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Mapping the electron correlation onto a model Hamiltonian for Cs/GaAs(110): a Mott–Hubbard insulator at quarter filling

Changfeng Chen† and X W Wang‡

† Department of Physics, University of Nevada, Las Vegas, NV 89154, USA

‡ Department of Physics, Florida International University, University Park, Miami, FL 33199, USA

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Abstract. We have constructed an effective model Hamiltonian in the Hubbard formalism for the Cs/GaAs(110) surface at quarter-monolayer coverage with all of the parameters extracted from constrained local-density-approximation (LDA) pseudopotential calculations. The single-particle excitation spectrum of the model has been calculated using an exact-diagonalization technique to help determine the relevant interaction terms. It is shown that the intersite interaction between the nearest-neighbour Ga sites plays the key role in determining the insulating nature of the system and must be included in the model, in contrast to suggestions of some previous work. Our results show that a reliable mapping of LDA results onto an effective model Hamiltonian can be achieved by combining constrained LDA calculations for the Hamiltonian parameters and many-body calculations of the single-particle excitation spectrum for identifying relevant interaction terms.

1. Introduction

The nature of the insulating state of the alkali-metal-covered GaAs(110) surface has attracted considerable interest and excited debate in recent years. Experimentally, it has been shown [1–4] that at sub-monolayer coverage up to $\theta = 0.25$ (corresponding to 0.5 alkali atoms per surface unit cell), the surface remains an insulator. On the theoretical side, it is known that the ideal GaAs(110) surface has a high density of surface electronic states consisting of the dangling bonds of surface atoms [5]. The surface valence (conduction) band has a large component of the As (Ga) dangling bond. Under monolayer Cs metal coverage, local-density-approximation (LDA) calculations [6] show that the conduction band width remains large, and that the alkali band stays above the conduction band. So the simple band picture suggests that with the alkali atoms donating the electron to the surface conduction band, the surface is a conductor under low alkali coverages. This can be clearly seen in figure 1 which shows the calculated LDA density of states (DOS) for the relaxed GaAs(110) surface under $\theta = 0.25$ Cs coverage with a c(2×2) pattern [6]. The DOS below the surface band gap is due to the filled As bands, the broad background above the band gap is contributed by the partially filled Ga bands, and the large spikes at energies above the Fermi energy are from the narrow two-dimensional Cs and unfilled surface conduction bands [6]. The Fermi level is within the broad peak of the DOS, indicating a metallic ground state. To explain this discrepancy between theory and experiment, electron correlation effects beyond conventional LDA treatment must be considered.

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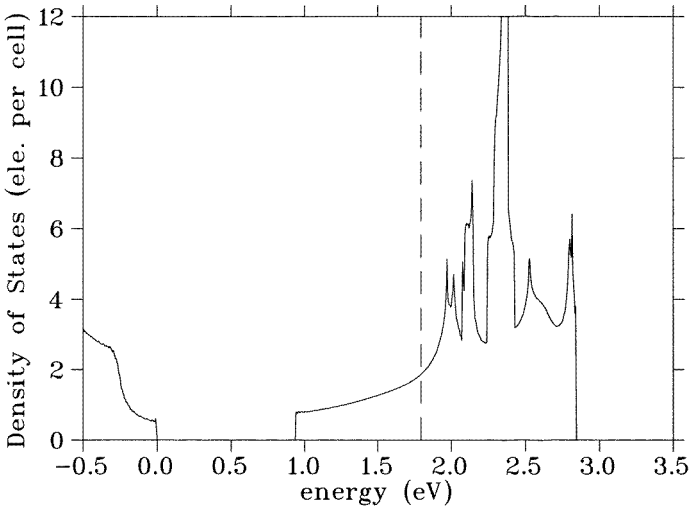

Figure 1. The calculated density of states of the relaxed c(2 × 2) Cs/GaAs(110) surface. The vertical dashed line indicates the position of the Fermi energy. The energy is shifted so that the top of the surface valence band is at $E = 0.0$ eV.

