# Hubbard Correlations and Charge Transfer at the GaAs(110) Surface with Alkali Adsorbates

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We have performed density-functional-theory (DFT) calculations for potassium adsorbed on GaAs(110). The results show that alkali adatoms mainly act as donors giving their electrons to Ga-derived surface states. We found that these states consist of well localized Ga dangling bonds, which allowed us to map the DFT results on a two-dimensional Hubbard model. To calculate the Hubbard $U$ and the charge-transfer parameter $\Delta$ we simulate the electron transfer between adjacent orbitals. We find that $U$ and $\Delta$ are of the same order as the hopping integral $t$, which brings the surface in the Mott-Hubbard regime.

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Although alkali-metal adsorbates on III-V semiconductors have been studied for many years [1], the understanding of the adsorption process on the microscopic level only starts to evolve. Recent experiments provide very stimulating information on the atomic geometry and electronic structure, mainly for alkalis on the GaAs(110) surface. The formation of Cs zigzag and Na linear chains, which merge with increasing coverage into two-dimensional ordered structures, is revealed by scanning tunneling microscopy (STM) [2,3]. The striking STM observation is that these one- and two-dimensional structures of the alkali metals are nonmetallic [2,3]. Also electron energy loss spectroscopy [4], and direct and inverse photoemission [5,6], show the nonmetallic behavior of the surface, which only changes when the one-monolayer coverage is clearly exceeded.

The geometric structures for alkali adsorbates on GaAs(110) are species dependent, whereas the dielectric state at low coverage seems to be a general property. In apparent contrast to this observation, *ab initio* calculations [7,8] show the existence of a partially filled single-particle surface band at the Fermi energy. Self-consistent tight-binding Hartree-Fock calculations [9] also predict a finite density of states at the Fermi level. A possible explanation of this apparent contradiction could be the formation of a Mott-Hubbard insulating state [4,8]. This idea was originally proposed [4] with a note, that the electron density in bulk alkali metals is already close to the Mott limit [10]. The enlargement of the interatomic distance in the alkali adlayer is therefore expected to promote the metal-insulator transition. However, *ab initio* calculations [7,8] demonstrated that this picture is not correct. Almost complete transfer of the alkali valence electron to the Ga-related surface state was found. This implies that electron correlation effects, if they really play an important role, should be referred not to the alkali, but to Ga orbitals.

In this paper we present density-functional-theory (DFT) calculations for GaAs(110) with adsorbed potassium. The local-density approximation (LDA) for the exchange-correlation functional was used. We found that a Ga-related surface state, which accepts the alkali valence electron, consists of well localized orbitals (Ga dangling bonds). The proper description of such a state therefore requires that Hubbard correlations are taken into account. In addition, the potential of the adatoms breaks the equivalence of the neighboring Ga dangling bonds and causes the charge transfer between them. This crystal-field splitting of the one-electron Ga states determines the charge-transfer energy parameter $\Delta$. Together with the Hubbard correlation energy $U$, this parameter controls the "conductivity gap," i.e., the energy of an excitation consisting of a spatially well separated electron and hole [11]. We use our DFT-LDA calculations to evaluate the parameters $U$ and $\Delta$. For this we simulate the electron transfer between the neighboring Ga dangling bonds and calculate the change in the total energy and self-consistent eigenvalues. The comparison with the mean-field solution of a two-dimensional Hubbard model then gives $U$ and $\Delta$.

To simulate the surface, a slab of seven GaAs(110) layers and a vacuum region with a thickness of five such layers were used. We exploited the exchange-correlation functional of Ceperly and Alder [12], and used fully separable, norm-conserving ionic pseudopotentials [13] and a plane-wave basis set with an energy cutoff of 8 Ry. The nonlinearity of an exchange-correlation energy as a function of the electron density [8,14] was taken into account when introducing the alkali ionic pseudopotential.

First we performed total-energy calculations for different structures of K adatoms to find the geometry with the lowest energy [15]. The calculations were carried out for a 2 × 2 surface elementary cell, which allows one to consider coverages as low as one adatom per four GaAs surface cells. The positions of the adatoms and the coordinates of substrate atoms in the three upper layers were fully relaxed. In these calculations we used a set of two-dimensional Monkhorst-Pack **k** points [16] to perform the summation over the Brillouin zone (BZ). The chosen set corresponds to four **k** points in the irreducible part of the BZ of a 1 × 1 surface elementary cell. At a coverage of one alkali atom per two GaAs surface cells, we found the lowest energy for the structure shown in Fig. 1. It reproduces the two-dimensional structure of closely packed zigzag chains observed by STM [2] for the Cs adsorbate. The calculated adsorption energy is 1.52 eV. For a smaller coverage of a single K adatom per four GaAs surface cells, the adsorption energy increases up to 1.72 eV, which indicates the repulsive interaction between adatoms. We obtained the increase of the adsorption energy with the decreasing coverage also for a Na adsorbate. Therefore at low coverages K and Na would rather prefer to form the low-density structures, like the linear chains observed for Na [3]. We have not studied a Cs adsorbate, because the large size and high polarizability of the Cs ion prevent generation of a reliable pseudopotential. Thus, the formation of high-density Cs chains [2] remains a challenge to the theory. Nevertheless, with respect to the nonmetallic behavior our theoretical results are also applicable to Cs, because regardless of the alkali species the electronic states of interest are the Ga dangling bonds.

