Magnetism and structure on the atomic scale: Small cobalt clusters in Cu(001)

Š. Pick,[1] V. S. Stepanyuk,[2,*] A. L. Klavsyuk,[3] L. Niebergall,[2] W. Hergert,[3] J. Kirschner,[2] and P. Bruno[2]
[1]*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-182 23 Prague 8, Czech Republic*
[2]*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*
[3]*Fachbereich Physik, Martin-Luther-Universität, Halle-Wittenberg, Friedemann-Bach-Platz 6, D-06099 Halle, Germany*
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The interplay between structure and magnetic properties of small cobalt clusters embedded in a Cu(001) surface is studied performing *ab initio* and tight-binding calculations in a fully relaxed geometry. We reveal that, despite the small macroscopic mismatch between Co and Cu, the strain relaxations at the interface have a profound effect on the structure of the clusters and the substrate. The physical mechanism responsible for the strain relaxations in embedded clusters is related to the size-dependent mesoscopic mismatch which has been recently introduced to understand homo- and heteroepitaxial growth at the mesoscale [O. V. Lysenko *et al.*, Phys. Rev. Lett. **89**, 126102 (2002)]. We show that the atomic relaxations strongly reduce the magnetic anisotropy energy (MAE) and the orbital magnetic moments of embedded clusters. The largest MAE of about 1.8 meV is found for a single Co atom in the Cu(001) surface. A strong enhancement of the spin magnetic moments in embedded clusters as compared to a single atom of Co incorporated in the Cu(001) surface is found. Magnetic properties of embedded and supported clusters are compared. While in supported clusters the MAE is strongly enhanced at the edge atoms, the immersion of the cluster into the surface and atomic relaxations make the distribution of the local MAE contributions and orbital-moment values almost homogeneous.

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I. INTRODUCTION

Recent remarkable experiments on small magnetic clusters on metal surfaces have opened up unprecedented opportunities for atomic engineering of new magnetic materials.[1–6] By increasing the cluster size in an atom-by-atom fashion, Gambardella *et al.*[1] have studied how the magnetization and the magnetic anisotropy energy (MAE) develop in cobalt nanoparticles on Pt(111). They have reported the MAE of 9 meV for single cobalt adatoms, which is about 200 times larger than that of cobalt atoms in a bulk crystal. The larger the MAE, the more stable is the magnet. These results suggest that only a few hundred atoms would be needed to make a stable magnetic bit. Experiments of the group of Crommie[2] have raised the possibility to study the Kondo effect in small clusters and interactions between magnetic adatoms. Very recently the superlattice of magnetic adatoms has been created by Schneider *et al.*[3] by exploiting the surface-state mediated long-range adsorbate interactions.[6] Rusponi *et al.*[4] have revealed that the MAE in supported clusters is nearly exclusively caused by the edge atoms alone. This finding opens new possibilities to tune the magnetic anisotropy and moment of nanostructures. The central role that have the edge cluster atoms in the MAE indicates that it could be possible to reduce the cluster size without running into the superparamagnetic limit and to use small clusters for single-bit magnetic data storage. The existence of both short- and long-range ferromagnetic order for finite monoatomic cobalt chains on a Pt substrate was reported by Gambardella *et al.*[5] It has been found that by decreasing the coordination of the magnetic atoms, values of the MAE are obtained that are two orders of magnitude larger than those in bulk. These results confirm the theoretical prediction of Dorantes-Dávila and Pastor about a strong enhancement of the MAE in the 3*d* transition-metal chains.[7] The first calculations for adatoms and small clusters on metal surfaces[8–10] have found very large orbital moments and MAE.