Some previous work [3, 7] suggested that the GaAs(110) surface under low alkali metal coverage is a Mott–Hubbard insulator and the insulating behaviour can be explained in a normal Hubbard model picture with an on-site interaction term assigned to each Ga site. The on-site Coulomb interaction U was estimated to be in the range 0.9–1.8 eV. Since the surface conduction band width is of the order of 1 eV [6, 7], it puts the system in the strongly correlated regime of the normal Hubbard model. However, a later calculation [8] has reported a much smaller value of 0.56 eV for the U-parameter, therefore casting doubt on the validity of the Mott–Hubbard description. Furthermore, a simple Mott–Hubbard insulator occurs at electron filling factor close to 1/2, while for the Cs/GaAs(110) surface the electron filling factor in the surface band is 1/4, thus favouring a metallic ground state regardless of the value of the on-site interaction U. The description of a half-filled Hubbard insulator could be valid if adsorbed alkali does not act as donors or upon low alkali coverage there are substantial changes in the surface relaxation. However, both scenarios were not supported by experimental [9, 10] and theoretical [6] studies. A bipolaron model [11] was proposed as an alternative mechanism for the insulating behaviour. In a recent work [12] we have investigated this problem using constrained LDA schemes [13] to map out the Hamiltonian parameters from first-principles pseudopotential calculations. It has been found necessary to include an intersite Coulomb interaction term for the nearest-neighbour Ga sites in the Hamiltonian to obtain a *consistent* set of interaction parameters independent of the various constraining schemes used in the mapping procedure, as required for a physically meaningful approach.

The inclusion of the intersite interaction term has solved the parameter consistency problem and has yielded reasonable values for the interaction terms for an Mott–Hubbard interpretation of the observed insulating behaviour of the Cs/GaAs(110) surface [12]. However, since the LDA results can be mapped onto various *effective* model Hamiltonians containing different interaction terms, further support is needed to make the choice of the interaction terms in the present Hamiltonian more convincing. It is also desirable to have a systematic way to test the suitability of the model Hamiltonian. In this paper, we

report calculations of the single-electron excitation spectrum (SEES) of the mapped model Hamiltonian with different parameter choices. An important conclusion is that constrained LDA calculations can yield a reliable mapping when combined with explicit many-body calculations of some physical property such as the SEES. We choose to calculate the SEES because it provides important insights into the fundamental electronic structure of the system and can be directly compared with photoelectron spectroscopy experiments. We have calculated the SEES of the Hubbard model for the Cs/GaAs(110) surface using an exact-diagonalization technique with and without the intersite interaction term. It is shown that a comparison between the calculated spectrum and experiment can clearly identify the relevant interaction terms. It also offers a clear physical picture as to what is the underlying mechanism responsible for the observed behaviour of the system. This approach, while explicitly applied to the Cs/GaAs(110) surface in this work, is not limited to a specific system and can be readily applied to a wide range of correlated electron systems.

In the next section, we describe the construction of the model Hamiltonian. In section 3, we present the calculated single-electron excitation spectrum and discuss issues related to the mapping of LDA results onto a model Hamiltonian. Conclusions are given in section 4.