At coverages of one alkali atom per two surface cells (see Fig. 1) and less, we found that the substrate relaxation is practically the same as for the clean surface. This is in contrast to the higher coverages, where the substrate relaxation is largely removed [8,17].

We used the structure of Fig. 1 to calculate the parameters of an effective Hubbard Hamiltonian. The surface elementary cell, indicated in Fig. 1 by dashed lines, contains two Ga atoms, which are inequivalent due to the presence of the adsorbate. The adatom potential splits the energy levels of these Ga orbitals and causes a charge transfer $\delta n_0$ between them. In our DFT-LDA calculation we neglect spin-correlation effects, i.e., every state is assumed to be occupied equally by the same amount of "spin up" and "spin down" electron; therefore we adopt the spinless Hubbard Hamiltonian

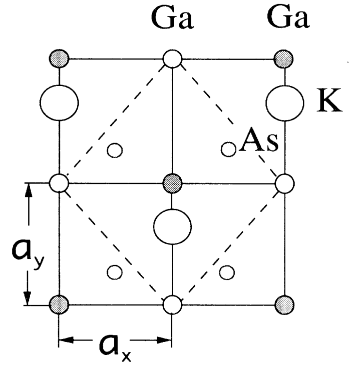

FIG. 1. The geometrical structure of the GaAs(110) surface with alkali adsorbate. Ga atoms, which are nonequivalent due to the presence of the adsorbate, are shown as the middle-sized shaded and empty circles. The elementary cell is indicated by the dashed lines.

$$H = \sum_{i \neq j} t_{ij} c_i^\dagger c_j + \frac{1}{2} U \sum_i \hat{n}_i^2 + \sum_i \Delta_i \hat{n}_i \,, \tag{1}$$

where $\hat{n}_i = c_i^\dagger c_i$ is the particle number operator for a Ga dangling bond at atom $i$. The bonds form a rectangular lattice (Fig. 1). The pertubation $\Delta_i$ due to the alkali adatom is defined as $\Delta_i = \pm\Delta$ for two adjacent sites. Obviously we deal with a bipartite lattice, which can be split into two sublattices, each sublattice consisting of the nearest neighbors to the other one. Therefore, in the case of an electron hopping to the nearest neighbors, the dispersion of the eigenvalues $\xi(\mathbf{k})$ of the kinetic energy term in (1) satisfies the condition

$$\xi(\mathbf{k}+\mathbf{Q}) = -\xi(\mathbf{k}) \,, \tag{2}$$

with $\mathbf{Q} = \pi(1/a_x, 1/a_y)$ and $a_x, a_y$ being the rectangular cell sides (see Fig. 1). We now use the mean-field approximation $\hat{n}_i^2 \rightarrow 2n_i\hat{n}_i$ and consider the charge fluctuation with $\delta n_i = \mp\delta n$ for the neighboring sites. The mean-field eigenvalues of the Hamiltonian Eq. (1) are

$$\varepsilon_\pm(\mathbf{k}) = \mp\sqrt{\xi^2(\mathbf{k}) + (U\delta n - \Delta)^2} \,. \tag{3}$$

From Eq. (2) and time-reversal symmetry it follows that at $\mathbf{k}_0 = \mathbf{Q}/2$, $\xi(\mathbf{k}_0) = 0$, and

$$\varepsilon_\pm(\mathbf{k}_0) = \mp\,(U\delta n - \Delta) \,. \tag{4}$$

The corresponding wave functions in Wannier representation are

$$\Phi_\pm(\mathbf{r}) = \sqrt{\frac{2}{N}} \sum_{\mathbf{R}_i} \left\{ \begin{array}{c} \cos \mathbf{k}_0 \cdot \mathbf{R}_i \\ \sin \mathbf{k}_0 \cdot \mathbf{R}_i \end{array} \right\} f(\mathbf{r} - \mathbf{R}_i) \,, \tag{5}$$

where $\mathbf{R}_i$ runs over the rectangular lattice of all Ga sites. From (5) it is easy to see that $\Phi_\pm(\mathbf{r})$ are built from the orbitals $f(\mathbf{r} - \mathbf{R}_i)$, which belong to different sublattices of nonequivalent Ga atoms.

