Quantum interference and long-range adsorbate-adsorbate interactions

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Density functional theory and scanning tunneling microscopy are used to resolve the long-range adsorbate interactions between Co adatoms on Cu(111), caused by the quantum interference of surface-state electrons. Our calculations and experimental results are in very good quantitative agreement. We reveal the effect of the quantum interference of surface state electrons on adatom motion, leading to the self-assembly of one-dimensional structures on metal surfaces.

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In condensed-matter physics, a topic of fundamental importance is how electronic states of a system are changed due to an external perturbation. More than 40 years ago, Friedel showed that the screening of impurities in the bulk should result in a long-range oscillatory behavior of period $\lambda_F/2$ in the electronic density.[1] The surface itself is a perturbation of the bulk. Lang and Kohn predicted Friedel oscillations for the charge density perpendicular to a surface.[2] Surface imperfections, such as steps and point defects, should also lead to periodic spatial oscillations of charge density.[3,4] These perturbations greatly affect adsorbate structures, dynamics, and chemistry.

The surface-state electrons on the (111) surfaces of noble metals form a two-dimensional (2D) nearly-free-electron gas. Such states are confined in a narrow layer at the surface. An electron in such a state *runs* along the surface, much like a 2D plane wave. The quantum interference between the electron wave traveling towards the scattering defect and the backscattered one leads to standing waves in the electronic local density of states (LDOS) around the defect.[5] These standing waves are the energy-resolved Friedel oscillations. The scanning tunneling microscope (STM) images, taken at low bias, directly reflect the oscillations in the LDOS close to E_F. The progress in STM made it possible to observe the Friedel oscillations in the vicinity of surface imperfections, such as step edges,[6] adsorbates,[7] and defects.[8] By using STM adsorbate manipulation techniques, it is possible to construct atomic-scale structures on metal surfaces and to study artificially confined quantum systems.[9]

The oscillations of the electron density around the adsorbates on a metal surface lead to a long-range, oscillatory, Friedel-type adsorbate-adsorbate interaction.[4] Only recently, low-temperature STM studies have allowed to resolve the long-range adsorbate interactions mediated by surface states up to 80 Å.[10,11] These remarkable experiments have raised the possibility of a direct study of interactions in 2D systems on the atomic scale. The model of Hyldgaard and Persson,[12] establishing a link between the interaction energy and the scattering properties of the adsorbates, has been used for a quantitative comparison with the theory. However, this model requires several parameters which depend on the properties of adsorbates and surface states. In the first *ab*

initio calculations by Bogicevic *et al.* and Fichthorn and Scheffler,[13,14] the indirect interactions on the (111) metal surfaces have been calculated. It was demonstrated that such interactions can significantly influence surface diffusion and the growth morphology. However, only the short-range part of the indirect interactions (up to 13 Å) has been determined in these calculations. It was not possible to discern the effect of the quantum interference of surface-state electrons on the interaction energies.

In this paper, we report on *ab initio* studies of the long-range adsorbate interactions caused by the quantum interference of surface-state electrons, and reveal that such interactions can lead to the self-assembly of the one-dimensional structures on metal surfaces.

While we concentrate on a particular system, Co adatoms on Cu(111), our results are of general significance because they show that the quantum interference on metal surfaces can strongly affect the growth process of the transition-metal nanostructures.

Our study demonstrates that the density-functional theory allows one to calculate adsorbate interactions at large distances in very good agreement with the STM experiments.

Our calculations are based on the density-functional theory and the multiple-scattering approach using the Korringa-Kohn-Rostoker Green's function method for low-dimensional systems.[15] The basic idea of this method is a hierarchical scheme for the construction of Green's function of adatoms on a metal surface by means of successive applications of the Dyson equation. We treat the surface as a two-dimensional perturbation of the bulk. For the construction of the ideal surface, the nuclear charges of several monolayers are removed, thus creating two half crystals, being practically uncoupled. Taking into account the 2D periodicity of the ideal surface, we calculate the structural Green's function by solving a Dyson equation self-consistently:

$$G_{LL'}^{jj'}(\mathbf{k}_\parallel, E) = \mathring{G}_{LL'}^{jj'}(\mathbf{k}_\parallel, E)$$
$$+ \sum_{j''L''} \mathring{G}_{LL''}^{jj''}(\mathbf{k}_\parallel, E) \Delta t_{L''}^{j''}(E) G_{L''L'}^{j''j'}(\mathbf{k}_\parallel, E).$$

(1)

Here $\mathring{G}$ is the structural Green's function of the bulk in a $\mathbf{k}_{\parallel}$-layer representation (j,j'-layer indices). The wave vector $\mathbf{k}_{\parallel}$ belongs to the 2D Brillouin zone. $\Delta t_L^j(E)$ is the perturbation of the t matrix with angular momentum $L=(l,m)$ in the jth layer.