The above mentioned experiments require low operating temperature down to several tens of Kelvins or even lower. With increasing temperature adatoms and small clusters would become unstable due to the thermally enhanced surface diffusion and the interfacial intermixing may take place. Atomic exchange processes for single adatoms and burrowing of clusters into the substrate have been reported in several experiments and calculations even for metals immiscible in the bulk.[11–13] Experiments of Kurnosikov *et al.*[14] have shown that it is possible to manipulate single atoms of Co embedded into a Cu(001) surface with scanning tunneling microscopy (STM) tip and to create in a controlled way small clusters which are stable at room temperature. In very recent scanning tunneling spectroscopy (STS) studies of Quaas *et al.*,[15] the Kondo resonance was revealed on single Co atoms embedded in the Cu(111) substrate. The Kondo temperature was reported to be about 400 K which is significantly higher than for Co adatoms.[16] We believe that the above experiments will undoubtedly stimulate experimental and theoretical studies of small clusters in subsurface layers. To the best of our knowledge there have been only a few calculations of magnetic properties of surface embedded clusters. For example, Klautau and Frota-Pessôa[17] have performed an *ab initio* study of spin magnetic moments of nonrelaxed Co agglomerates of different sizes and shapes embedded in Cu(001). They have found that the variation of the local moments in the clusters is mainly governed by the position of the site relative to the surface and the number of Cu neighbors. *Ab initio* calculations[18] have demonstrated that

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the coating of the Co clusters by Cu atoms strongly reduces spin magnetic moments. Robles *et al.*[19] have shown by performing a self-consistent tight-binding study that, unlike the free clusters, magnetic Co clusters embedded in Cu do not exhibit "magnetic magic numbers," i.e. their spin magnetic moments per atom decrease essentially monotonically as cluster size increases. There are also some reports of calculations of magnetic moments of cobalt clusters embedded in a copper matrix.[20–23]

Our goal in this work is to present *ab initio* and tight-binding (TB) calculations of spin and orbital magnetic moments, and MAE for small Co clusters embedded into the Cu(001) surface in a fully relaxed geometry. To the best of our knowledge, for the first time we demonstrate how embedding and atomic relaxations at the Co-Cu interface affect magnetic properties. We show that the mesoscopic relaxations in the island and the substrate lead to a strongly inhomogeneous strain distribution at the interface which is determined by the size-dependent mismatch. We discover that the mesoscopic relaxations strongly reduce the MAE and orbital magnetic moments. In contrast to supported clusters,[10] the MAE of the edge atoms and the central atoms of embedded clusters are close. The largest MAE and orbital magnetic moment are found for a single Co atom in Cu(001), and they strongly decrease in small clusters.

II. COMPUTATIONAL METHODS

For *ab initio* calculations of electronic states and spin magnetic moments of embedded clusters we apply the Korringa-Kohn-Rostoker (KKR) Green's function method in the full potential approximation.[24] This approach is also used to construct interatomic potentials for atomic-scale relaxations and to fit the TB parameters for calculations of the MAE and orbital moments of embedded clusters in a fully relaxed geometry.

In the KKR Green's function method the surface is considered as a two-dimensional perturbation of the bulk. First, we calculate the structural Green's function of the ideal surface by solving the Dyson equation self-consistently. 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 self-consistent calculation of the Green's function of clusters on(in) the surface using an algebraic Dyson equation:

$$G_{LL'}^{nn'}(E) = \mathring{G}_{LL'}^{nn'}(E) + \sum_{n''L''} \mathring{G}_{LL''}^{nn''}(E)\Delta t_{L''}^{n''}(E) G_{L''L'}^{n''n'}(E), \quad (1)$$

where $G_{LL'}^{nn'}(E)$ is the energy-dependent structural Green's function matrix and $\mathring{G}_{LL''}^{nn''}(E)$ 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 clusters. The Green's function of embedded clusters is used to find the local density of states (LDOS), spin magnetic moments, charge density, total energy and the Hellmann-Feynman (HF) forces acting on atoms in clusters.

Atomic relaxations in clusters and the substrate are performed with *ab initio* based n-body interatomic potentials formulated in the second moment tight-binding approximation.[25]

The band energy (attractive term) E_B^i contains many-body interactions. The repulsive term E_R^i is described by pair interactions (Born-Mayer form). The cohesive energy E_{coh} is the sum of band energy and repulsive part:

$$E_{coh} = \sum_i (E_R^i + E_B^i), \quad (2)$$

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

$$E_B^i = -\left(\sum_j \xi_{\alpha\beta}^2 \exp\left(-2q_{\alpha\beta}\left(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1\right)\right)\right)^{1/2}, \quad (4)$$

r_{ij} is the distance between the atoms i and j. $r_0^{\alpha\beta}$ is the first neighbors distance in the crystalline structures of pure metals for atom-like interactions and becomes an adjustable parameter in the case of different atom interaction. ξ is an effective hopping integral; $p_{\alpha\beta}$ and $q_{\alpha\beta}$ describe the decay of the interaction strength with the distance of the atoms.

