only a uniform relaxation of the top copper layer was possible, and simulations where a different vertical relaxation for the copper atoms in the top layer was possible (*i.e.* substrate rumpling).

Four adsorption sites were considered (see Fig. 1): the top adsorption site with K sitting vertically above a copper atom in the top layer, the bridge site with K sitting above the middle of two copper atoms in the top layer, and two different threefold hollow sites where the potassium atoms are placed vertically above a copper atom in the second (third) copper layer. These threefold hollow sites can not be distinguished when only the adsorbate and the positions of the atoms in the top copper layer are given, but instead the position of the atoms in the second and third layer under the adsorbate layer must be considered. The first of the threefold hollow sites is referred to as the hcp (hexagonal close-packed) hollow site because the potassium atom is vertically above a copper atom in the second copper layer. The second of the threefold hollow sites is referred to as fcc hollow site because the potassium atom is vertically above third layer copper atoms. In the following, we will use the notion hcp (fcc) hollow site to distinguish between these two adsorption sites. This is closely connected to the notion of hcp (*versus* fcc) lattices where there are atoms two (*versus* three) layers vertically below atoms in a certain layer of a solid.

With a Pack-Monkhorst net of shrinking factor 16, the number of points in the reciprocal lattice was 30 for the fcc hollow site and the hcp hollow site, and 73 for the bridge and top site. The Fermi function was smeared with a temperature of 0.01 E_h ($1E_h = 27.2114$ eV) to make the integration numerically more stable. For an extensive test of the various computational parameters for metallic systems with a local basis set technique, see reference [17].

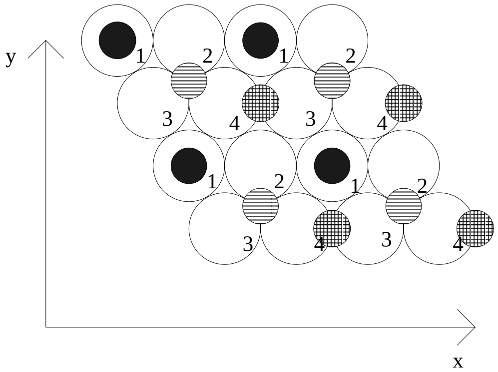

Fig. 1. The structures considered for K, adsorbed on the Cu(111) surface, at a coverage of one fourth of a monolayer, (2×2) unit cell. The copper atoms in the top layer are displayed by open circles. In the top adsorption site, potassium occupies the sites above the copper atoms with number 1 (filled circles). Alternatively considered adsorption sites were the threefold hollow sites above atoms 2, 3, 4 (fcc or hcp hollow, circles with horizontal lines) or the bridge site above atoms 3 and 4 (circles with horizontal and vertical lines). Note that fcc and hcp hollow sites can not be distinguished in this figure. The positions of the second and third layer copper atoms underneath the potassium layer are necessary to differentiate between fcc and hcp hollow sites.

3 Summary of previous experimental and theoretical results

The adsorption of K on Cu(111) has been studied with surface-extended X-ray absorption fine-structure (SEXAFS) measurements [8]. At a nominal coverage of 0.25 ± 0.01 monolayer, a (2×2) pattern was observed. The adsorption site was identified as the top site and a bond-length from K to the nearest Cu atom of 3.05 ± 0.02 Å was deduced.

Cluster models [18] with Cu_7 as the adsorbate gave in Hartree-Fock and density functional calculations the top site as the preferential one. However, the energy splitting was found to be relatively large (*e.g.* ∼0.5 eV at the DFT level), the computed bond length was in good agreement with the experimentally observed. The computed K charge was relatively large with 0.7–0.8 $|e|$ at the DFT level. Similar results for the energy splitting and bond length were then found when potentials were fitted to model the interaction of the adsorbate with the infinite surface.

