



# Alkali metal adsorption on graphite: Calculation of a work function variation in the Anderson–Newns–Muscat model

Sergei Yu. Davydov\*

Ioffe Physico-Technical Institute, Russian Academy of Sciences, 194021, Polytekhnicheskaya str. 26, St. Petersburg, Russia

## ARTICLE INFO

### Article history:

Received 31 August 2009

Accepted 21 August 2010

Available online 19 September 2010

### PACS:

71.20.Dg

73.20.Hb

### Keywords:

Alkali metals

Work function

Coverage dependence

Graphite

## ABSTRACT

Within the scope of the Anderson–Newns model of adsorption the Na, K, and Cs submonolayer films on graphite are considered. The adatoms dipole–dipole repulsion is taken into account with the use of the Muscat approach. The calculated work function variations are in a reasonable agreement with the experimental data. We have found that the charges of K, Na, and Cs adatoms are  $Z_0 = 0.22, 0.38,$  and  $0.41$  for the zero coverage limit and  $Z_{ML} = 0.09, 0.15,$  and  $0.16$  for the monolayer coverage correspondingly. The crude estimations of the single adatom binding energies got  $E_b = 0.76, 0.67,$  and  $0.37$  eV for Na, K, and Cs accordingly.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

It is well known that the AM atoms adsorbed on graphite can form two-dimensional (2D) commensurate superstructures [1–5]. AM adatoms act as donors changing the free carriers concentration of graphite. AM deposition on graphite results also in the decrease of the system work function  $\phi$ . The main goal of our work is to describe work function variations  $\Delta\phi$  for the AM/graphite system within a semi-empirical simple model.

Alkali metals (AM) adsorbed on solid surfaces have been traditionally considered as the model adsorbates [6]. One of the first theoretical approach to the problem has been put forward by Newns [7], who applied Anderson Hamiltonian [8] (see Appendix A) for the description of a single one-electron atom adsorption on metal surface. Later Muscat and Newns have generalized this approach for the adsorbed overlayer [9], taking into account dipole–dipole repulsion of adatoms. This permits them to calculate the work function decrease  $\Delta\phi$  as a function of the coverage  $\Theta$  for AM submonolayers on a model metallic substrate. In what follows we will refer to this approach as to the Anderson–Newns–Muscat (ANM) model.

It is well known that in the case of AM deposition work function variations  $\Delta\phi(\Theta)$  demonstrate the same qualitative character for

metallic [6], semiconductor [10–12], and semimetallic [1–5] substrates. The main features of  $\Delta\phi(\Theta)$  variations are as follows: (i) fast initial drop at small coverages ( $\Theta \ll 1$ ); (ii) saturation for nearly monolayer (ML) coverages ( $\Theta \rightarrow 1$ ); (iii) possible pronounced minimum at intermediate coverages [13–15]. Thus, one may conclude that for all AM adsorption systems some unified scheme for the  $\Delta\phi(\Theta)$  calculation can be applied. One of such a scheme is the use of ANM model.

## 2. Model

We begin postulating adatom density of states (see Appendix A) in the form:

$$\rho_a(\omega) = \frac{2}{\pi} \frac{\Gamma}{(\omega - \varepsilon_a)^2 + \Gamma^2}, \quad (1)$$

where  $\varepsilon_a$  and  $\Gamma$  are the quasilevel position and half-width;  $\omega$  is the energetic variable; the factor 2 is due to the two possible electron spin orientations. This expression is exactly the same as in the case of an adsorption on metals within the wide-band and non-magnetic approximations for the Anderson model [7] (see Appendix A).

Now it is easy to find the adatom occupation number  $n$  for zero temperature by the integration of Eq. (1):

$$n = \frac{2}{\pi} \cot^{-1} \frac{\Omega}{\Gamma}, \quad (2)$$

where  $\Omega = (\varepsilon_a - E_F)$  is the energy gap between the adatom  $\varepsilon_a$  and Fermi  $E_F$  levels. The adatom charge  $Z = 1 - n$ . If the dipole–dipole

\* Tel.: +7 812 2927125; fax: +7 812 2921017.

E-mail address: [sergei.davydov@mail.ru](mailto:sergei.davydov@mail.ru).

repulsion between adatoms is taken into account [9], than Eq. (2) becomes

$$Z(\Theta) = \frac{2}{\pi} \tan^{-1} \frac{\Omega - \xi \Theta^{3/2} Z(\Theta)}{\Gamma}. \quad (3)$$

Here the coverage  $\Theta = N/N_{ML}$ , where  $N$  and  $N_{ML}$  are the adatom surface concentrations in the layer and the 1 ML correspondingly;  $\xi = 2e^2\lambda^2 N_{ML}^{3/2} \bar{A}$  is the constant of the dipole–dipole repulsion;  $\lambda$  is the adatom–substrate separation;  $e$  is the positron charge;  $\bar{A} \sim 10$  is the structural factor, which is 2D analog of the bulk Madelung constant [16].

