# Magnetic nanostructures stabilized by surface-state electrons

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Performing state of the art *ab initio* studies, we predict that new 3*d* magnetic nanostructures and superlattices on Cu(111) can be stabilized by surface-state electrons. We reveal that magnetic states in these systems are determined by long-range exchange interaction between adatoms. Atomic scale simulations indicate that 3*d* superlattices on Cu(111) can be stable up to 25–30 K.

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In recent years there has been a strong interest in the physics of magnetic nanostructures deposited on metal surfaces.[1,2] It is believed that such structures can be of great importance for the development of advanced atomic scale magnetic devices. The control and manipulation of magnetism and structure on the atomic scale is an ongoing challenge of materials science.

Very recently a method in atomic engineering was demonstrated by a group headed by W.-D. Schneider.[3] They have shown that cerium adatoms, deposited on Ag(111), can self-assemble into large ordered superlattice. These remarkable experiments raise the possibility for achieving new magnetic structures on metal surfaces.

The key idea of the experiment of Silly *et al.*[3] is connected to long-range adsorbate interaction mediated by surface-state electrons. The quantum interference between the electron wave traveling towards the scattering defect, for example to an adatom, and the backscattered one leads to standing waves in the electronic local density of states (Fig. 1) and to Friedel-type indirect adsorbate-adsorbate interaction.[4] Recently, low-temperature scanning tunnel microscope (STM) experiments[5,6] and *ab initio* studies[7–9] have resolved substrate-mediated interactions between adatoms. At short distances, the indirect electronic interactions are dominated by a rapidly decaying repulsive part (see Fig. 1). If the thermal energy of adatoms is not sufficient to overcome the repulsive barrier A, the dimers are not formed. In this case, as it was proposed by Knorr *et al.*[6] and proved by experiments of Silly *et al.*,[3] a hexagonal superlattice with the first nearest-neighbor (NN) adatom position corresponding to the first minimum of the interaction energy can be formed.

In this paper, performing state of the art *ab initio* studies, we predict that new magnetic nanostructures and superlattices on Cu(111) can be stabilized by the surface-state electrons. Adatom bonding in these structures is determined by a long-range interaction between adatoms. We reveal that spin-spin correlations at large adatom-adatom separations are caused by surface-state electrons. Our study demonstrates that magnetic states in nanostructures stabilized by surface-state electrons are dominated by an indirect exchange interaction between the magnetic adatoms. Atomic scale simulations show that magnetic superlattices on Cu(111) can be stable up to 25–30 K.

Our *ab initio* studies are based on density-functional theory in the local spin density approximation (LSDA) and the multiple-scattering approach in the framework of the Korringa-Kohn-Rostoker (KKR) Green's function method for adatoms and supported clusters.[9–11] For short and intermediate distances, fully self-consistent total energy calculations are performed to find the interaction energies. However, for large adatom-adatom separations we calculate the interaction energy using the single-particle energies alone, as was proposed by Hyldgaard and Persson.[12] Our studies have shown that such an approach is well justified due to the screening of the Coulomb potentials of adatoms by the substrate electrons. The details of our approach have been given in our previous publications.[9–11,13]

We have performed calculations for the interaction energy between 3*d* adatoms on Cu(111) for adatom-adatom separations up to 50 Å. In all cases we have found that the interaction energy is oscillatory with a period of $\lambda_F/2=15$ Å [$\lambda_F$ is a surface-state Fermi wavelength of Cu(111)] and has the repulsive barrier A (cf. Fig. 1).[14] The first minimum is found to be about 12 Å for all 3*d* pairs. The repulsive barrier B at 19 Å is considerably smaller than barrier A. Therefore, the

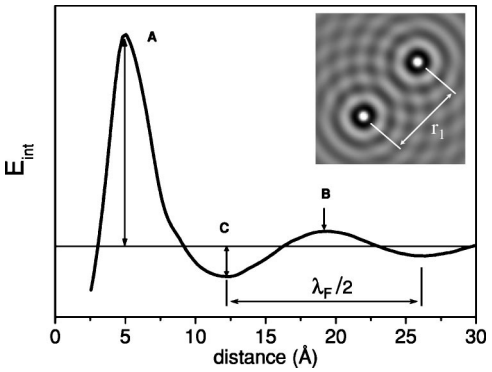


FIG. 1. Schematic description of the interaction energy between adatoms. Such form of the interaction energy has been found in *ab initio* calculations for all 3*d* pairs. Repulsive barriers A and B, and the depth of the potential C for all 3*d* pairs are presented in Table I. The inset shows, as an example, standing waves of the local density of states (LDOS) between the two Co adatoms separated by a distance $r_1$ equal to the minimum of the potential C.

