Burrowing of Co clusters on the Cu(001) surface: Atomic-scale calculations

V. S. Stepanyuk,[1,2,*] D. V. Tsivline,[3] D. I. Bazhanov,[3,2] W. Hergert,[1] and A. A. Katsnelson[3]
[1]*Fachbereich Physik, Martin-Luther-Universität, Halle-Wittenberg, Friedemann-Bach-Platz 6, D-06099 Halle, Germany*
[2]*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany*
[3]*Solid State Physics Department, Moscow State University, 119899 Moscow, Russia*
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Scenario of burrowing of the Co adatoms and clusters on the Cu(001) is considered. Performing atomic scale calculations we find that the Co/Cu interface is stabilized when the Co clusters reside in the surface layer. We demonstrate that coating the Co islands with the Cu substrate material leads to large capillary forces, which promote burrowing. A vacancy mechanism of burrowing is discussed. The effect of magnetism on the atomic relaxations at the Co/Cu interface is revealed.

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Recent experimental studies have demonstrated that the place-exchange processes can result in the formation of surface alloys even for metals immiscible in bulk form. For example, it was concluded that Co and Fe atoms intermix with Cu on the Cu(001) surface.[1,2] Similar results were obtained for Fe/Ag(001),[3] Fe/Au(001),[4] Cr/Fe(001),[5] and Rh/Ag(001) (Ref. 6) interfaces. Common to all these findings is the tendency for the adsorbate atoms to replace substrate atoms within the top atomic layer. Embedded atoms can form clusters[1] or disordered surface alloys.[7] Tersoff showed that surface-confined intermixing arises in systems dominated by atomic size mismatch.[8] Both kinetics and energetics determine the structure of the interface. In the case of transition-metal heteroepitaxy the alloying at the interface can strongly influence magnetic properties.[9]

One of the most striking features of the interface mixing has been discovered in the last year.[10,11] Zimmermann *et al.*[10] have found that Co particles burrow into clean Cu(001) and Ag(001) substrates at 600 K, while no burrowing was observed at room temperature. Padovani *et al.*[11] have reported that cobalt clusters burrow themselves into the Au(111) surface at a temperature about 450 K. These experiments have revealed a novel mechanism of mass transport in transition-metal heteroepitaxy, which can lead to surface smoothing and can have a strong impact on magnetic properties at the interface. It was suggested[10] that burrowing may occur in many systems where the adsorbates have significantly higher surface energy than the substrate. It was also demonstrated that burrowing is fundamentally different from the capping behavior. However, an argument based on such macroscopic properties as surface and interface energies of components are rather questionable when applied to individual adatoms and small clusters on metal surfaces. It is important to note that cohesive energies of components are often not appropriate to predict surface-confined intermixing. For example, an intermixing at Au/Ni(001),[12] Ag/Pt(111),[13] and Cr/Fe(001)[14] interfaces cannot be described in terms of cohesive energies of bulk materials. Therefore, theoretical investigations of surface intermixing on an atomic scale are of fundamental interest.

The main goal of this paper is to give insight into the mechanism of burrowing on an atomic scale. Performing atomic scale simulations we find a strong tendency for the embedding of the Co clusters into the Cu substrate. The coating of the Co clusters with the substrate material is found to be energetically favorable and leads to a large pressure at the bottom interface of the cluster. The vacancy mechanism of burrowing is proposed. We demonstrate that magnetism has a strong effect on the atomic relaxations at the Co/Cu interface and promotes burrowing.