Work function variation due to adsorption is determined as follows:

$$\Delta\phi(\Theta) = -\Phi Z(\Theta), \quad (4)$$

where the scaling factor for work function variation  $\Phi = 4\pi e^2 N_{ML} \lambda$ .

We have to underline here that the ANM model completely ignores any structural transitions which take place for the real AM/graphite systems with the increase of the coverage [1–5]. Thus, we consider the  $\Theta$  increase effect as a purely continuous compression of the adatoms overlayer. As we suppose, it can be done since the dominant channel of the interactions within the adlayer is the dipole–dipole repulsion, which is a long-range one and possesses cylindrical symmetry. Moreover, as it has been shown in Ref. [16], parameter  $\bar{A}$  depends only slightly on the overlayer geometry.

### 3. Estimations of the ANM model parameters and calculations

#### 3.1. Potassium on graphite

We begin with the K adsorption since it is this case that is studied most thoroughly. Let accept the monolayer adatoms concentration  $N_{ML} = 4.8 \times 10^{14} \text{ cm}^{-2}$  as in Refs. [1,3]. It is worthy to note here that if we take the bulk nearest neighbor (n.n.) separation as  $d_{n,n} = 4.525 \text{ \AA}$  [17] and estimate the concentration  $N_{ML}$  as  $(d_{n,n}(K))^{-2}$ , we get  $4.88 \times 10^{14} \text{ cm}^{-2}$ , i.e., very close to the preceding value. Accepting the atomic radii of K and C to be equal to  $r_a(K) = 2.36$  and  $r_a(C) = 0.77 \text{ \AA}$  [18], we find that the C–K bond length is  $r_a(C) = d = r_a(K) + r_a(C) = 3.13 \text{ \AA}$ . Since the n.n. separation in graphite is  $b = 1.42 \text{ \AA}$ , then the perpendicular K–graphite spacing  $d_{\perp} = \sqrt{d^2 - b^2} = 2.79 \text{ \AA}$ . In what follows we will consider two possible schemes for the estimation of  $\lambda$ . First one is based on the assumption that in the zero coverage limit ( $\Theta \rightarrow 0$ ) adatom is in nearly ionic state, while for the ML its state transfers to nearly atomic. Therefore, it is natural to put  $\lambda = [r_a(K) + r_i(K)]/2$ , where  $r_i(K) = 1.33 \text{ \AA}$  is the K ionic radius [18]. That gives  $\lambda = 1.845 \text{ \AA}$  (case I). From the other hand we can take  $\lambda = d_{\perp} - r_a(C) = 2.02 \text{ \AA}$  (case II). In both cases we assume that mirror plane coincides with the “tops” of the surface C atoms.

We will estimate energy parameter  $\Omega$  using the following expression:

$$\Omega = I - \phi + \frac{e^2}{4\lambda}, \quad (6)$$

where the ionization energy  $I$  for potassium is 4.34 eV and the graphite work function  $\phi$  is 4.7 eV [1,3]. The last term in the right-hand-side of Eq. (3) describes the shift of the adatom quasilevel due to the Coulomb repulsion between adatom and substrate electrons [19]. This gives  $\Omega = 2.31$ ,  $\Phi = 16.02$ ,  $\xi = 10.31$  eV for the case I and  $\Omega = 2.14$ ,  $\Phi = 17.54$ ,  $\xi = 12.36$  eV for the case II. Note that in both cases we put  $\bar{A} = 10$ .

Now turn to the analyses of the experimental data [3] and consider the initial drop of the work function, described by the derivative  $(\partial \Delta\phi / \partial \Theta)$  in the zero coverage limit  $\Theta \rightarrow 0$ . Using Eq.

**Table 1**

Model parameters and calculated adatom charges ( $\lambda$  in  $\text{\AA}$ ;  $\Omega$ ,  $\Gamma$ ,  $\xi$ , and  $\Phi$  in eV,  $Z_0 = Z(0)$ ,  $Z_{ML} \equiv Z(\Theta = 1)$ ).