The adsorbate atoms on the surface destroy the translation symmetry. Therefore, Green's function of the adsorbate adatom on the surface has to be calculated in a real-space formulation. The structural Green's function of the ideal surface in a real-space representation is then used as the reference Green's function for the calculation of the adatom-surface system from an algebraic Dyson equation

$$G_{LL'}^{nn'}(E) = \mathring{G}_{LL'}^{nn'}(E) + \sum_{n''L''} \mathring{G}_{LL''}^{nn''}(E) \Delta t_{L''}^{n''}(E) G_{L''L'}^{n''n'}(E),$$
(2)

where $G_{LL'}^{nn'}(E)$ is the energy-dependent structural Green's function matrix and $\mathring{G}_{LL''}^{nn''}(E)$ is the corresponding matrix for the ideal surface, serving as a reference system. $\Delta t_L^n(E)$ describes the difference in the scattering properties at site n, induced by the existence of the adsorbate atom. A self-consistent one-electron potential for the adatom on the surface is obtained by solving the Kohn-Sham equations, taking into account the atomic structure of the substrate. Exchange and correlation effects are included in the local-density approximation.[15] The full charge density and the full potential approximation can be used in the calculations.

Using Green's function for the adatoms on the surface, the charge density and the density of electronic states $n(\varepsilon)$ can be calculated.[15]

The total energy of adatoms on a surface is presented as[16]

$$E_{tot} = E_{sp} + E_{DC},$$
(3)

where the single-particle energy E_{sp} is

$$E_{sp} = E_F N - 2 \int^{E_F} d\varepsilon N(\varepsilon),$$
(4)

E_{DC} is the double-counting term obtained using the self-consistent charge density and the self-consistent potential for the adatom on the surface,[16] $N(E)$ is the integrated density of states per spin direction, and N is the number of particles.

For two adsorbates at separation r, the interaction energy between them is defined as the total-energy difference between the two states: The final state where the two adatoms are located at a distance r and the initial state where both adatoms are infinitely far away.

At large adsorbate-adsorbate separation of 10–100 Å, the interaction energies are only of a few meV. Therefore, there is the problem of substracting huge total-energy values to obtain the resulting small interaction energies. Hyldgaard and Persson[12] have suggested that due to the screening of adatoms by the substrate electrons, the interaction energy is determined by the single-particle energies alone. Our calculations show that such approximation is well justified for the Co-Co distances larger than 6–7 Å. For example, for the adatom-adatom distance 6.76 Å, the interaction energy calculated with the total energies is 6.6 meV, which is very close to the value 5.5 meV obtained using only the single-particle energies. For larger distances, this difference becomes smaller than 0.1 meV. The agreement of our results for large distances with the model of Ref. 12 (cf. Fig. 2) gives us confidence that we have performed very accurate energy calculations. In our studies, we apply the "force theorem"[17] and use the self-consistent spin-polarized potential of the single adatom.

Adatom relaxation is calculated using the Hellman-Feynman theorem.[18] In a fully relaxed geometry, the distance of the Co adatom from the surface is reduced by 14% compared to the ideal layer distance of Cu. However, we find that the substrate-mediated interactions at large distances are essentially unmodified by the inclusion of the relaxation.

The corresponding experiments were performed using a UHV-STM with a base temperature of 6 K. The Cu(111) single-crystal surface was prepared by Ar sputtering and annealing cycles. Co adatoms were deposited from a filament with the substrate held below 20 K. Deposition of $\Theta=1 \times 10^{-3}$ ML, where ML denotes monolayer, resulted in well-separated monomers on the surface. To obtain the interaction energy, we studied the adatom diffusion in a temperature interval of 14–16 K. The diffusing adatoms sample the potential landscape produced by their neighbors therefore an adatom will be found more likely on a site with a low rather than with a high interaction potential. Statistically independent snapshots of the diffusive motion were taken by STM, and from them a site-occupation probability as function of adatom pair distance was obtained. Using a Boltzmann distribution for the ratio of the experimental site-occupation probabilities with that of a hypothetical system without an adatom interaction yields the interaction energy quantitatively without any further assumptions. In this process, care was taken to exclude many-body interactions and any influence that the STM tip might have on the diffusion of the adatoms.[11]