Atomic scale simulations are performed using a quasi–*ab initio* molecular-dynamics method.[15] This approach is based on fitting the many-body potentials at the Co/Cu interface to accurate first-principle calculations of selected cluster-substrate properties. The potentials are formulated in the second moment tight-binding approximation. The cohesive energy E_{coh} is the sum of the band energy E_B and the repulsive part E_R:

$$E_{coh}=\sum_i (E_R^i+E_B^i), \tag{1}$$

$$E_B^i=-\left\{\sum_j \xi_{\alpha\beta}^2 \exp\left[-2q_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}}-1\right)\right]\right\}^{1/2}, \tag{2}$$

$$E_R^i=\sum_j \left[A_{\alpha\beta}^1\left(\frac{r_{ij}}{r_0^{\alpha\beta}}-1\right)+A_{\alpha\beta}^0\right]\exp\left[-p_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}}-1\right)\right], \tag{3}$$

where r_{ij} represents the distance between atoms i and j, and $r_0^{\alpha\beta}$ is the first-neighbor distance in the $\alpha\beta$ lattice structure, while it is just an adjustable parameter in the case of the cross interaction. ξ is an effective hopping integral that depends on the material, and $q_{\alpha\beta}$ and $p_{\alpha\beta}$ describe the dependence of the interaction strength on the relative interatomic distance.

The first-principle Korringa-Kohn-Rostoker (KKR) Green's-function method[16] is applied to calculate binding energies of small Co clusters on the Cu(001), which are used in fitting of interatomic potentials. Magnetic effects are included implicitly performing the spin-polarized calculations for all clusters. Several applications of this method, the parameters of the potentials, and the computational details have been presented in our recent publications.[15,17]

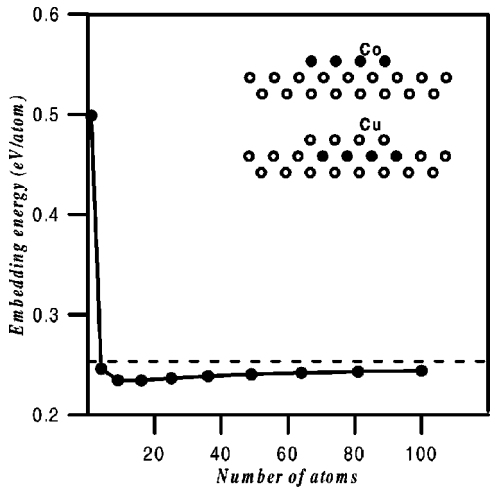

FIG. 1. Embedding energies of the Co square islands on Cu(001); the dashed line corresponds to results for the Co monolayer.

In surface calculations periodic boundary conditions are employed in two orthogonal directions in the plane. No periodic boundary conditions are applied in the direction perpendicular to the plane. The slab representing the substrate is 12 layers thick with 2000 atoms per layer. The two atomic layers are fixed at the bottom. Starting from a terminated bulk configuration, we find a total potential energy minimum of Cu(001) surface by employing the conjugate gradient method. The two-dimensional (2D) Co clusters are formed on the relaxed substrate and the whole system (surface with clusters) is relaxed again.

Molecular-dynamics simulations at various temperatures are performed in the microcanonical ensemble. The equation of motion is integrated by means of the Verlet algorithm. The system is equilibrated at a desired temperature during 50 000 time steps (250 ps).

First, we concentrate on the molecular static calculations of the embedding energy for Co clusters on the Cu(100) surface. We have found that the substitution of a Cu substrate atom with the Co adatom significantly lowers the energy of the interface. Figure 1 summarizes the calculated energy differences for the plane square islands. For large islands the structures embedded in the substrate and adsorbed on the surface are closer in energy compared to a single adatom. The relaxation of edge atoms of the islands is a dominating process only for small islands. With the increasing island size the effect of edge atoms becomes less important and the curve in Fig. 1 approaches the embedding energy for the Co monolayer. One should note that our definition of the embedding energy does not include the additional energy gain due to the possible adsorption of the Cu atoms at a step, since we are interested only in the exchange probability for the islands on the terrace, which is considered as infinitely large. It is necessary to note that the Co islands embedded in the Cu substrate and coated with the Cu atoms can also be formed due to the exchange processes for single Co atoms which prefer to form clusters in the surface layer and act as pinning centers for further adsorption of Cu (and Co) atoms.[15] Regardless of the mechanism of the formation,