 

TABLE I. Magnetic moments and parameters of the interaction energy.

| Adatom | Ti | V | Cr | Mn | Fe | Co | Ni |
|---|---|---|---|---|---|---|---|
| M ($\mu_B$) | 1.77 | 3.15 | 4.28 | 4.32 | 3.17 | 1.92 | 0.36 |
| A (meV) | 72.4 | 44.1 | 26.4 | 30.5 | 32.2 | 28.3 | 26.5 |
| B (meV) | 0.13 | 0.20 | 0.24 | 0.49 | 0.57 | 0.61 | 0.54 |
| C (meV) | −0.49 | −1.02 | −0.69 | −1.48 | −1.80 | −2.02 | −2.06 |

thermal energy of atoms, even at very low temperatures, may be sufficient to overcome this barrier. Results presented in Table I show that the barrier A and the depth of the potential well change nonmonotonically from the Ti to the Ni.[15] We find that all 3*d* adatoms, except Ni, have large local magnetic moments on Cu(111) (see Table I). The largest moments are found for the Cr and the Mn. If nonspin polarized calculations are performed, the barrier A and the depth of the well C change monotonically among 3*d* adatoms. These results demonstrate that, similar to the direct interaction,[16] the substrate-mediated interaction between magnetic adatoms is affected by magnetism. However, the effect of magnetism is rather weak: the difference between magnetic and nonmagnetic calculations is about 0.1–0.2 meV.

Analysis of experimental results for Ce adatoms on Ag(111) performed in Ref. 3 shows that the first minimum at 32 Å and −0.8 meV depth corresponds to the position of the NN of the hexagonal superlattice. The repulsive barrier A was found to be small, less than 1 meV. Such large distance between adatoms and the small repulsive barrier indicate a very limited range of thermal stability of the hexagonal superlattice. Indeed, the hexagonal Ce superlattice on Ag(111) was reported to be most stable only at 4.8 K. In contrast, our calculations for 3*d* adatoms on Cu(111) show that the binding of adatoms at the separation corresponding to the first minimum of the potential well is considerably stronger. Additionally, the repulsive barriers A for all 3*d* pairs are significantly larger than for Ce on Ag(111). Thus, one can expect that hexagonal nanostructures and superlattices of 3*d* adatoms on Cu(111) with the NN distance at 12 Å may exhibit enhanced stability compared to the Ce superlattice on Ag(111). We will address this problem later in this paper.

Now we turn to the discussion of the magnetic interaction between adatoms on a hexagonal surface. As an example, we present in detail our *ab initio* calculations for the exchange interaction between the two Cr adatoms on Cu(111) for different adatom-adatom separations. Results, shown in Fig. 2, clearly demonstrate that the exchange interaction is oscillatory. Negative energies mean that the spins of both adatoms are ferromagnetically coupled, while positive energies correspond to an antiferromagnetic correlation between spins. We find that for the NN sites (2.55 Å) the two Cr adatoms would like to couple their spins antiparallel to each other. Increasing the distance between adatoms to the second or third NN distances changes the sign of the exchange interactions, i.e., the Cr adatoms at such separations are coupled ferromagnetically.

One very important issue predicted by these results is the possible impact of the adatom-adatom separations on the Kondo effect. Antiferromagnetic coupling between adatoms may yield a net singlet ground state removing the Kondo resonance. Recent experiments of the group of Crommie[17] have raised the possibility to study the evolution of the Kondo resonance as a function of interatomic separations. Therefore, we believe that our results may be further tested by STS experiments at low temperatures.