Let us now consider the results of the DFT-LDA calculations. In Figs. 2(a) and 2(b) the electron-density contour plots for two Ga-related surface states at $\mathbf{k}_0$ are shown. The two states practically do not overlap and obviously belong to different Ga sites. We can therefore identify them with functions $\Phi_\pm(\mathbf{r})$ of Eq. (5) and use the corresponding localized orbitals $f(\mathbf{r} - \mathbf{R}_i)$ as the basis states for the Hubbard Hamiltonian of Eq. (1). At any other $\mathbf{k}$ point surface states are well represented by a linear combination of $\Phi_\pm$ [Fig. 2(c)]. The charge transfer between sublattices of two nonequivalent Ga sites can be written as $\delta n = (n_+ - n_-)/2$ , where $2n_\pm$ are the occupation numbers of two Ga-derived surface states at $\mathbf{k}_0$. The factor 2 in $2n_\pm$ accounts for the two sides of a slab, so that $n_\pm$ are the occupation numbers for Ga orbitals on one side and $n_+ + n_- = 1$ for the considered coverage (Fig. 1). To simulate the electron transfer between the neighboring Ga dangling bonds, we concentrate the sur-

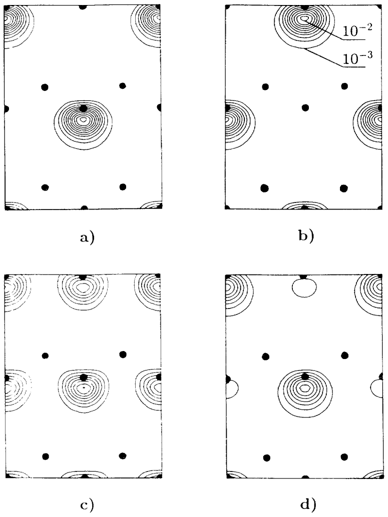

FIG. 2. Contour plots (in bohr$^{-3}$) of (a) $|\Phi_+(\mathbf{r})|^2$, (b) $|\Phi_-(\mathbf{r})|^2$, (c) $|\Phi_+(\mathbf{r})|^2$ at $\mathbf{k} = \pi(3/4a_x, 1/4a_y)$ (one of the Monkhorst-Pack special points), and (d) the surface state electron density $n_+^{(0)}|\Phi_+|^2 + n_-^{(0)}|\Phi_-|^2$ in a ground state. All contour plots are in the $x$-$y$ plane passing through the maximum of a Ga dangling bond between Ga and K.

face state electrons in a single $\mathbf{k}$ point, $\mathbf{k}_0$, keeping the four-$\mathbf{k}$-point sampling for all other states. The method of Car and Parrinello [18], which we used, enables such a calculation, because each state is treated individually. We then transfer the electron between neighboring Ga sites changing gradually the occupation numbers of two Ga surface states. The atomic positions during the electron transfer are kept frozen.

The total energy (per one elementary cell with two surface Ga atoms) as a function of an electron transfer $\delta n$ is depicted in Fig. 3. The curve is well fitted by a parabola with a minimum at the equilibrium charge transfer $\delta n_0 \approx -0.42$. As the average would be 0.5 electron per Ga dangling bond, this means almost complete transfer to one of the Ga atoms [Fig. 2(d)].

Figure 4 shows Kohn-Sham eigenvalues of the Ga surface states at $\mathbf{k}_0$ vs $\delta n$. We evaluate $U$ and $\Delta$, identifying these eigenvalues with the mean-field Hubbard eigenvalues of Eq. (4). This allows us to avoid the evaluation of the kinetic energy of Hubbard electrons, which is necessary if one makes the mapping of Hubbard and LDA total energies [19]. Our mapping procedure is conceptually similar to the constrained LDA calculations by Hybertsen, Schlüter, and Christensen [19] and McMahan, Annett, and Martin [20], and is justified by the mean-field-like structure of the LDA [21].

From Eq. (4) and Fig. 4 we find the following set of parameters:

$$U \approx 0.56\ \text{eV}, \quad 2\Delta \approx -0.42\ \text{eV}\ . \tag{6}$$

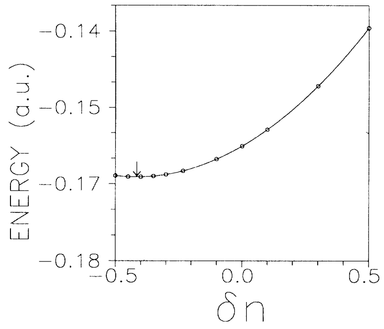

FIG. 3. The total energy as a function of electron transfer between states $\Phi_+$ and $\Phi_-$. The origin of the energy scale corresponds to $-120$ hartrees.