GGA calculations have been performed for the systems Cu(111) (2×2)-Na and Cu(111) $(3/2\times3/2)$-Na [5]. It was found that hollow sites were preferred. Substrate rumpling was found to be strongest for the top site; in general copper atoms below sodium atoms moved into the substrate, whereas copper atoms without sodium in the vicinity moved outwards. The top site was the one which gained most energy from rumpling and thus the energy

Table 1. Adsorption of K on the Cu(111) surface, GGA results, if not stated otherwise. d_1 is the relaxation of those atoms in the Cu top layer which are nearest neighbor to the adsorbed potassium, d_2 is the relaxation of those atoms which are not nearest neighbor to the adsorbed potassium. The relaxations are given with respect to the bulk value, a negative sign means a contraction relative to the bulk. The bond length $d_{\mathrm{K-Cu\ nn}}$ is the distance from potassium to the nearest copper atom. The adsorption energy is the difference $E_{\mathrm{K\ at\ Cu(111)}} - E_{\mathrm{Cu(111)}} - E_{\mathrm{K}}$. The numeration of the atoms is like in Figure 1.

site	nearest atoms to K	relaxation d_1 [Å]	atoms not under K	relaxation d_2 [Å]	$d_{\mathrm{K-Cu\ nn}}$ [Å]	$E_{\mathrm{adsorption}}$ $\left[\frac{E_h}{\mathrm{K\ atom}}\right]$
hcp hollow[a]	2, 3, 4	–0.045	1	+0.06	3.11	0.0464
fcc hollow[b]	2, 3, 4	–0.050	1	+0.07	3.11	0.0465
bridge	3, 4	–0.068	1, 2	+0.03	3.04	0.0465
top	1	–0.14	2, 3, 4	+0.025	2.83	0.0473
top (LDA)	1	–0.13	2, 3, 4	+0.012	2.73	0.0660

[a] note: Cu atom in third layer vertically under K atom.
[b] note: Cu atom in second layer vertically under K atom.

Table 2. Adsorption of K on the Cu(111) surface, GGA results, without rumpling. The relaxation of the atoms in the Cu top layer with respect to the bulk is given, the negative sign means a contraction relative to the bulk, *i.e.* an inwards relaxation. The bond length $d_{\mathrm{K-Cu\ nn}}$ is the distance from potassium to the nearest copper atom. The adsorption energy is the difference $E_{\mathrm{K\ at\ Cu(111)}} - E_{\mathrm{Cu(111)}} - E_{\mathrm{K}}$.

site	relaxation [Å]	$d_{\mathrm{K-Cu\ nn}}$ [Å]	$E_{\mathrm{adsorption}}$ $\left[\frac{E_h}{\mathrm{K\ atom}}\right]$
hcp hollow	–0.026	3.10	0.0457
fcc hollow	–0.028	3.11	0.0459
bridge	–0.026	3.02	0.0457
top	–0.028	2.80	0.0451
free K layer			$E_{\mathrm{cohesive}} = 0.0229$

difference between the different adsorption sites was reduced.

The adsorption of sodium and potassium on the Al(111) surface has been studied theoretically with the LDA [4] and it was found that, whereas sodium adsorbed on a substitutional site, the fcc hollow site and the top adsorption site were degenerate for potassium for both structures considered ($\sqrt{3} \times \sqrt{3}$ R30° and 2 × 2). Again, rumpling was most important for the top site.

4 Results for K adsorption

In this section, the results of the calculations on the system Cu(111) (2×2)-K are presented and discussed. Firstly, in Tables 1 and 2, the adsorption geometry and energy are displayed. We notice that the adsorption at the top site is energetically most favorable, *i.e.* the experimental situation is reproduced. For this site, the computed adsorption energy per potassium atom is 47 mE_h (1.28 eV). However, the other considered sites are only slightly higher in energy (by less than 1 mE_h). This is close to the limit of what can be resolved and there are still parameters which might have an influence on the prediction of the adsorption site (*e.g.* numbers of layers in the slab model, a possible horizontal relaxation of the copper atoms, basis set deficiencies due to the lack of availability of f-functions). The magnitude of the energy splitting is thus much lower as previously found for halogens [6,7], but in good agreement with findings for Na on Cu(111) [5] and Na or K on Al(111) [4].

