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Electronic structure of $(\sqrt{3} \times \sqrt{3})$R30°-Na and -K on Al(111): comparison of "normal" and substitutional adsorption sites

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Recently, it was shown that Na and K on Al(111) will kick out a surface Al atom and occupy the substitutional site. For K also the on-top position is possible. In this contribution, we give an analysis of the adsorbate wave functions, surface density of states, and surface band structures. Different adsorption sites are considered, and it is shown that the mechanism of bonding in the substitutional geometry on Al differs from that in the "normal" on-surface geometry. In the first case the adatom–substrate interaction dominates, and the surface electronic structure is largely determined by the character of the Al surface vacancy, whereas in the second case the adatom–adatom interaction dominates. The theoretical results are compared with experimental studies of direct and inverse photoemission, suggesting the need of a re-analysis of the data.

1. Introduction

Recently [1,2], it was shown that Na and K on Al(111) will kick out a surface Al atom, occupying the substitutional site and forming ordered islands. For K the adsorption at the on-top position is possible, as well as a metastable geometry [3]. These unexpected results question the validity of the present understanding of alkali adsorption on metal surfaces [4]. So far, it was generally assumed that the adsorption of alkali metals on a close-packed substrate surface takes place exclusively at highly coordinated atomic positions on the nearly undistorted substrate. The principal mechanism behind the adsorption-induced change of the work function also needs to be reconsidered. This change induced by alkali metals was described in terms of a decrease of the alkali–alkali distance with increasing coverage, but the growth of islands was not discussed [5,6]. A proper description of the chemical bonding of Na and K

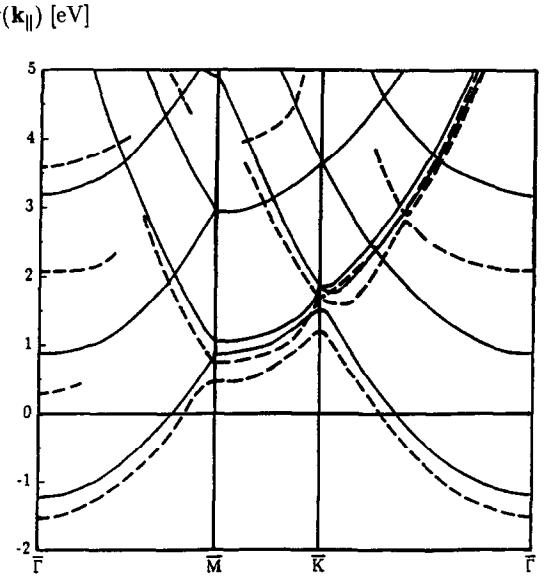

Fig. 1. Surface electronic structure, $\epsilon(\boldsymbol{k}_{\parallel})$ in eV, for a $(\sqrt{3} \times \sqrt{3})$R30°-Na adlayer on Al(111) with Na atoms adsorbed at the fcc hollow site (dashed line) compared with a hexagonally coordinated Na monolayer of nearest-neighbor distance d = 4.87 Å (solid line). The energy is referred to the Fermi level (indicated by a solid line at $\epsilon = 0$).

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on Al(111) has to take into account the different nature of substitutional and "normal" adsorption.

In the following, a detailed analysis of the adsorbate wave functions, surface density of states, and surface band structures for $(\sqrt{3} \times \sqrt{3})R30°$-Na and -K on Al(111), i.e., with a coverage $\Theta = \frac{1}{3}$, is given. Different adsorption geometries are considered, and the theoretical results are compared with available experimental data.