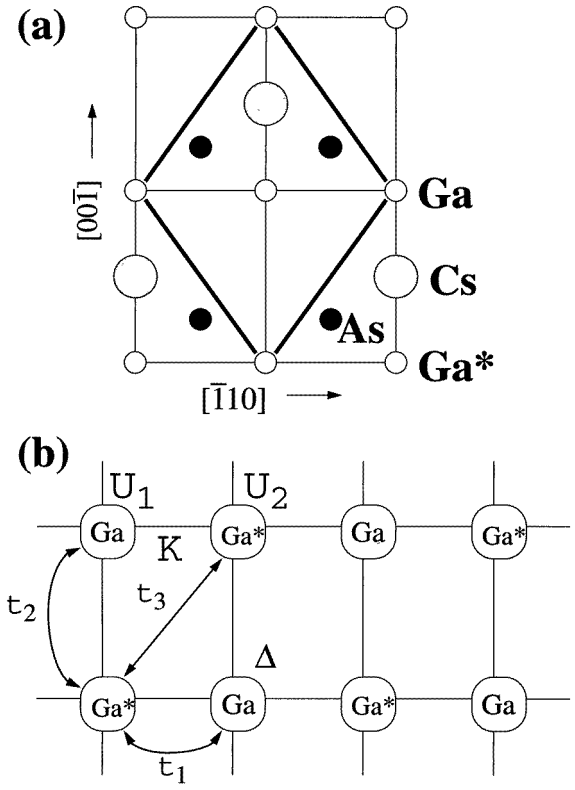

Figure 2. (a) The Cs/GaAs(110) surface at $\theta = 0.25$ coverage. The c(2×2) cell is outlined with bold lines. The Ga atom that has a Cs atom at its tetrahedral bond direction is denoted by Ga*. (b) The two-dimensional Ga-only lattice with the Hamiltonian parameters indicated. Periodic boundary conditions are applied to this eight-site, (4×2) cluster, which is compatible with the (2×2) relaxation pattern of the Cs/GaAs(110) surface.

2. The model Hamiltonian

The GaAs(110) surface structure with $\theta = 0.25$ Cs coverage is shown in figure 2(a). This surface exhibits a simple c(2×2) relaxation pattern as indicated in the figure. It is known from LDA calculations [6] that the As band is completely filled and below the surface band gap (see figure 1), and the surface conduction band is highly localized on the surface layer Ga. Therefore we model the surface with a two-dimensional rectangular lattice of the Ga sites (see figure 2(b) for the lattice structure and Hamiltonian parameters). Our model concentrates on the dangling bonds of Ga, so there is only one orbit per surface unit cell. With the adsorption of alkali atoms, the surface periodicity changes, so we consider two inequivalent Ga atoms, with Ga* denoting the Ga atom that has an alkali atom at its tetrahedral bond direction. The model for this system thus is a two-dimensional Hubbard model defined by the following Hamiltonian:

$$H = \Delta \sum_{i\in Ga;\sigma} c^\dagger_{i\sigma} c_{i\sigma} + \sum_{ij;\sigma} t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \frac{1}{2} \sum_{i\sigma} U_i c^\dagger_{i\sigma} c_{i\sigma} c^\dagger_{i-\sigma} c_{i-\sigma} + \sum_{\langle ij\rangle;\sigma\sigma'} K_{ij} c^\dagger_{i\sigma} c_{i\sigma} c^\dagger_{j\sigma'} c_{j\sigma'}. \tag{1}$$

Here Δ is the on-site energy difference between the Ga and Ga* sites. We consider three neighbouring hopping terms: t_1 for hopping between Ga and Ga* sites along the surface Ga−As chain, t_2 for interactions perpendicular to the chain, and t_3 for interactions along the diagonal of the surface rectangular lattice. Our LDA calculations show [6] that the relaxation of Ga and that of Ga* are almost identical. This is due to the highly ionic bonding between Cs and the GaAs(110) surface. It is also expected that the hopping term t_3 for interactions between Ga sites and that for interactions between Ga* sites are similar. In addition, we consider two intrasite Coulomb interaction terms with parameters U and U^*, and one nearest-neighbour intersite interaction term K along the surface chain. The Hamiltonian parameters have been determined by constrained LDA pseudopotential calculations [12]. The values are $t_1 = 0.17$ eV, $t_2 = -0.072$ eV, $t_3 = 0.049$ eV, $\Delta = 0.10$ eV, $U = 1.5$ eV, $U^* = 1.5$ eV, and $K = 0.61$ eV. We have checked the consistency of these parameters by using various constraining schemes in the mapping procedure and by performing the LDA calculations for different relaxed surface structures and at different points in the surface Brillouin zone. The parameters are found to be insensitive to the variation of the mapping procedure. The interaction parameters indeed put the system in the strong-interaction regime. However, since there is some ambiguity in choosing the interaction terms to be included in the model Hamiltonian, it is not *a priori* clear that we have included all of the relevant interaction terms in the Hamiltonian necessary to provide a proper description for the insulating behaviour of the system. In the following section, we use the above parameter set to calculate the single-electron excitation spectrum to directly test the above Hamiltonian through an explicit calculation of the gap and a comparison of the calculated spectrum with experimental photoemission results.