Our calculation for the Cu(111) surface gives a surface-state Fermi wavelength $\lambda_F = 29$ Å. The scattering of surface-state electrons by Co adatoms leads to the quantum interference patterns around the adsorbate. Figure 1 shows the calculated LDOS at E_f displaying the $\lambda_F/2 \approx 15$ Å period oscillations.[19] The concentric rings surrounding the Co adatom (cf. Fig. 1, inset) are standing waves due to the quantum interference. The calculated Friedel oscillations nicely mimic the experimental STM observations,[6,10,11] exemplified in Fig. 2(a) for the Co/Cu(111) system.

Now we turn to the discussion of our results for the long-range interactions between Co adatoms on Cu(111). An example of a STM image of two Co adatoms at a distance of about 60 Å from each other is shown in Fig. 2(a). One can see that the atoms share LDOS oscillations with each other. Thus, the adsorbates should interact via Friedel oscillations. Our experimental results and calculations for the energy interaction between Co adatoms are presented in Fig. 2(b), and they show that the interaction energy is oscillatory with a period of about 15 Å. The *ab initio* results are in good quantitative agreement with the experiment.[20] Only for distances <8 Å, deviations are observed where the experiment finds a systematically lower $E(r)$. Statistical error (in this regime,
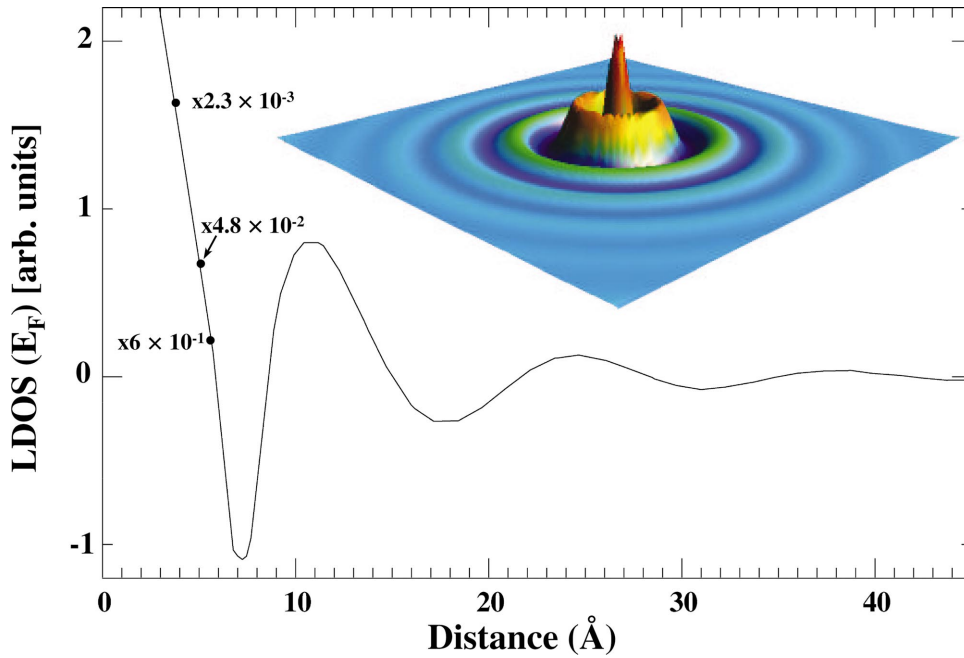
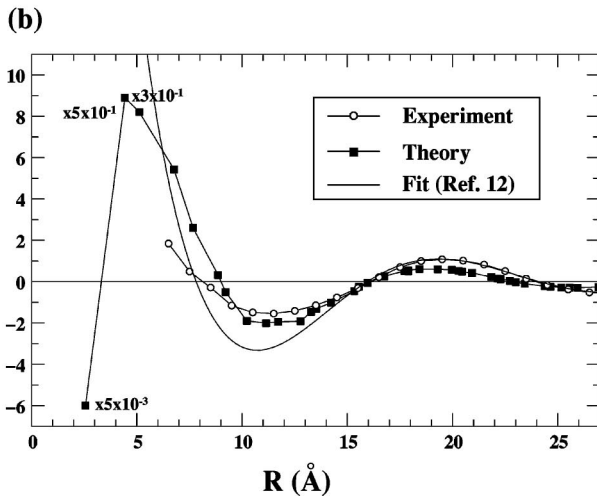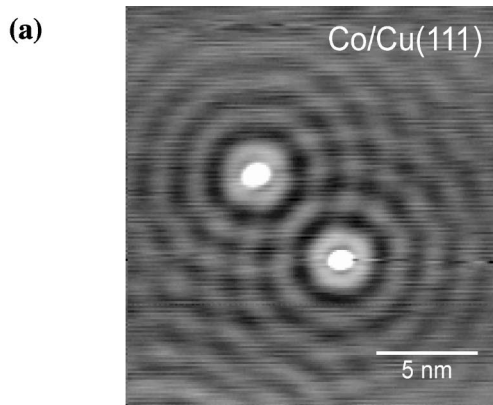FIG. 1. (Color) Calculated standing waves in the LDOS around single Co adatom on Cu(111).