2. Computational methods

The problem is treated by the method of the surface Green function (SGF). The Green function, $G^{\sigma'\sigma}_{\boldsymbol{R}'L',\boldsymbol{R}L}(\boldsymbol{r}', \boldsymbol{r}; \epsilon, \boldsymbol{k}_\parallel)$, with the layer index σ, the atomic index $\boldsymbol{R}$, the index $L = (l, m)$ of angular momentum, and for the position $\boldsymbol{r}$ in real space, the energy argument ϵ, and the Bloch vector $\boldsymbol{k}_\parallel$ within the surface Brillouin zone (SBZ), is obtained by the layer KKR method [7,8]. The two important quantities to characterize the electronic structure are the spectral and partial local density of states (LDOS), also called the spectral function,

$$A^{\sigma}_{\boldsymbol{R}L}(\epsilon, \boldsymbol{k}_\parallel) = -\frac{2}{\pi} \mathrm{Im} \int_{\Omega_{ws}} d^3\boldsymbol{r}\, G^{\sigma\sigma}_{\boldsymbol{R}L,\boldsymbol{R}L}(\boldsymbol{r}, \boldsymbol{r}; \epsilon + \mathrm{i}0, \boldsymbol{k}_\parallel), \tag{1}$$

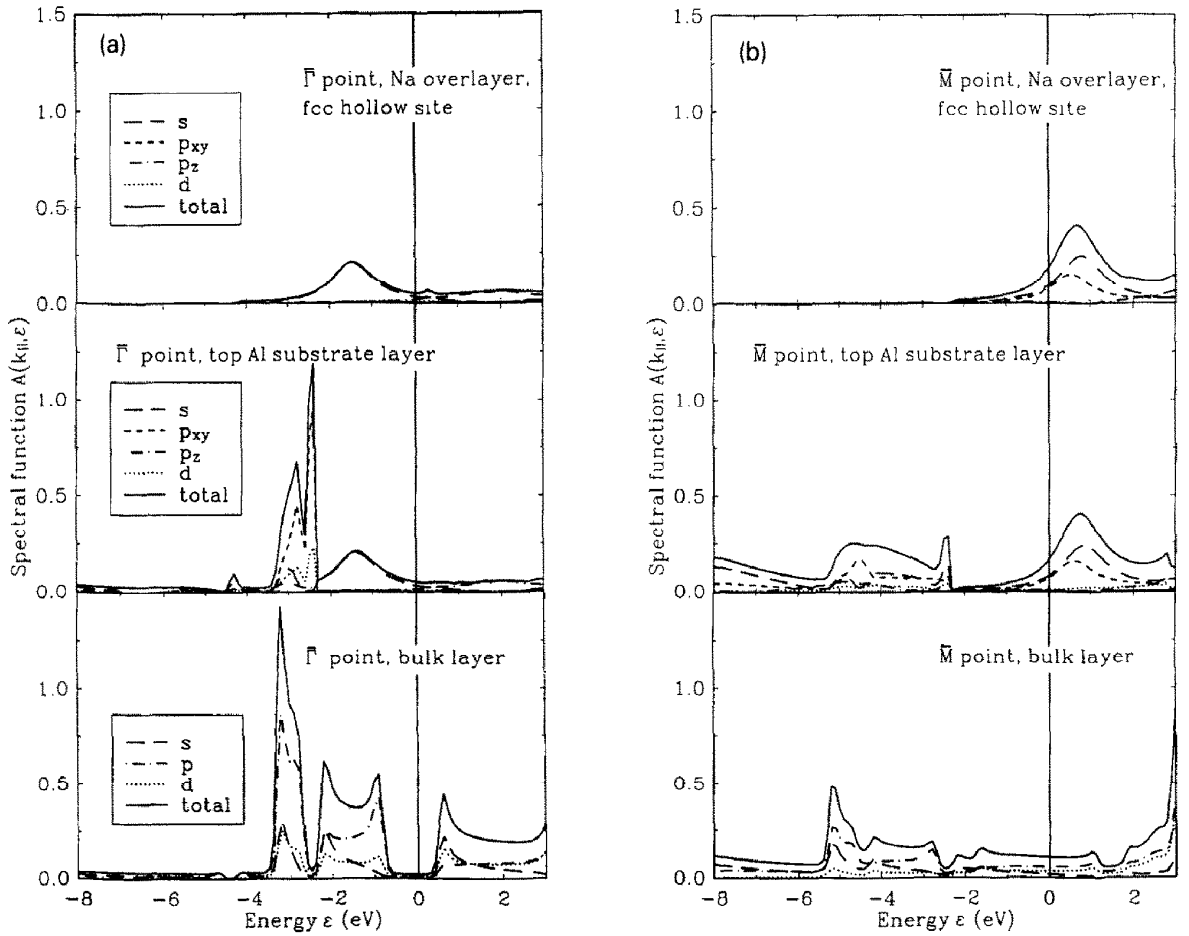

Fig. 2. $\boldsymbol{k}_\parallel$-resolved local density of states (spectral function $A(\epsilon, \boldsymbol{k}_\parallel)$) at (a) the $\bar{\Gamma}$ point, (b) $\bar{M}$ point, (c) $\bar{K}$ point of the SBZ for a $(\sqrt{3} \times \sqrt{3})R30°$-Na adlayer on Al(111) with the Na atoms adsorbed at the fcc hollow site. The energy is referred to the Fermi level (indicated by a solid line at $\epsilon = 0$). Continued on next page.

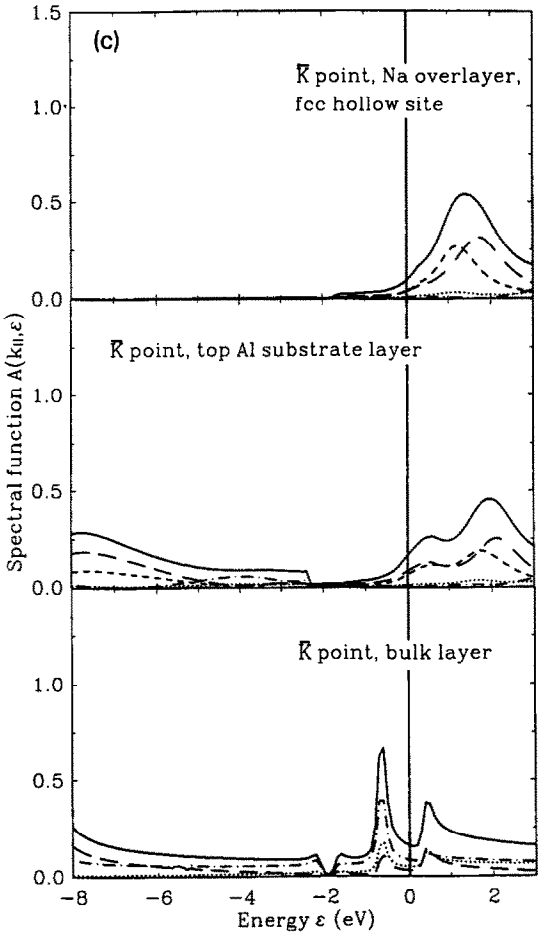

Fig. 2. Continued.

and the spectral and partial "charge density",