In the last decade a number of new schemes to construct interatomic potentials from a large amount of data produced by first-principle calculations have been developed.[26] They have significantly increased the range of systems and types of process that can be studied in material science. In the present work we use the KKR Green's function method to construct the interatomic potentials. It is important to include in fitting data relative to different geometries and physical situation (supported and embedded clusters, bulk, defects, etc.) to achieve a good potential transferability.[26,27] Parameters of potentials are fitted to *ab initio* spin-polarized calculations of binding energies of supported and embedded clusters of different sizes and geometries, and to the HF forces acting on adatoms on the surface. To link the interaction between atoms near the surface to that in the bulk the set of data used for fitting includes such bulk properties as bulk modulus, lattice constant, the solution energy of a single Co impurity in bulk Cu, energy of interaction of two Co impurities in Cu bulk, cohesive energy and elastic constants.[25,27] The interatomic potentials based on fitting to an *ab initio* database for surface and bulk properties can be used for the calculations of supported and embedded clusters on the same footing. Our very recent studies have demonstrated that atomic relaxations in magnetic supported clusters calculated fully *ab initio* and determined using our interatomic potentials are in very good agreement mutually.[28] Thus, we believe that the interatomic potentials constructed by fitting to an *ab initio* data pool can be used to find an equilibrium structure of clusters and the substrate. The combination of *ab initio* and TB methods allows one to construct many-body potentials for low-dimensional structures and to perform atomic relaxations for very large systems which still are out of possibilities of *ab initio* methods. Parameters of potentials and several applications of our approach can be found in the recent publications.[25,29–32] The relaxed atomic configuration of the cluster and the substrate is used to perform *ab initio*

self-consistent calculations by means of the full potential KKR Green's function method.

The electronic TB calculations are similar to those described in Ref. 10. The semi-empirical $s+d$ electron Hamiltonian parameters are checked to reproduce a number of literature data and finally are fitted to KKR results (LDOS, spin magnetic moments) for Co clusters embedded into the Cu(001) surface. The self-consistent adjustment of parameters is performed for 11 nonequivalent atoms containing the Co cluster and Cu atoms in its neighborhood (57 atoms altogether); for more distant Cu atoms, values derived for semi-infinite Cu(001) are taken. The evaluation of the LDOS is performed by the standard recursion-method[33] technique with modifications appropriate[34] for models including the spin-orbit coupling.

For nonhomogeneous systems with high peaks in the LDOS at the Fermi level E_F a large number of moments might be necessary[10] to obtain accurate values of such a small quantity as is the MAE. We employ 600 moments (300 levels of the continued fraction) to construct the LDOS in final evaluations. To make the calculation feasible, the semi-infinite fcc(001) crystal is approximated by a 6-layer slab with 49×49 atoms in each (001) layer. For these calculations, Coulomb integrals (diagonal matrix elements of the Hamiltonian) on all Co atoms are carefully recalculated to ensure the postulated d-electron occupation.

The local electronic contribution to the MAE is expressed as the difference of band energies corresponding to the perpendicular and in-plane direction of magnetic moments, respectively. Let us begin our considerations with the (local) one-electron band energy:

$$E_{band}(E_F) = \int^{E_F} E\rho(E)dE. \tag{5}$$

Above, $\rho(E)$ is LDOS at site i. (For the sake of simplicity we omit the site index i.) Although the self-consistent Coulomb integrals are well adjusted for the perpendicular orientation of the magnetic moment, the local charge changes by δq (which is usually a small quantity) when the magnetic moment becomes parallel to the surface. It is easy to see that to the 2nd order in δq the correction to band energy reads[10] as

$$\delta E_{band}(E_F) = E_F\delta q + 0.5(\rho(E_F))^{-1}\ \delta q^2. \tag{6}$$