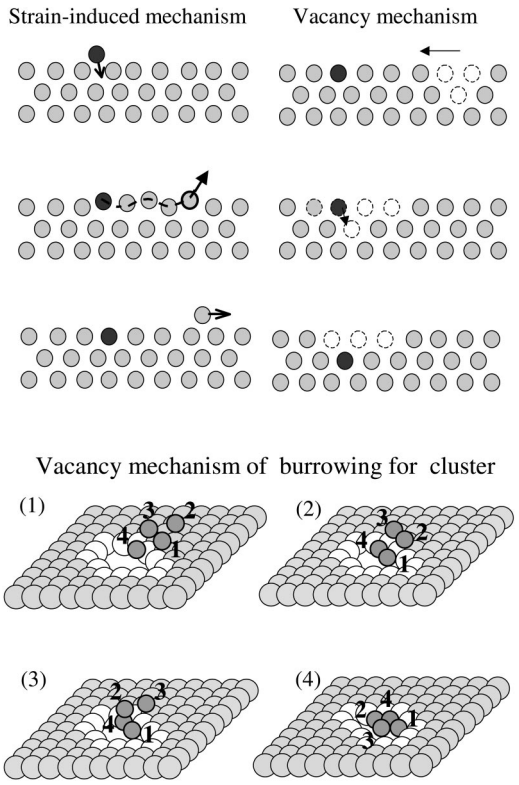

FIG. 2. Strain-induced and vacancy mechanism of burrowing for adatoms and clusters on Cu(001).

it appears that the Co islands embedded in the substrate are energetically favorable compared to the clusters adsorbed on the surface.

Our *ab initio* KKR calculations showed that the Co adatoms and the Co clusters are magnetic on Cu(001).[15,16] To understand the influence of magnetism on the exchange process at the Co/Cu interface, we performed the KKR calculations of the embedding energy for hypothetical nonmagnetic Co adatoms on Cu(001). We found that in this case the gain of energy due to intermixing for a single nonmagnetic Co adatom with a Cu substrate atom is 1.15 eV, which is considerably larger than for a magnetic Co atom (0.5 eV, cf. Fig. 1). Thus, magnetism tends to stabilize Co adatoms and clusters on Cu(001) and to prevent intermixing. Similar effects were found for different transition metal monolayers on noble-metal substrates.[18]

Let us consider the possible scenario of burrowing. According to Ref. 10 the burrowing time at room temperature is of the order of months, while this is less than 100 s at 600 K. The time scale of molecular-dynamics (MD) simulations is much shorter than the time used in the real experiments. Therefore it is unlikely to observe burrowing of large Co islands in MD simulations. Due to this reason we concentrate on burrowing of a single Co adatom and small Co clusters, which is easily observed in our calculations. The MD simulations are performed at 800 K. We find that there are two possible paths for a Co adatom to exchange its place with a Cu substrate atom. The first exchange mechanism is based on the strain-induced model.[19] The scenario of the strain-induced exchange is shown in Fig. 2. The Co adatom enters

into the substrate and introduces strain. Due to the strain propagation in the top surface layer, one or two Cu substrate atoms are pushed out from the surface and the strain is relieved. The second mechanism of burrowing into the first surface layer is based on diffusion of vacancies or vacancy clusters. If place-exchanges occur at many surface sites the vacancies can be created.[20] Once the vacancies are formed, they can diffuse and agglomerate to form vacancy clusters. We have observed that the vacancies and the vacancy clusters diffuse to the Co adatoms (and to Co clusters) to reduce the local stress. The vacancy becomes filled by a Co atom (cf. Fig. 2). Burrowing into the second surface layer proceeds by the diffusion of a vacancy cluster as demonstrated in Fig. 2.