$$\rho^{\sigma}_{RL}(\boldsymbol{r}, \epsilon, \boldsymbol{k}_{\parallel}) = -\frac{2}{\pi} \mathrm{Im}\, G^{\sigma\sigma}_{RL,RL}(\boldsymbol{r}, \boldsymbol{r}; \epsilon + \mathrm{i}0, \boldsymbol{k}_{\parallel}), \tag{2}$$

reflecting the character of wave functions.

The electronic structure of alkali adsorbate systems is calculated for a semi-infinite substrate, using the adsorption geometries and potentials derived by self-consistent slab calculations [2]. A spherical averaging of these potentials was performed for using them within the muffin-tin approximation.

3. Results and discussion

We start with the $(\sqrt{3} \times \sqrt{3})R30°$-Na adlayer on Al(111) with Na atoms adsorbed at the "normal" fcc threefold hollow position. In fig. 1, we compare its surface band structure with that of a hexagonally coordinated monolayer of Na atoms having the same nearest-neighbor distance of $d = 4.87$ Å. Both band structures are very similar, which reflects the fact that the electronic structure for the on-surface adsorption is dominated by the character of the adatom–adatom interaction. For the valence electrons of the Na atom, we find a partially occupied s-band, beginning at $\epsilon = -1.5$ eV below the Fermi level at the $\bar{\Gamma}$ point of the SBZ, and an unoccupied p_z-band hybridizing with s-states in its lower part, giving rise to dangling-orbital-like wave functions pointing into the vacuum (cf. figs. 1 and 2a). The charge density induced by the adsorbate is mainly localized between the adsorbate and the top substrate layer. This is reflected both in the character of the adsorbate wavefunctions and the LDOS (cf. fig. 2). Below the top substrate layer there are practically no changes in the charge density.