We also calculated the dispersion of a Ga surface band for the equilibrium charge distribution and after the complete electron transfer to the Ga orbital, which was almost empty in the ground state. The bands are shown in Fig. 5. The inset shows the surface Brillouin zone, where the outer rectangle corresponds to the clean surface and the inner part is the Brillouin zone in the presence of the adsorbate. The two bands, which are practically degenerate at $\mathbf{k}_0 = \mathbf{Q}/2$ (the $\bar{L}$ point), correspond to the ground state charge distribution [see Fig. 2(d)]. The approximate degeneracy of these states can be understood if we write the variation of the total energy as

$$\delta E \approx U\delta n^2 - 2\Delta\delta n\ . \tag{7}$$

Here the kinetic energy contribution is neglected. The minimum of $\delta E$ occurs at $\delta n = \Delta/U$, where the one-electron levels of Eq. (4) cross. As a result of the approximation in Eq. (7), $\delta n$ differs from $\delta n_0 \approx -0.42$, but with the parameters of Eq. (6) we obtain a very close value $\Delta/U = -0.375$. Qualitatively, this means that electron flow between neighboring Ga orbitals continues until the one-electron levels $\varepsilon_\pm$ (Fig. 4) equilibrate.

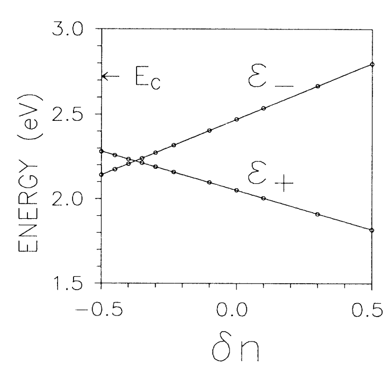

FIG. 4. The eigenvalues for states $\Phi_\pm$ as a function of an electron transfer between them. $E_c$ shows the position of a conduction band edge.

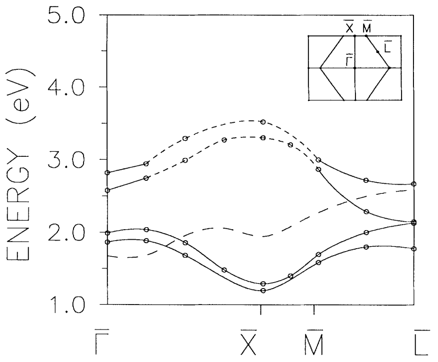

FIG. 5. The dispersion of Ga-derived surface states. The two curves, almost degenerate at the $\bar{L}$ point, represent the surface states at the equilibrium charge density distribution. After the complete electron transfer to the $\Phi_+$ state ($\delta n = 0.5$) the two states split, with the largest splitting occurring at $\bar{L}$. The dashed upper part of surface bands refers to the substantial mixing with bulk states. The broken line shows the conduction band edge for a projected bulk GaAs band structure.

From Fig. 5 it can be seen how the charge transfer splits the two surface bands. The largest splitting of about 1 eV occurs at the $\bar{L}$ point. In other parts of the Brillouin zone it is significantly smaller, because when the eigenfunctions become delocalized [see Fig. 2(c)], the charge redistribution induces much smaller changes of the eigenvalues.

Figure 5 shows that the surface bands have a noticeable dispersion. The bandwidth $\approx 2$ eV at the equilibrium charge distribution, compared to the bandwidth $4t$ for the two-dimensional Hubbard model, gives an estimate of the hopping integral $t \approx 0.5$ eV. For higher alkali coverage the surface bands were found to be much less dispersive [6,8]. The reason is a different geometry of the surface. Whereas at high coverage it is close to the truncated bulk, in our case the surface is still substantially relaxed. The corresponding tilting and rehybridization of the Ga bonds increase the hopping integral.

The experimental study of the electronic excitation spectra of the GaAs(110) surface with adsorbed alkalis [2–6] reveals the appearance of empty and filled surface states in a region of $\sim 1.5$ eV around the Fermi energy. In the Hubbard picture one would expect two peaks split by $U$ (upper and lower Hubbard subbands) detectable by inverse and direct photoemission. Such a spectrum was indeed observed for GaAs(110):K [5]. In the case of Cs [6] the inverse photoemission reveals two peaks in the conduction band (one is obviously derived from the Ga dangling bond state) and a filled state 1.6 eV below this empty state.

In conclusion, our calculations support the description of the GaAs(110) surface with alkali adsorbates as a Mott-Hubbard system with a large charge transfer. The calculated value of the Hubbard correlation energy $U \approx 0.56$ eV is assigned to be a property of the Ga dangling orbital and therefore should be largely adsorbate independent. On the other hand, the parameter $\Delta$ depends on the nature of the adsorbate as well as on the adsorption site.

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