Indeed, $dE_{band}/dq=(dE_{band}/dE)(dq/dE)^{-1}=E_F$ at $E=E_F$. Similarly, $d^2E_{band}/dq^2=dE_F/dq=(dq/dE_F)^{-1}=(\rho(E_F))^{-1}$. The term linear in δq in Eq. (6) represents the content of the well-known force theorem: one calculates the band-energy difference for two systems that differ by a small perturbation. The change of E_F and of atomic potentials are neglected, but the error in the charge is compensated by changing the multiplier E into $(E-E_F)$ in the integrand in Eq. (5). The quadratic corrections in Eq. (6) are easily incorporated into the computer code and their values give some idea about the accuracy of results. Let us stress that they are not used to reach an unjustified "extremely high" accuracy but to avoid gross error for non-negligible δq. In our calculations, δq (in absolute value) does not exceed 0.05 and is typically about 0.03 at noncentral atoms in Co clusters. By similar manipulations, also corrections of first-order in δq to magnetic orbital-moment values have been introduced.[10] As compared with the Co clusters *above* the Cu surface,[10] the "new" corrections are a good deal less important here even for the case of a single Co atom.

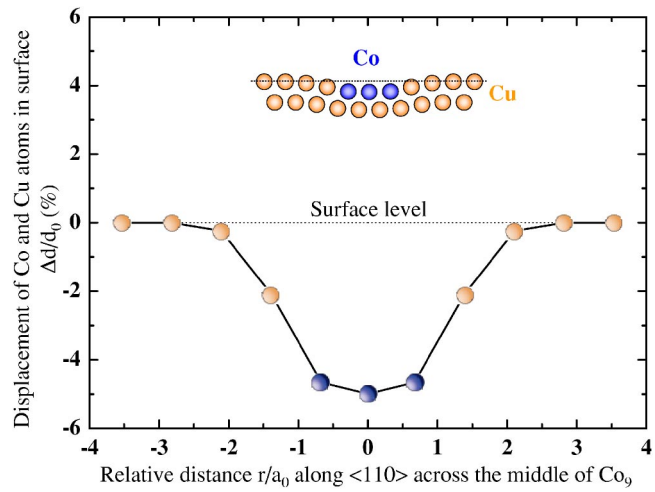

FIG. 1. (Color online). The shape of the embedded Co_9 island and the Cu substrate; vertical displacements in the island and the Cu(001) substrate across the (110) direction are shown; interlayer distance $d_0=1.8075$ Å and lattice constant $a_0=3.615$ Å; the surface level corresponds to the atomic position of the relaxed Cu(001) surface without the Co cluster

III. RESULTS AND DISCUSSION

First, we discuss strain relaxations in embedded Co islands and the Cu surface.

It has been believed that strain relaxations at the Co/Cu interface are determined by the small mismatch which is only ≈2%. However, as we have recently shown,[29,31,32,35,36] if the deposited system is of mesoscopic size, its intrinsic bond lengths are different from the bond length in the bulk and the strain effects at the mesoscale cannot be predicted from the macroscopic lattice mismatch. Even in homoepitaxy the island growth can be drastically influenced by mesoscopic strain relaxations. It has been demonstrated that the mesoscopic mismatch between small Co islands and the Cu substrate is considerably larger than the mismatch calculated from the lattice constants of the two materials and depends on the size of islands. Therefore, the strain induced at the interface can locally be larger and may more strongly affect structural, electronic and magnetic properties, than expected. Recent atomic scale calculations and stress measurements have revealed that the size-dependent mismatch between Co islands and the Cu substrate leads to stress oscillations in a growing Co film.[37]

To give a demonstration of the impact of the mesoscopic mismatch on the structure of the Co/Cu interface, we show in Fig. 1, as an example, the shape of the Co_9 island and the substrate in the fully relaxed geometry for the cluster and the substrate atoms. The vertical displacements at the interface

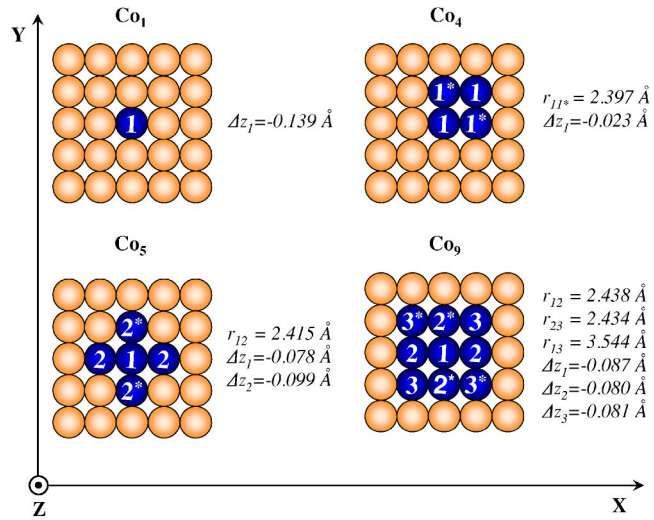

FIG. 2. (Color online) The bond lengths r_{ij} in embedded clusters and the vertical displacement Δz relative to the clean surface. The bond length in the ideal structure is 2.556 Å. The asterisk (*) is used to distinguish atoms $n=1-3$ that become nonequivalent for an in-plane magnetization orientation. In that case, the atomic couple n-n is oriented parallel and n^*-n^* perpendicularly to magnetization.