These two characteristic features for the on-surface adsorption – namely, (i) adsorbate-induced states mainly close to the Fermi level and (ii) practically no charge density changes below the top substrate layer – are not found for adsorption at a substitutional site. As shown recently [1,2], this adsorption site is energetically preferred for the $(\sqrt{3} \times \sqrt{3})R30°$-Na on Al(111). For the substitutional geometry, we find changes in the LDOS also close to the bottom of the Al valence band. The character of this state is mainly s-like (cf. fig. 3). Further details are a broad p_z-band and two p_{xy}-like states at energies $\epsilon = +1.1$ and $+2.1$ eV. A comparison with the electronic structure of a surface vacancy [9] shows that these features also are present without the Na monolayer. The calculated single-particle energies agree well with the inverse photoemission data by Heskett et al. [10], showing peaks at 1.1 and 2.1 eV. However, their interpretation that the dispersion of these states can be understood mainly in terms of that of a free Na monolayer with corresponding nearest-neighbor spacing, is

not valid. We conclude instead that their peaks and the measured dispersion is that of the ($\sqrt{3} \times \sqrt{3}$)R30°-Al surface vacancy structure. The effect of the Na is mainly to create this vacancy structure, but the electronic structure of the vacancies is modified only very little by the adatom.

A further difference between the substitutional and the on-surface adsorption is that for the substitutional geometry the perturbation reaches deeper into the substrate, due to the opening of the surface by the vacancies. An analysis of the wave functions shows that the adsorbate is more ionic for the substitutional adsorption: due to the reduced adsorbate height for this site, the electron density between the adsorbates is higher, thus, enhancing the screening and reducing the repulsion of the partially positively charged adatoms.

In general, the same conclusions also hold for the adsorption of ($\sqrt{3} \times \sqrt{3}$)R30°-K on Al(111), with only the following modification: for the on-surface adsorption, the LDOS at the adatom and the dispersion of the surface band structure is larger than for Na, due to the larger adatom–substrate distance and the larger atomic radius of K, respectively.