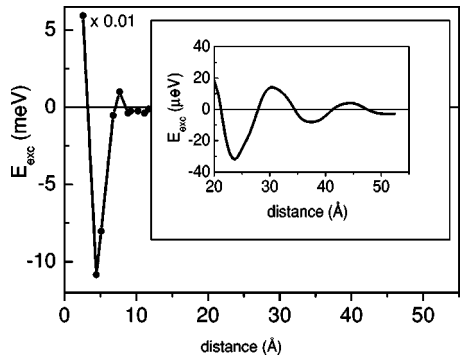


FIG. 2. Exchange interaction between two Cr adatoms. The interaction for the first nearest-neighbor position is considerably larger than for other different positions, therefore, it is scaled by a factor 0.01.

For small separations between adatoms, the direct interaction between spins of adatoms dominates the magnetic interactions. However, if the two adatoms are placed sufficiently far apart, an indirect exchange interaction through the substrate electrons is expected. Here, for the first time, we give clear evidence that the exchange interaction between magnetic adatoms at large distances is caused by surface-state electrons. Results presented in Fig. 2 show that the exchange energy oscillates with a period of 15 Å. In other words, the long-range spin-spin correlations between adatoms are strictly determined by the surface band of Cu(111). We find that the magnitude of the exchange interaction energies asymptotically decays as $1/d^2$. The results presented above demonstrate that spins of adatoms at large distances are coupled by the two-dimensional electron gas at the Cu(111) surface. While predicted surface-state mediated oscillatory exchange interactions are considerably smaller than electronic ones (cf. Table I), they can be studied at very low temperatures.

In order to gain insight into the effect the exchange interaction between adatoms might have on magnetic states of nanostructures and superlattices, we calculate these energies for all 3*d* pairs for the adatom-adatom separation corresponding to the first minimum of the potential (cf. Fig. 1). The results presented in Table II show that, for Ti, V, Cr, and Ni pairs, the magnetic coupling mediated by surface-state electrons is ferromagnetic, while for Mn, Fe, and Co pairs antiferromagnetic states are more stable. These results sug-

TABLE II. Exchange energies for the adatom-adatom distances equal to the first minimum of the potential energy, see Fig. 1.

| Adatom | Ti | V | Cr | Mn | Fe | Co | Ni |
|---|---|---|---|---|---|---|---|
| $E_{exc}$ (meV) | −0.184 | −0.457 | −0.067 | 0.151 | 0.246 | 0.345 | −0.032 |

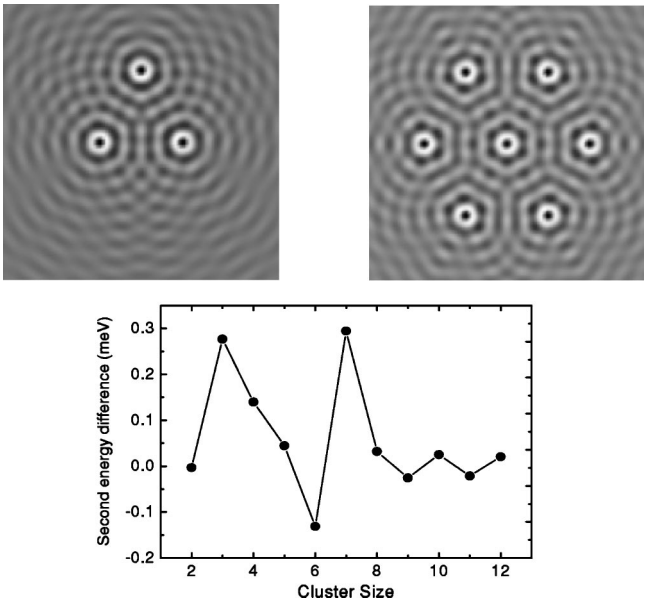


FIG. 3. Second derivative of the binding energy for Fe clusters on Cu(111) stabilized by the surface-state electrons.

gest that nanostructures and superlattices of Ti, V, Cr, and Ni with the period of about 12 Å can be ferromagnetically ordered. However, for Mn, Fe, and Co hexagonal nanostructures magnetic frustration is expected, which can lead to noncollinear magnetic states.[17,18]