are presented in Fig. 1 and demonstrate that due to the strain relaxation the substrate and the island atoms are pushed down. The edge atoms in the Co island are highest. These results reveal that the island and the surface layers are not flat. The island locally distorts the surface and induces a strongly inhomogeneous displacement pattern in the substrate. None of the above results could be predicted by the classical theory of cluster growth based on the macroscopic lattice mismatch which is small in the present case. The size-dependent mismatch between Co islands and the substrate determines unusual strain relaxations at the interface.[29] For example, our studies showed that for small Co clusters the mesoscopic mismatch can be as large as 8–9%[29] and it decreases as the size of the clusters increases. In other words, atomic displacements at the interface depend on the size of the island.

In Fig. 2 we present atomic bonds and the vertical displacements (with respect to the clean surface) of small Co clusters embedded in Cu(001). One can see that the largest vertical relaxation is found for the single Co atom in Cu(001), i.e. the Co atom enters into the substrate deeper than the clusters. One of the reasons for this effect is that an attractive interaction between atoms in Co clusters weakens their bonds to the surface and with increasing size, the embedded clusters approach the surface layer. However, similar to results of Bogicevic[38] for ad-clusters, only the rebonding view would be oversimplified in our case, because cluster and substrate relaxations strongly determine the positions of clusters in the surface and their bonds. Due to the atomic relaxations in the substrate the bond lengths in small clusters and the position of clusters in the surface layer do not change notably with an increase the size.

Now we turn to the discussion of the magnetic properties of embedded clusters. Our results for the MAE of a single Co atom and the average MAE for Co_4, Co_5 and Co_9 clusters in the Cu substrate are shown in Table I for the ideal and fully relaxed geometries.[39] In all cases, the MAE prefers the in-plane orientation of the magnetic moment. We present only the electronic part of the anisotropy energy, because the shape anisotropy originating from dipole-dipole interactions is very small for small clusters, e.g. 0.03 meV/atom for the nine-atom cluster. Our results clearly demonstrate that the atomic relaxations in embedded clusters and the substrate strongly reduce the MAE (Table I). The largest effect is found for the single Co atom and the Co_4 cluster which exhibit the largest atomic displacements due to the strain relief (see Fig. 2). These results correlate with some reduction of the minority-spin LDOS in the very vicinity of E_F in the relaxed geometry. For example, in Fig. 3 we show the LDOS for the single Co adatom in the Cu substrate before and after relaxations calculated by the KKR Green's function method. Similar changes in the minority LDOS are found for other clusters.

TABLE I. The average MAE ΔE for embedded clusters; the MAE are calculated for the magnetization switch from the normal Z towards the in-plane X and $X+Y$ directions, as shown in Fig. 2. Calculations without relaxation are shown in parentheses. Negative MAE values mean preferred in-plane magnetization.

Cluster	$\Delta E(X,Z)$ (meV/atom)	$\Delta E(X+Y,Z)$ (meV/atom)
Co_1	−1.82 (−2.58)	−1.75 (−2.42)
Co_4	−0.30 (−0.60)	−0.32 (−0.65)
Co_5	−1.22 (−1.47)	−1.20 (−1.51)
Co_9	−0.78 (−0.91)	−0.68 (−0.86)

Calculations of the orbital and spin moments (Table II) reveal that the single embedded Co atom has the largest orbital moment in both the unrelaxed and relaxed geometry. However, its spin moment is strongly reduced as compared to the spin moments of embedded islands. This effect can be explained by the fact that the d-d interaction in Co (and Ni) nanostructures broadens the d-states and can enhance spin