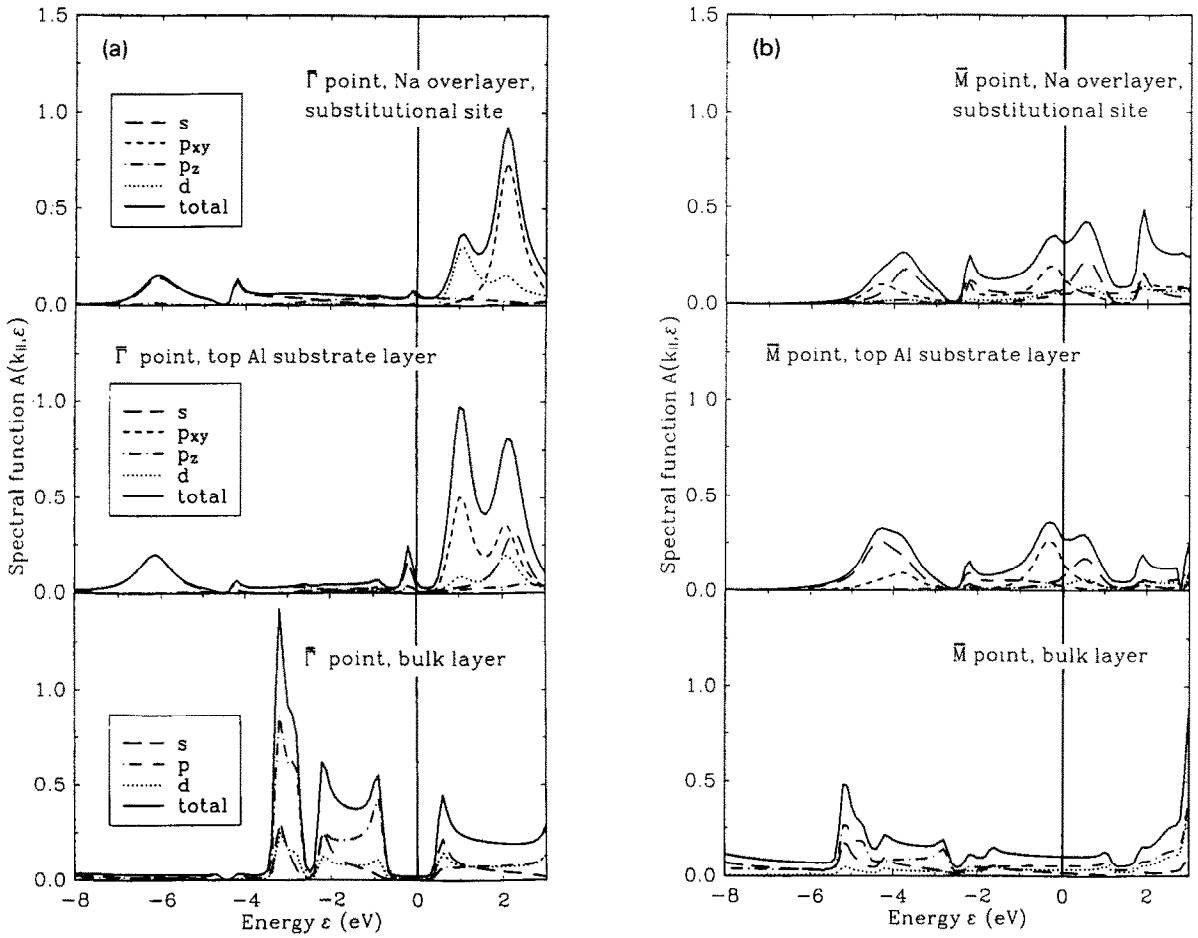

Fig. 3. Same as fig. 2, but for Na atoms adsorbed at the substitutional site. Continued on next page.

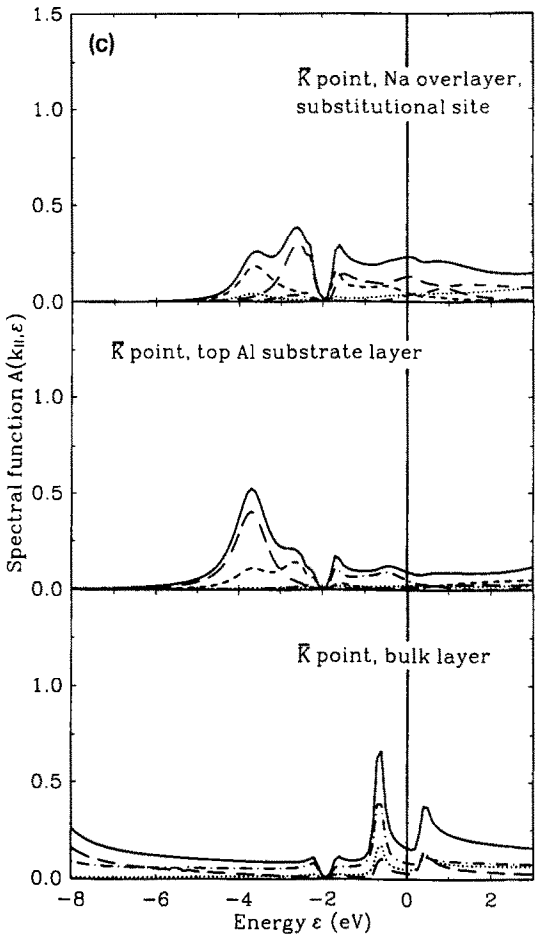

Fig. 3. Continued.

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