The value for the adsorption energy is in the range of that for potassium on graphite (0.48 to 0.89 eV, depending on the coverage and the relaxation [19]), or that for Na on Cu(111) which was computed to be 1.8 to 1.9 eV [5].

The binding energy of a free K layer (with a K-K nearest neighbor distance as in the adsorbate system, 5.13 Å) was computed for comparison and a value of 0.0229 E_h, *i.e.* 0.62 eV was obtained. This is in reasonable agreement with previous calculations (0.56 eV [19], LDA, K-K nearest neighbor distance 4.94 Å; or 0.83 eV [20], LDA, K-K nearest neighbor distance 4.52 Å; in the latter work the energy of the free atom was obtained from a calculation without spin-polarization).

We notice that the K-Cu bond length increases from 2.83 Å (top site) < 3.04 Å (bridge site) < 3.11 Å (fcc, hcp hollow site). This is in agreement with the argument that the bond should be the stronger and the bond length therefore the shorter, the lower the number of copper neighbors [21]. It is consistent with results from simulations for halogens on metal surfaces [6,7]. In addition, we note that those atoms in the Cu surface, which are closest to the K atom, relax inwards. This relaxation is strongest for the structure with the lowest number of nearest

Table 3. Orbital-projected charge of K on different adsorption sites.

site	charge, in $\|e\|$					
	s	p_x	p_y	p_z	d	total
with rumpling						
top	6.484	4.155	4.155	4.072	0.012	18.879
hcp hollow	6.481	4.149	4.149	4.072	0.012	18.863
fcc hollow	6.481	4.150	4.150	4.072	0.012	18.865
bridge	6.481	4.147	4.155	4.072	0.013	18.867
without rumpling						
top	6.493	4.151	4.152	4.079	0.013	18.886
hcp hollow	6.483	4.149	4.149	4.072	0.012	18.863
fcc hollow	6.484	4.149	4.149	4.074	0.012	18.866
bridge	6.485	4.146	4.151	4.074	0.014	18.868
free K layer						
	6.806	4.094	4.094	4.006	0.000	19.000
free K atom						
	7.000	4.000	4.000	4.000	0.000	19.000

neighbors underneath the K atom – in full agreement with the findings in the case of Na on Cu(111) [5]. The order of magnitude (0.165 Å inwards relaxation of copper atom 1 under the potassium atom, relative to atoms 2,3,4) is in line with Na on Cu(111) (0.1 Å) [5] and with one experiment for K on Ni (111) (0.12 Å) [16], less with the other experiment for K on Ni(111) (0.01 ± 0.09 Å) [22].

The computed bond length is shorter than measured in the experiment (3.05 ± 0.02 Å) [8]. To estimate the errors due to the choice of the functional, calculations with the LDA were performed for the top site, for comparison. The LDA bond length (2.73 Å) is slightly shorter as the GGA bond length. If we assume a copper radius of $3.63/2\sqrt{2}$ Å, we obtain an effective radius, at the GGA level, of 1.55 Å which is in the range of the experimentally observed value for top adsorption of potassium (1.77 Å for K on Cu(111), 1.57...1.77 Å for K on Ni(111)) – see reference [2] and references therein.

In addition, calculations for the same adsorption sites were performed when rumpling was not allowed, but instead only a uniform relaxation of the copper atoms in the top Cu layer (Tab. 2). In these simulations, the fcc hollow site was found to be lowest in energy, with the hcp hollow site and the bridge site of the order of ∼0.2 mE_h higher in energy, *i.e.* nearly degenerate. The top site was highest in energy, but only by less than 1 mE_h, however. The bond lengths are relatively similar to the case where rumpling was allowed, the atoms in the top Cu layer relaxed inwards by ∼0.03 Å. We can thus conclude that rumpling is crucial to obtain the top site as the preferred site – the top site gains > 2 mE_h due to rumpling, whereas all the other sites gain less than 1 mE_h.