An important problem we are going to address next is related to growth and stability of the hexagonal structures of 3*d* adatoms on Cu(111). One of the key assumptions of the classical scenario of growth is that long-range interactions between adatoms can be neglected. However, several theoretical works showed that such interactions can significantly affect the growth of nanostructures.[7,8] Very recent studies of Fichthorn *et al.*[19] and our own calculations[9] have clearly demonstrated that short linear structures on a hexagonal lattice can grow more easily than compact clusters at very low temperatures. The driving force for this preferential growth is associated with the repulsion barrier in the energy of the adatom-adatom interaction at the intermediate distances. This repulsion leads to the self-assembling of adatoms into short chains.[9] As was shown by Fichthorn *et al.*,[19] compact clusters with high symmetry have the highest repulsive barriers and it is increasingly difficult for an adatom to aggregate with a cluster as the cluster size increases. The same is true for linear structures—for example, the repulsion surrounding a linear trimer is greater than that around a dimer.

In view of these results we expect that at very low coverages and low temperatures there are many pairs of adatoms separated by 12 Å. Let us call them "dimers." Binding energies of these dimers are determined by the depth of the minimum of the potential presented in Table I, i.e., they are between 1 and 2 meV. If new adatoms deposited on the surface are far apart from dimers and their thermal energy is sufficient to overcome the repulsive barrier B (cf. Fig. 1) new dimers may be formed. However, if adatoms move towards dimers they are repelled by the repulsive potential and tend to be incorporated to dimers at the end forming linear "trimers" and "tetramers" with the interatomic distance close to 12 Å, i.e., the kinetics, rather than energetics, leads to the formation of linear structures. Knorr *et al.*[6] have indeed observed many short linear chains in their STM experiments on Co/Cu(111).

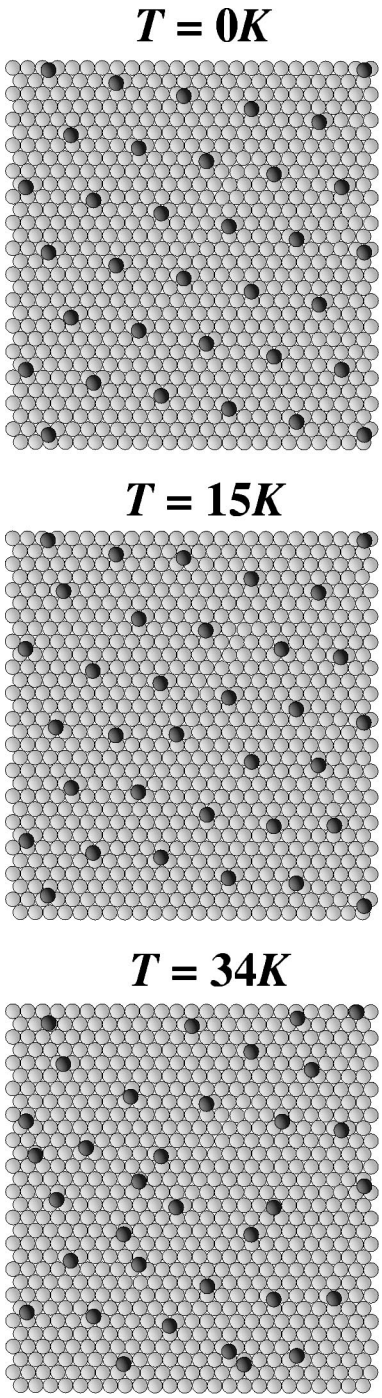


FIG. 4. Thermal evolution of the Fe superlattice.

The relative energetical stability of clusters can be understood in terms of the second derivative of the binding energies: $D_2(N)=E_b(N+1)+E_b(N-1)-2E_b(N)$. A positive peak in $D_2$ indicates that clusters of size $N$ are more abundant than clusters with $N+1$ or $N-1$ atoms. In other words, such calculations allow us to find "magic" clusters stabilized by

surface-state electrons.[20] As shown in Fig. 3, calculated spectrum $D_2$ shows the enhanced stability of clusters of three and seven atoms. These results are supported by recent experiments. For example, the formation of Cu clusters on Cu(111) with a local hexagonal structure and a closest distance between adatoms of about 12 Å has been observed by Repp *et al.*[5] Knorr *et al.*[6] have also detected Co hexagonal islands on Cu(111) with a large bond length. Our results show that in these experiments unusual hexagonal nanostructures have been stabilized by the surface-state electrons.