FIG. 2. (a) Constant current STM image of two Co adatoms on Cu(111), which interact via the standing waves $I = 2$ nA, $V = -50$ mV, $T = 6$ K; (b) experimental and calculated interaction energies between two Co adatoms on Cu(111); a fit based on the model of Ref. 12 is presented and the first three theoretical points have been rescaled.

less then ten occurrences out of 10 000 were found) and unfavorable imaging conditions (relatively large area scans with quickly moving adsorbates), which introduce an error in the determination of the adatom pair distance, could explain this deviation.

In the above results, we take into account that the adatoms couple to the 3D bulk bands. It is known[4] that the interaction energy in the bulk asymptotically falls off as the inverse fifth power of the interatomic distance. However, our calculations and experiments show that the envelope of the magnitude of the interaction energies asymptotically decays as $1/d^2$, in agreement with the prediction for the interaction caused only by the surface-states electrons. At the same time, the bulk states can significantly affect the interaction energies at short distances. For example, former comparisons between the experiment[10,11] and theory[12] found discrepancies concerning the strength of the first interaction minimum, which was overestimated in the theory of Ref. 12. Only by including a cutoff parameter, the experiment[11] and theory could be brought into agreement [cf. Fig. 2(b)].

In contrast, our *ab initio* calculations are in perfect agreement with the experimental data, and predict a first minimum of the interaction energy -1.5 meV. We believe that the drawback of the scattering theory[12] to describe correctly the first interaction minimum is connected with the neglect of the effect of bulk electronic states on the scattering of the surface electrons.

Despite the fact that the interactions probed in this work are small, they can affect atomic motion and growth processes. In our experiments, Co chains are often seen in STM images (cf. Fig. 3).[21] To examine how Co adatoms self-assemble into one-dimensional structures, we calculate the diffusion barriers for the Co adatom in the presence of short chains, taking into account the long-range interactions caused by the quantum interference. The barriers for jump diffusion in the direction of the chain and parallel to the
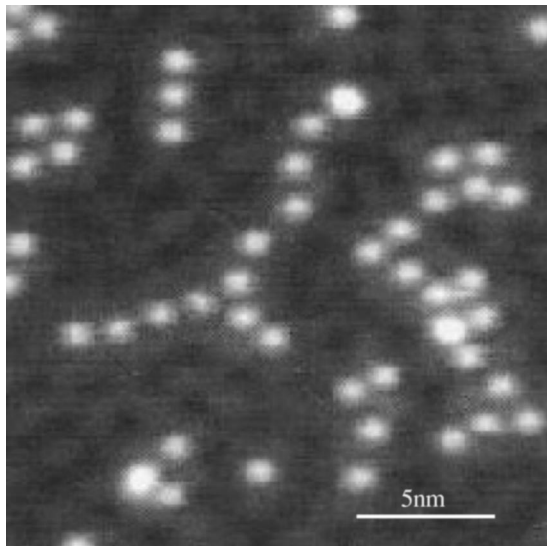
FIG. 3. Constant current STM image of metastable one-dimensional structures of Co atoms on Cu(111), formed upon deposition of 0.006 ML at 11 K ($I = 0.1$ nA, $V = 50$ mV).

chain are determined.[22] The first mechanism of the diffusion should lead to the formation of compact island, while the second one should promote the incorporation of Co adatoms at chain ends. The starting point for the diffusion of Co adatom is taken beyond 8 Å, where the repulsive interaction occurs (cf Fig. 2). The trace of the path for Co adatom near the chain is shown in Fig. 4. We study two configurations of the chain: The distance between Co atoms in the chain corresponds to the first nearest-neighbor distances [Fig. 4(a)]; and to the position of the first minima in the long-range interaction potential [Fig. 4(b)]. Atomic scale calculations are performed with the potential shown in Fig. 2 in a fully relaxed geometry. Our results reveal that the adatom moving towards the chain is repelled by the repulsive potential created by atoms of the chain. For both the configurations of the chain, Co adatoms tend to move parallel to the chain, as proved by the calculations of diffusion barriers presented in Fig. 4.[21] Incorporation of Co adatoms to the chain takes place only at the end regions of the chain, thus leading to the growth of one-dimensional structures. Note that the above results can be explained qualitatively using Fig. 2(b), assuming that pair-interaction energies can be added.