We have easly observed in our MD calculations the burrowing of small Co islands into the Cu substrate due to the vacancy mechanism. Figure 2 demonstrates such a mechanism for the plane island of the four Co atoms. Our results show that burrowing is a collective atomic process, rather than a motion of individual atoms. We found that the burrowing of small Co clusters is initiated by the shear motion of a dimers belonging to the Co island. Recently, dimer shearing has been discovered in cluster diffusion on metal surfaces.[21]

First (cf. Fig. 2), the dimer 3-4 diffuses to the vacancy cluster and the vacancy is filled by the atom 4; then, the second dimer 1-2 follows the motion of the first dimer and the second vacancy is filled by the atom 1; finally, the motion of the dimer 2-3 to the vacancy cluster is observed through a crisscross configuration.

Padovani *et al.*[11] suggested that propagation of vacancies along the interface can drive burrowing. The above results support such a mechanism of burrowing.

The central concept used in the experiments to explain the burrowing of Co clusters is based on the following ideas:[10] the coating of the Co particles with the Cu atoms occurs; the extremely large capillary forces act on the Co particles.

In order to test these assumptions we perform the energy calculations and find that the coating is energetically preferable being the result of a higher cohesive energy of the Co compared to the Cu. In fact, the coating is similar to a ''surfactanlike'' behavior which was recently investigated.[22]

Figure 3 shows that the coating significantly increases the pressure at the bottom interface of the Co islands and can promote burrowing, as was suggested in Ref. 10.

The following important questions arrise: What is the role of magnetism in the burrowing of Co clusters into the Cu substrate? Does magnetism have any influence on the structure of the Co/Cu interface? To answer these questions, first we performed *ab initio* KKR calculations for hypothetical nonmagnetic Co clusters on Cu(001). We found that binding energies in the nonmagnetic clusters are reduced compared to the magnetic ones. As an example, in Table I we present binding energies of magnetic and nonmagnetic Co clusters on an ideal Cu(001) surface. Second, many-body potentials for nonmagnetic Co clusters on Cu(001) are constructed by fitting the parameters of the potential (1-3) to the binding energies of different nonmagnetic Co clusters on Cu(001) (linear chains and plane islands up to nine atoms, and embedded nonmagnetic clusters).[15] We find that in the hypotetical nonmagnetic case the pressure on the Cu substrate atoms under the Co clusters is reduced by $\approx 30\%$ compared to the magnetic case (cf. Fig. 3). This result indicates that magnetism has a profound effect on burrowing.

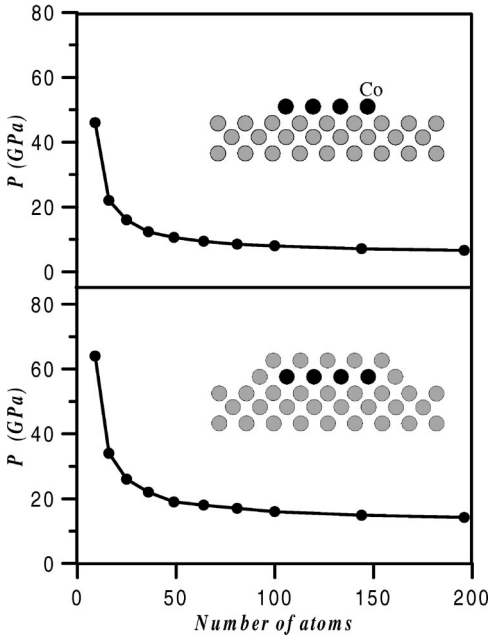

FIG. 3. Pressure under the Co square plane islands.

In order to get a deeper insight into the effect of magnetism on burrowing we calculate the displacement of atoms in the Co islands and the Cu substrate in both magnetic and nonmagnetic cases. Recently, we demonstrated that the Co islands and the Cu surface under the islands are not flat due to the strain relief.[25] In Fig. 4, as an example, we present the vertical displacement of Co atoms in the square island of 36 atoms and the surface atoms in the topmost layer under the island for the magnetic and nonmagnetic cases. The deformation of the substrate is found to be larger for the magnetic Co cluster. Both magnetic and nonmagnetic Co clusters are not flat. The interaction between atoms in the magnetic cluster is stronger than in the nonmagnetic one (cf. Table I) which leads to a significant ''bending'' of the magnetic cluster.