3. The single-particle excitation spectrum

A symmetry-projected exact-diagonalization scheme [14] is applied in the context of the finite-cluster approach to an eight-site Ga lattice with periodic boundary conditions (see figure 2). This approach has been widely used in the study of strongly correlated electron systems, and has proved to be very good at describing many spectroscopic processes [15–17]. The structure of the periodic cluster is chosen to be compatible with the (2×2) relaxation pattern of the Cs/GaAs(110) surface. Here we consider four electrons in the neutral state

of the cluster. This electron filling factor of 0.25 corresponds to GaAs(110) with $\theta = 0.25$ coverage of Cs. The Hamiltonian is restricted to the Hilbert space of the paramagnetic ($S = 0$) state, corresponding to the experimental situation of the GaAs(110) system. We have used spin and space-group symmetries of the system to project out states transforming according to various irreducible representations. Since the matrix element theorem of group theory [18] guarantees that Hamiltonian matrix elements connecting states belonging to different irreducible representations are always zero, the original Hamiltonian matrix of order 4368 is now decomposed into smaller Jordan blocks with distinct particle-number, spin and spatial symmetries. These Jordan blocks, the largest of which is of order 504, are then numerically diagonalized to obtain all of the eigenvalues and eigenstates of the system. This procedure is applied to the neutral state ($N = 4$) as well as the photoexcited final states ($N = 3$ and 5) of the system to calculate the single-electron excitation spectrum, or many-body density of states, which is defined as

$$\rho(\omega,\sigma) = \sum_{n,k} |\langle\phi_n^{N-1}|c_{k,\sigma}|\phi_0\rangle|^2 \delta(\omega + E_n^{N-1} - E_0^N + \mu) + \sum_{n,k} |\langle\phi_n^{N+1}|c_{k,\sigma}^\dagger|\phi_0\rangle|^2 \delta(\omega - E_n^{N+1} + E_0^N + \mu) \tag{2}$$

where $|\phi_0\rangle$ is the ground state in the subspace of N electrons ($N = 4$ in the reported calculation) with energy E_0^N, and $|\phi_n^{N\pm1}\rangle$ are eigenstates in the subspace of $N \pm 1$ electrons with energies $E_n^{N\pm1}$. The operator $c_{k,\sigma}$ ($c_{k,\sigma}^\dagger$) destroys (creates) an electron with spin σ and composite index k, where k may include orbital and momentum indices. In the above equation, the first term corresponds to the occupied states, or the photoemission spectrum, and the second term corresponds to the empty states, or the inverse photoemission spectrum. The chemical potential μ is determined from [16] $\mu = (1/2)[E_0^{N+1} - E_0^{N-1}]$.

The discrete spikes in the calculated spectra, which are characteristic of finite-cluster calculations, are broadened with Gaussian functions of width 0.05 eV. The calculated results are checked against the sum rule

$$\int \rho(\omega,\sigma)\ \mathrm{d}\omega = M \tag{3}$$

where M is the total number of sites in the cluster. This sum rule is satisfied in the reported calculations.

The calculated single-electron excitation spectrum for the Cs/GaAs(110) surface is shown in figure 3. It is seen that there is a gap between the occupied and unoccupied part of the spectrum and that the system is an insulator. The magnitude of the gap, commonly defined as the separation between the occupied and unoccupied peaks with the lowest binding energy, is about 0.6 eV, in excellent agreement with the experimental values of the one-electron excitation gap [2, 3]. We have, therefore, demonstrated that the present model Hamiltonian not only yields a consistent set of parameters mapped from the LDA results, but also generates the insulating ground state with the correct gap value. The explicit calculation of the band gap provides convincing evidence that our model has captured the essential physics of the Cs/GaAs(110) surface, and can serve as a good starting point for further many-body study of low-energy dynamics of this system. Notice that the gap E_g coincides with the value of the intersite interaction K. We will show below that, in fact, the insulating behaviour of the Cs/GaAs(110) surface is entirely driven by the intersite interaction K that determines the size of E_g.