In summary, we have performed *ab initio* calculations for the long-range adsorbate-adsorbate interactions caused by
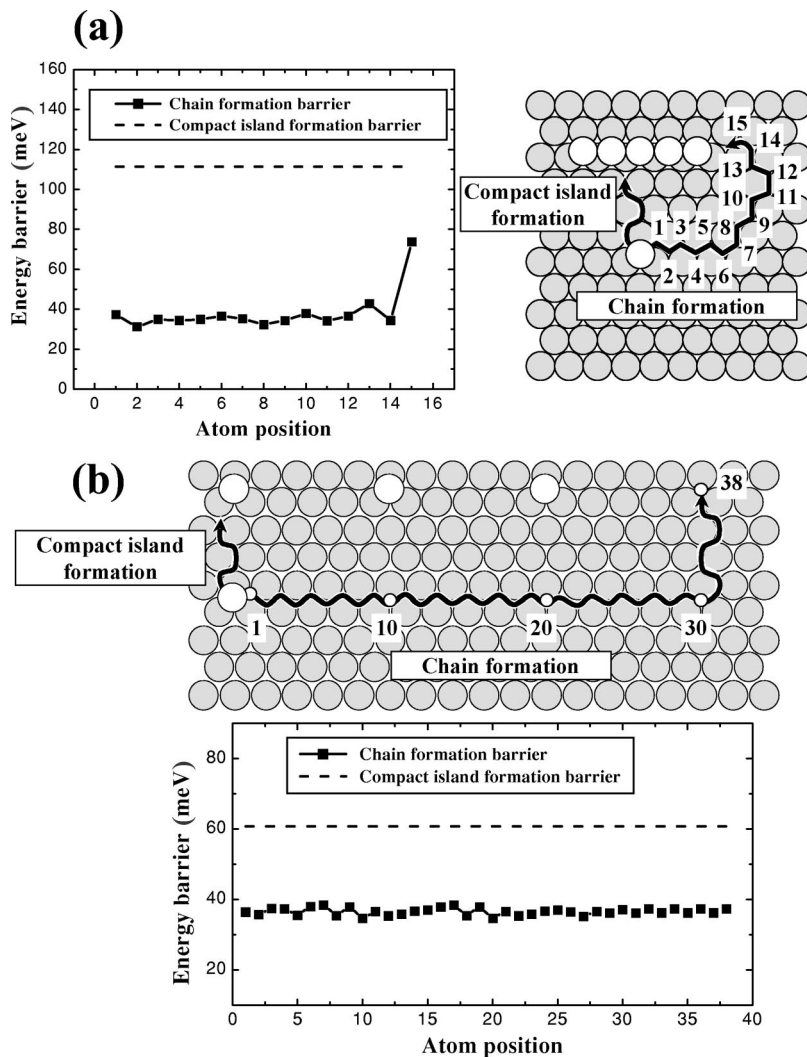

FIG. 4. The effect of the long-range interaction on the self-assembly of one-dimensional Co structures on Cu(111).

the quantum interference of surface-state electrons. Our calculations and experimental results performed by STM are in very good agreement. We have revealed the effect of long-range interactions on atomic motion on metal surfaces. We demonstrated that such interactions lead to the self-assembly of one-dimensional Co structures on Cu(111). We believe that our work opens up new possibilties for investigations of many important effects determined by the long-range interactions on metal surfaces.

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[19] The LDOS is calculated at the Fermi energy and 5 Å above the surface which is close to the tip-substrate distance in STM experiments. The LDOS near the Co adatom (1.8 Å above the surface) exhibits the same oscillations with larger amplitudes.

[20] We have also calculated the interaction energies between Cu atoms on Cu (111), and have found that at large distances they are very close to the interaction between Co adatoms. This result agrees with the conclusion of the experiment (Ref. 11), and shows the generality of surface-state mediated interactions between adsorbates.

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[22] Both the experiment and the calculation reveal that fcc sites are more stable than hcp sites.