Adsorbate	Parameter	$\lambda$	$\Omega$	$\Gamma$	$\xi$	$\Phi$	$Z_0$	$Z_{ML}$
Na	Case I	1.39	2.05	5.45	11.66	19.12	0.23	0.10
	Case II	1.44	1.96	5.41	12.51	19.80	0.22	0.09
K	Case I	1.85	2.31	3.45	10.31	16.03	0.38	0.15
	Case II	2.02	2.14	3.57	12.36	17.55	0.34	0.12
Cs	Case I	2.24	2.32	3.11	10.70	15.40	0.41	0.16
	Case II	2.31	2.27	3.17	11.38	15.88	0.40	0.14

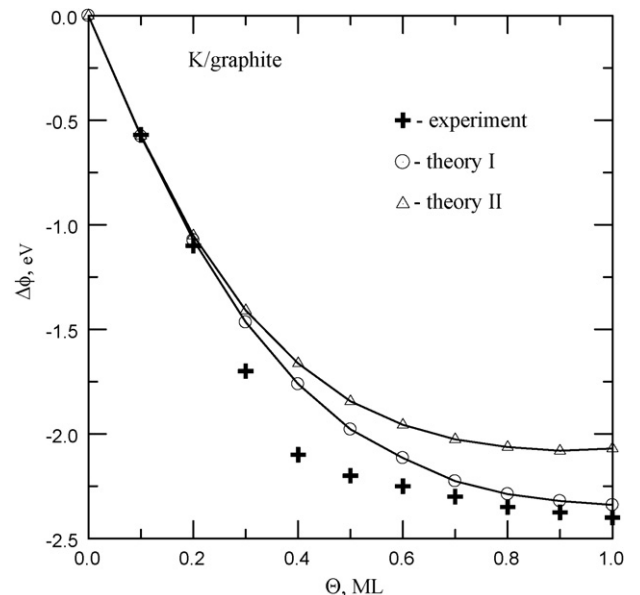
(4) we get

$$\left( \frac{\partial \phi(\Theta)}{\partial \Theta} \right)_{\Theta \rightarrow 0} = -\Phi Z_0, \quad (7)$$

where  $Z_0 \equiv Z(\Theta = 0)$  is the initial adatom charge. Taking from the data the ratio  $\Delta\phi / \Delta\Theta$  for the linear part of the  $\Delta\phi(\Theta)$  dependence, we can calculate  $Z_0$ . Than, using Eq. (3), we find  $\Omega / \Gamma = \text{tg}(\pi Z_0 / 2)$ . This ratio gives 0.67 (case I) and 0.60 (case II). Now we obtain  $\Gamma = 3.45$  and 3.57 eV for the cases I and II correspondingly. All the parameters are listed in Table 1. The results for the  $\Delta\phi(\Theta)$  dependence are show in Fig. 1 in comparison with the experimental data [3] (see this paper for the much more details of the experimental  $\Delta\phi(\Theta)$  dependence). It is easy to see from Fig. 1 that the case I gives the better correspondence with the experiment than the case II. But in the limit  $\Theta \rightarrow 1$  it is the case II that describes the derivative  $(\partial \Delta\phi / \partial \Theta)$  better than the case I. The largest discrepancy occurs at the intermediate coverage ( $\Theta \sim 0.3\text{--}0.6$ ), where the maximal relative error  $\eta = |(\Delta\phi_{\text{exper.}} - \Delta\phi_{\text{theor.}}) / \Delta\phi_{\text{exper.}}|$  for the case I is less than 15%. Fig. 2 demonstrates the  $Z(\Theta)$  dependence for the case I. The obtained charge decrease with  $\Theta$  corresponds the adatoms depolarization due to their dipole repulsion.

#### 3.2. Sodium on graphite

The adsorption of Na atoms on graphite has been experimentally studied in Ref. [4]. Following [1,4], we accept  $N_{ML} = 7.6 \times 10^{14} \text{ cm}^{-2}$ . Taking for the bulk n.n. spacing  $d_{n,n}(\text{Na}) = 3.659 \text{ \AA}$  [17], we arrive at  $N_{ML} = 7.47 \times 10^{14} \text{ cm}^{-2}$ , which is again rather close to the preceding value. Since  $r_a(\text{Na}) = 1.86 \text{ \AA}$  [18], we find that the C–Na distance



**Fig. 1.** Work function variation  $\Delta\phi$  vs. coverage  $\Theta$  for K adatoms on graphite.

Download English Version:

<https://daneshyari.com/en/article/5359500>

Download Persian Version:

<https://daneshyari.com/article/5359500>

[Daneshyari.com](https://daneshyari.com)