Further comparison with the experimental photoemission spectrum (PES) shows that our calculated single-electron excitation spectrum matches the experiment quite well. The

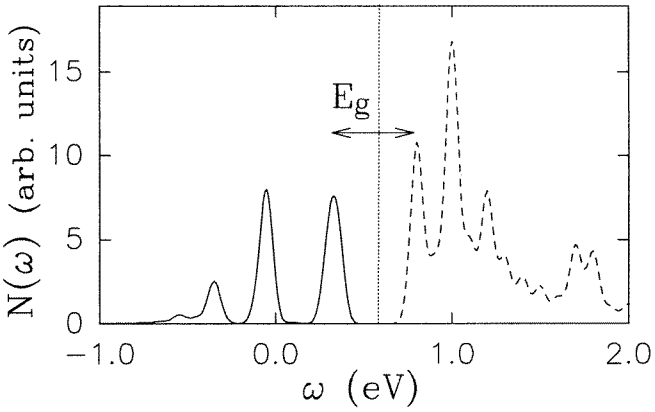

Figure 3. The calculated single-electron excitation spectrum with the parameter set extracted from constrained LDA calculations as explained in the text. The vertical dotted line indicates the position of the chemical potential. The gap E_g, defined as the separation between the occupied and unoccupied peaks with the lowest binding energy, is also indicated.

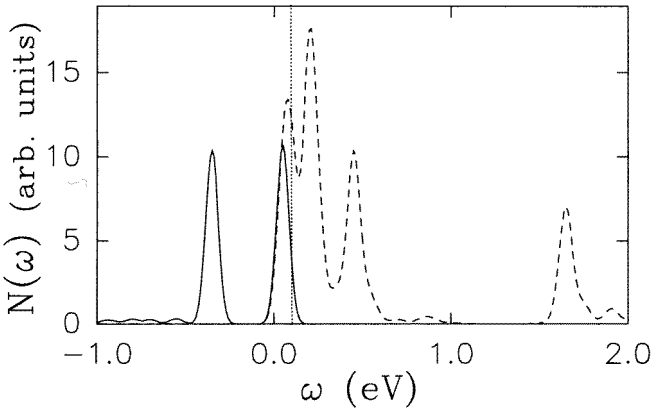

Figure 4. As figure 3, except that here $K = 0$.

comparison with the PES experiment is straightforward since the occupied states above the surface band gap are from the surface Ga states [6] which are explicitly considered in the present model. Although the limited energy resolution of the photoemission experiments prevents a detailed comparison of fine features in the spectrum, a surface feature (labelled as S_1' in reference [19]) is clearly observed at coverages up to quarter of a monolayer, consistent with the results of our model calculation. A similar surface feature is also observed in the K/GaAs(110) surface around quarter-monolayer coverage [19]. This indicates that, as long as the overlayer alkali atoms serve only as the carrier donors without affecting the geometric and electronic structures of the GaAs(110) surface, the present model can be applied to describe the low-energy physical processes of the system. The match between the calculated spectrum of the effective model Hamiltonian and the experimental PES provides further evidence that the model is appropriate for the alkali-metal-covered GaAs(110) surface. Meanwhile, a direct comparison of the calculated spectrum with the inverse photoemission spectrum (IPES) experiment is difficult in the present work since there is large contribution

to the observed IPES from the Cs 5p states [19], which are not explicitly included in the present model.

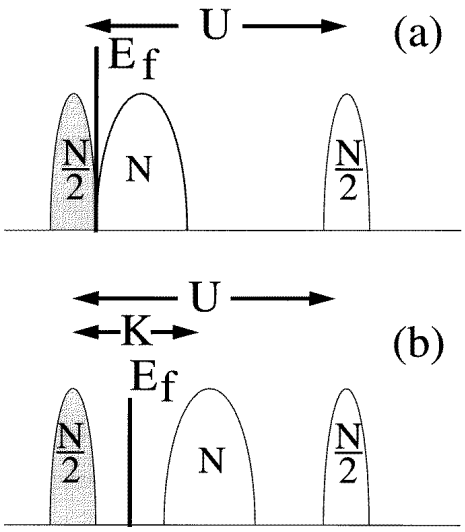

Figure 5. A schematic representation of the density of states (DOS) for an N-site (a) normal ($K = 0$) and (b) extended Hubbard model at quarter filling in the localized limit. The shaded (unshaded) area represents the occupied (unoccupied) DOS. The Fermi energy (E_f) and the spectral weight are indicated.