In Table 3, Mulliken charges for the potassium atom are given, projected on the different basis functions. The free atom in its ^2S state has 7 s and 12 p electrons, obviously p_x, p_y and p_z are degenerate. In the free and neutral K layer, p_x, p_y and p_z population slightly increase whereas the s population decreases. Finally, in the adsorbate systems, p_x, p_y and p_z charges are slightly above 4, the number of s-electrons is ∼6.5, and the total charge is ∼+0.1 $|e|$. Charges in p_x and p_y orbitals are identical except for the bridge site – as in the case of Cl on Ag(111) [7], the p_x orbital which has more overlap with the substrate layer (in our choice of geometry – Fig. 1) is slightly less occupied than the p_y orbital. However, the difference is much smaller than in the case of Cl on Ag(111), and it is hardly visible in the density of states (DOS) – see the discussion in the following paragraph. In addition, the overlap population is very small: for K and next neighbor Cu, it is 0.06 $|e|$, and it rapidly decreases for the copper atoms further apart. All this indicates that there is no evidence for hybridisation and covalent bonding.

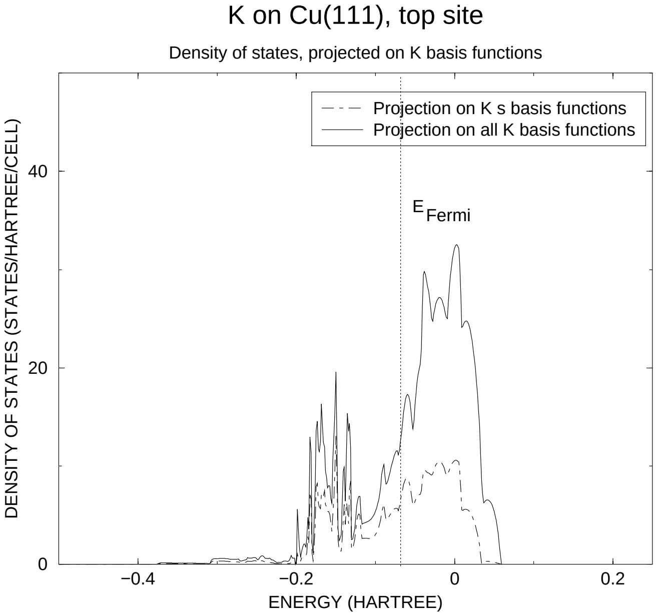

Fig. 2. Density of states, on K projected, top adsorption site. The displayed structure is the broad K 4sp band. The density of states, projected on all K basis functions, is shown with a full line. A projection onto the K s-basis functions only is shown with a dashed-dotted line. The Fermi energy is indicated with a dotted line.

In Figure 2, the DOS, projected on the potassium basis functions, is displayed for the top adsorption site. The Fermi energy is in a regime with a relatively large contribution from K 4s and 4p bands, so that the overlayer is clearly metallic. It is interesting that the projected DOS does not depend on the adsorption site: it looks virtually identical for top, hcp hollow, fcc hollow and bridge site. This is different from the case of chlorine as an adsorbate, where the projected DOS clearly depended on the adsorption site [7]. Another feature which was found for the bridge site in the chlorine adsorption was the different projected DOS for p_x and p_y orbitals: however, this is hardly visible for potassium and the DOS for p_x and p_y is virtually identical.

Also, the values of the K 3s level (–1.19 E_h with respect to the Fermi level) and 3p levels (–0.59 E_h with respect to the Fermi level) are practically independent of the adsorption site. This is again in contrast to chlorine: for chlorine, the core eigenvalue depended on the adsorption site, and it was correlated with the charge of the chlorine atom [7]. For K, the variation of the Mulliken charges with adsorption site is much smaller (Tab. 3) as for chlorine. This is consistent with the finding that the core eigenvalue does not vary for the different sites. The Mulliken charge for K at the top site is ∼+0.12, *i.e.* K is slightly positive charged. This is in reasonable agreement with the findings for K on graphite, where, depending on the coverage and the relaxation, charges in the range from 0.17 to 0.38 $|e|$, were obtained [19].