We want to discuss, finally, the thermal stability of the hexagonal superlattice of *3d* adatoms on Cu(111). As an example, we concentrate on the Fe superlattice on Cu(111). The hexagonal superlattice with the period of 12 Å is constructed covering the entire Cu(111) surface by Fe adatoms. The long-range interaction between adatoms is taken into account using the asymptotic expression of the interaction energy proposed in Ref. 12. For short adatom-adatom separations, the interatomic interactions are well described by potentials formulated in the second-moment approximation of the tight binding (TB) theory.[21] All parameters of interactions are obtained by fitting parameters of potentials to our *ab initio* results for the long-range interactions, forces acting on adatoms, binding energies of supported and embedded clusters, and bulk properties.[21–23]

In Fig. 4 we show the geometry of the superlattice at 0 K. To study the stability of the superlattice we perform MD simulations at different temperatures. Several snapshots showing the thermal evolution of the superlattice are presented in Fig. 4. One can see that at 15 K the thermal energy is still not sufficient to overcome the repulsive barrier of the potential energy, so the superlattice is still stable. We have found that temperature between 25–30 K gives to the adatoms the thermal energy necessary to go beyond the repulsive barrier and to form dimers. At a temperature of about 35 K we observe the disappearance of the superlattice. One should note that results of Silly *et al.*,[3] indicate that sample temperature, low adatom diffusion barrier, and adatom concentration are the key parameters for a successful self-assembly of the superlattice. We believe that future atomic-scale simulations with the adatom-adatom potentials presented in our work will help to find recipes on how to create different magnetic superlattices that will present a new state of matter with fascinating properties.

In summary, we have shown that the adatom-adatom interactions mediated by surface-state electrons can stabilize new magnetic nanostructures and superlattices of *3d* adatoms on Cu(111). Magnetic states in these nanostructures are determined by long-range exchange interactions. Molecular dynamics simulations show that *3d* superlattices can be stable up to 25–30 K. We believe that advanced techniques such as atomic-scale manipulation and the spin-polarized STM may enable researchers to directly study new magnetic nanostructures predicted in this paper.

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[13] Important details of our studies: We take into account that adatoms couple to 3D bulk bands. The full charge density is used in calculations. The atomic sphere and the full potential approximations give essentially the same results for the substrate-mediated interactions. Calculations beyond the LDA, for example, the GGA (generalized gradient approximation), do not affect the interaction energies at large distances. Relaxations of the atomic position of adatoms are performed by calculating the Hellman-Feynman forces in the full-potential approximation. We have not found any substantial effects of relaxations on the substrate-mediated interactions.

[14] We find that the *sp* surface states have a parabolic dispersion relation, described by an onset below the Fermi level at $E_0 = 0.5$ eV and an effective mass $m^* = 0.39 m_e$, see also our results in Ref. 11.

[15] Due to the exchange splitting of potentials of adatoms a non-monotonic behavior for A and C is found; calculations of the LDOS for all *3d* adatoms reveal that for Ti, V, and Cr adatoms the surface-state electrons scatter more strongly at the majority potentials of adatoms, while starting from Mn, the scattering of surface-state electrons by the minority potentials is dominated.

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[18] Frustration can arise due to a close competition between different interactions. A simplest example of local geometrical magnetic frustration is the arrangement of three identical spins on an equilateral triangle for the case of the antiferromagnetic pair coupling between atoms, see Ref. 17. The individual interaction energies of all spin pairing in the structure with the hexagonal short-range order cannot be minimized simultaneously if the pair-wise interactions are antiferromagnetic. We note that magnetic coupling in hexagonal nanostructures stabilized by surface-state electrons is mainly determined by the pair-wise exchange interaction.

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[22] Binding energies of the hexagonal nanostructures calculated by a pair-wise summation are very close to the *ab initio* KKR results taking into account many-body interactions, i.e., the using of the pair-wise approximation is well justified.

[23] We use *ab initio* fitted interatomic potentials because fully *ab initio* calculations of the thermal stability of nanostructures stabilized by surface-state electrons are still out of the possibility of modern computational methods.