Additionally, the following two factors influence atomic relaxations in magnetic clusters: the coordination number and the magnetic energy. The closer the cluster is to the substrate, the larger the average coordination number is and the smaller the gain in magnetic energy is. The competition

TABLE I. Binding energies of magnetic and nonmagnetic Co clusters on the Cu(001).

	Magnetic Co E (eV)	Nonmagnetic Co E (eV)
Dimer	−1.04	−0.88
Trimer	−2.06	−1.72
Island	−3.84	−3.58

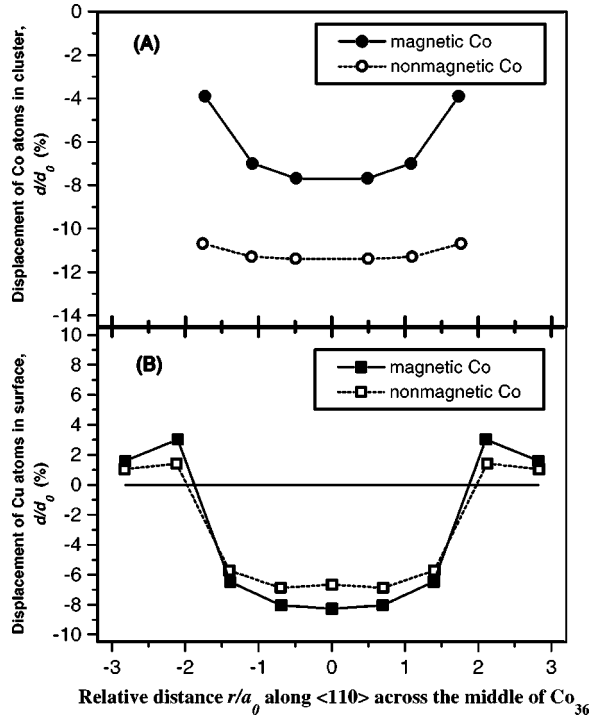

FIG. 4. The vertical displacement of atoms in the Co_{36} square island (*A*) and the surface atoms (*B*) in the topmost layer under the island; interlayer distance $d_0 = 1.8075$ Å and lattice constant $a_0 = 3.615$ Å. Magnetic and hypothetical nonmagnetic Co islands are presented.

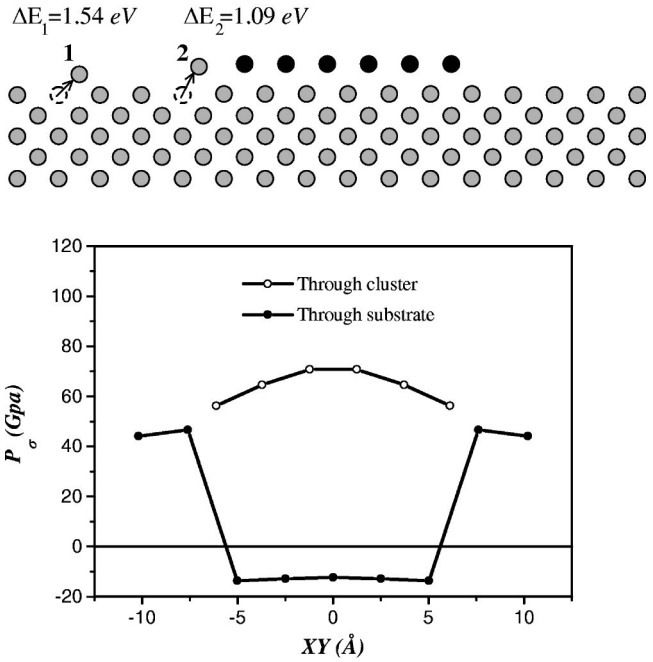

FIG. 5. Stress distribution at the Co/Cu interface for the Co_{36}. Energy barriers for vacancy formation on a flat substrate (1) and near the edge of the Co_{36} cluster (2) are shown.