5 Summary

In this article, all-electron full-potential density functional calculations were applied to compute properties of the system Cu(111) (2 × 2)-K. The top site was found as the preferable adsorption site, with the other considered sites being nearly degenerate. Substrate rumpling was crucial to obtain this result. The bond length was computed to be 2.83 Å, the binding energy 1.28 eV. The potassium charge was computed to be +0.1 $|e|$. Charge and projected density of states varied only very little for the different adsorption sites, and similarly the position of the K 3s and 3p core eigenvalues did not vary. No evidence for a covalent contribution to the binding was found, so that the mechanism should rather be a metallic bond.

References

1. S.Å. Lindgren, L. Walldén, J. Rundgren, P. Westrin, J. Neve, Phys. Rev. B **28**, 6707 (1983).
2. R.D. Diehl, R. McGrath, Surf. Sci. Rep. **23**, 43 (1996).
3. R.D. Diehl, R. McGrath, J. Phys. Cond. Matt. **9**, 951 (1997).
4. J. Neugebauer, M. Scheffler, Phys. Rev. B **46**, 16067 (1992).
5. J.M. Carlsson, B. Hellsing, Phys. Rev. B **61**, 13973 (2000).
6. K. Doll, N.M. Harrison, Chem. Phys. Lett. **317**, 282 (2000).
7. K. Doll, N.M. Harrison, Phys. Rev. B **63**, 165410 (2001).
8. D.L. Adler, I.R. Collins, X. Liang, S.J. Murray, G.S. Leatherman, K.-D. Tsuei, E.E. Chaban, S. Chandravarkar, R. McGrath, R.D. Diehl, P.H. Citrin, Phys. Rev. B **48**, 17445 (1993).
9. V.R. Saunders, R. Dovesi, C. Roetti, M. Causà, N.M. Harrison, R. Orlando, C.M. Zicovich-Wilson, *Crystal 98 User's Manual* (Theoretical Chemistry Group, University of Torino, 1998).
10. M.D. Towler, R. Dovesi, V.R. Saunders, Phys. Rev. B **52**, 10150 (1995).
11. M. Prencipe, A. Zupan, R. Dovesi, E. Aprà, V.R. Saunders, Phys. Rev. B **51**, 3391 (1995).
12. This is different for the atom where a larger basis set is necessary to compute properties of the atom. For calculations on the free K atom itself and for the calculations on the free two-dimensional K layer, a [6s5p1d] basis set was used (with outermost sp-exponents 0.39, 0.21, 0.03 instead of 0.29 and 0.08). Calculations for the free atom were done with spin-polarized DFT, all the other calculations were performed with non-spin-polarized DFT.
13. J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
14. P.A.M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930); J.C. Slater, Phys. Rev. **81**, 385 (1951);
15. J.P. Perdew, A. Zunger, Phys. Rev. B **23**, 5048 (1981).
16. D. Fisher, S. Chandavarkar, I.R. Collins, R.D. Diehl, P. Kaukasoina, M. Lindroos, Phys. Rev. Lett. **68**, 2786 (1992).
17. K. Doll, N.M. Harrison, V.R. Saunders, J. Phys. Cond. Matt. **11**, 5007 (1999).
18. L. Padilla-Campos, A. Toro-Labbé, J. Maruani, Surf. Sci. **385**, 24 (1997).
19. F. Ancilotto, F. Toigo, Phys. Rev. B **47**, 13713 (1993).
20. E. Wimmer, J. Phys. F **13**, 2313 (1983).
21. L. Pauling, *The nature of the chemical bond and the structure of molecules and crystals* (Cornell University Press, 1960).
22. R. Davis, X.-M. Hu, D.P. Woodruff, K.-U. Weiss, R. Dippel, K.-M. Schindler, Ph. Hofmann, V. Fritzsche, A.M. Bradshaw, Surf. Sci. **307**, 632 (1994).