One important feature of the construction of a model Hamiltonian mapped from LDA results is the uncertainty in identifying all of the relevant terms in the Hamiltonian. While the single-particle terms can be mapped out in a tight-binding form in a straightforward manner, the determination of the relevant interaction terms is not *a priori* clear since the mapped values of all of the interaction terms are sensitive to the number and nature of the interactions considered [12, 13]. This is exactly the case for the alkali-metal-covered GaAs(110) surface. In the previous work [7, 8] the normal Hubbard model with only the on-site interaction term was used. It has led to inconsistent parameter sets that are sensitive to the mapping procedure, indicating that the model is inappropriate. We have carefully analysed this problem and identified the intersite interaction K between the nearest-neighbour Ga sites as an important term that must be included in the model Hamiltonian. Furthermore, an analysis of the many-body wavefunction reveals that the intersite Coulomb interaction K is crucial in stabilizing the ground state that, for the present Hamiltonian parameters, essentially has four electrons at the four Ga^* sites. The insulating behaviour arises naturally in the Mott–Hubbard picture once the intersite interaction is explicitly included. The insulating ground state does not critically depend on specific values of the U-parameters, as long as their values are large enough to prevent double occupancy. As mentioned above, the insulating gap is essentially determined by K. Since the single-electron excitation spectrum should be sensitive to various interaction terms, it is expected that the calculated spectrum will be able to be used to distinguish Hamiltonians containing different interaction terms. In figure 4, we present the calculated spectrum for the Cs/GaAs(110) surface with the same parameter set as was used above, except that the intersite interaction K is now turned off. It is seen that the gap observed in figure 3 now completely collapses. This confirms the above analysis concerning the role of K in opening up the gap and stabilizing the

insulating ground state. The high sensitivity of the calculated spectrum to changes in the Hamiltonian interaction terms suggest that it can be used as an effective tool to distinguish different model Hamiltonians and identify relevant interaction terms in the procedure of mapping LDA results onto a model Hamiltonian. Another advantage of using the single-electron excitation spectrum is that it can be directly compared to photoelectron spectroscopy experiments for a 'reality check'.

Finally, we discuss the calculated results in the localized limit to gain further physical insight. In the localized limit, the single-electron excitation spectrum can be summarized in a schematic plot as shown in figure 5. This provides a clear picture as a basis for understanding the underlying physics. In the normal Hubbard model picture ($K = 0$), the system is actually a conductor at quarter filling regardless of the value of the on-site interaction parameter U. It is well known that an insulating state can be realized at quarter band filling in a charge-transfer insulator [20] in the parameter region where the orbital energy difference between the correlated electron site and the uncorrelated ligand site is smaller than the on-site Coulomb interaction U. However, in the present model constructed for the Cs/GaAs(110) surface, there are no ligand band states available. It is shown that the nearest-neighbour intersite Coulomb interaction K opens up an additional gap in the single-electron excitation spectrum and drives the system into an insulating state. Since this conclusion is based on very general physical considerations, this type of nonlocal-interaction-driven insulating behaviour can be expected to occur in other correlated electron systems.

4. Conclusions

We have used a consistent parameter set for an extended Hubbard model derived from first-principles constrained pseudopotential LDA calculations in a many-body calculation of the single-electron excitation spectrum for the GaAs(110) surface under one quarter monolayer of Cs coverage. The calculation produces the experimentally observed insulating behaviour with the correct band gap, and the results agree with the spectral features of photoemission measurements. A comparison between the calculated spectrum and photoelectron spectroscopy experiments reveals that the intersite interaction between the nearest-neighbour Ga sites is of crucial importance in determining the insulating ground state, and must be explicitly included in the model Hamiltonian. The most important conclusion of this work is that a reliable mapping of the LDA results onto a model Hamiltonian can be achieved by combining the constrained LDA calculations for Hamiltonian parameters and many-body calculations of the single-electron excitation spectrum, which can be directly compared with photoelectron spectroscopy experiments, for identifying the relevant interaction terms. This approach is expected to be applicable to a wide range of correlated electron systems.

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