to gain magnetic energy between atomic relaxations with larger coordination numbers and atomic relaxations with smaller coordination numbers determines the atomic structure of magnetic clusters in a fully relaxed geometry. In nonmagnetic clusters the scenario of atomic relaxations is determined by increasing their coordination number. This should favor the displacement of atoms in the nonmagnetic cluster towards the substrate. Such effect is well seen in Fig. 4: the nonmagnetic Co cluster is considerably closer to the substrate than the magnetic one. The competition between Co-Co and Co-Cu interaction in the nonmagnetic cluster is also a driving force for the atomic relaxations. In both magnetic and nonmagnetic Co clusters Co-Co interaction is stronger than Co-Cu. Therefore, the magnetic and nonmagnetic clusters assume a ''platelike shape,''[25] while the bending of the nonmagnetic cluster is considerably reduced. Thus, the magnetism tends to increase the curvature of the clusters and the substrate and leads to a higher pressure under the cluster.

Finally, we turn to the stress distribution in the Co islands and the uppermost Cu substrate layer. We perform calculations of the atomic level stress components[23]

$$\sigma_{\alpha\beta}(i) = -\frac{1}{\Omega_0}\left[\frac{p_i^\alpha p_i^\beta}{m_i} + \frac{1}{4}\sum_j (r_{ij}^\beta f_{ij}^\alpha + r_{ij}^\alpha f_{ij}^\beta)\right], \qquad (4)$$

where $(\alpha\beta) \equiv (x,y,z)$, m_i and $\vec{p}_i$ are the mass and momentum of atom i, $\vec{r}_{ij}$ means the distance between atom i and j, and $\vec{f}_{ij}$ is the force acting on atom i due to j; Ω_0 defines the average atomic volume.

Figure 5 shows the atomically resolved hydrostatic stress $P_\sigma = \mathrm{Tr}(\sigma_{\alpha\beta})$ at the Co/Cu interface. The Co_{36} island coated with the Cu is considered as an example. One can see that the substrate layer under the island exhibits compressive stress, while at the edge, the stress is highly tensile. The inhomogeneous stress distribution in the substrate can affect an atom motion near the Co island. For example, we find that the vacancy formation barrier is drastically reduced near the cluster edge compared to a flat substrate (cf. Fig. 5).

To understand these results we recall the recent calculations of atom diffusion on strained surfaces.[24,26,27] It was demonstrated that when the corrugation of the potential acting on atoms on a surface increases, the barrier for the exchange diffusion decreases. However, it is important to note such simple interplay between stress and diffusion is not always valid.[28].

In our case, similar to Refs. 24, 26, and 27, the increased tensile stress at the edge of the island reduces the exchange barrier. Thus, vacancies can be formed near the Co islands promoting burrowing. We expect that higher growth temperatures may activate diffusion of the most highly strained substrate material to regions of lower strain. Such mechanism has been recently observed in Ge/Si(100) islands.[29] It was reported that due to the strain-relief mechanism trenches in the Si substrate at the base of the Ge island are formed. It is important to note that the vacancy mechanism of burrowing found in the present work is similar to the results obtained for the incorporation of Mn atoms at steps on a Cu(001).[30] Also, it was suggested that vacancy segregation should favor exchange at the Ni/Ag interface.[31]

In summary, we have found that Co clusters lower the

energy of the total system when they are embedded in the Cu substrate. The coating of the Co clusters with substrate material leads to a large pressure at the interface and can promote burrowing. The vacancy mechanism is proposed to explain burrowing. Magnetism has a strong effect on the shape of Co clusters and leads to a strong enhancement of the pressure at the interface promoting burrowing.

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*Email address: stepan@valinux.physik.uni-halle.de

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