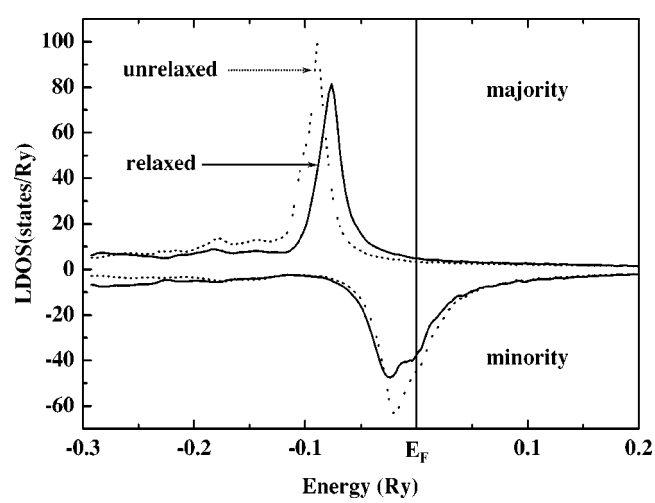

FIG. 3. The LDOS on a single Co atom embedded in the Cu(001) surface

TABLE II. Orbital magnetic moments L^m for Z, X, and $X+Y$ orientation of magnetization, and spin magnetic moments M of particular Co atoms in embedded clusters (see Fig. 2), both for relaxed and unrelaxed geometries; see the details in Table I. All values are in μ_B.

Cluster	Atom	L_Z^m	L_X^m	L_{X+Y}^m	M
Co_1	1	0.51	0.61	0.60	1.26
		(0.67)	(0.80)	(0.79)	(1.54)
Co_4	1	0.15	0.20	0.16	1.68
		(0.19)	(0.27)	(0.22)	(1.70)
	1*	0.15	0.20	0.24	1.68
		(0.19)	(0.27)	(0.31)	(1.70)
Co_5	1	0.09	0.15	0.15	1.78
		(0.13)	(0.20)	(0.20)	(1.82)
	2	0.22	0.40	0.35	1.51
		(0.30)	(0.46)	(0.43)	(1.63)
	2*	0.22	0.27	0.35	1.51
		(0.30)	(0.38)	(0.43)	(1.63)
Co_9	1	0.10	0.19	0.19	1.76
		(0.13)	(0.24)	(0.25)	(1.80)
	2	0.13	0.19	0.18	1.70
		(0.16)	(0.24)	(0.22)	(1.73)
	2*	0.13	0.17	0.18	1.70
		(0.16)	(0.21)	(0.22)	(1.73)
	3	0.18	0.28	0.25	1.65
		(0.21)	(0.32)	(0.29)	(1.66)
	3*	0.18	0.28	0.26	1.65
		(0.21)	(0.32)	(0.30)	(1.66)

magnetic moments.[40] In other words, spin magnetic moments in embedded clusters are stabilized and enhanced by the interaction between Co atoms. However, the orbital moments of embedded clusters are drastically suppressed by interactions between atoms. For example, we found that the orbital moments of the central and edge atoms in the Co_9 clusters are about 3–5 times smaller than for the single Co atom.

When the embedded and supported[10] Co_9 islands are compared, one finds that both immersion of the island into the copper surface and relaxation strongly reduce the MAE and make the distribution of local MAE contributions and orbital-moment values more homogeneous (Table III). Particularly, the MAE contribution from corner Co atoms (atoms 3, 3*) is reduced about twice by the embedding, It is remarkable, however, that the local values of the magnetic orbital moment for the perpendicular magnetization are less sensitive to the above mentioned changes. We would like to note that it is well known that the calculated MAE might be sensitive to the model details. However, as a rule, quantitative rather than qualitative results are expected to be sensitive to them. Our studies have proved that the above discussed results on the MAE of supported and embedded clusters do not indicate any instabilities and trends found look natural.

A naive argumentation suggests that the MAE scales roughly inversely proportionally to typical energy level separations (denominators in the 2nd order perturbation theory), i.e. as $(d/d_0)^{-5}$. The latter value reads as 0.7–0.8 in our case, that agrees quite well for Co_9, Co_5 and single Co. It is difficult to say, however, whether the agreement is not partly accidental. For Co_4, the MAE is reduced to one half due to the relaxation (cf. Table I and Fig. 2). Let us consider the corresponding LDOS. In Fig. 4 the LDOS peak at E_F in minority-spin states is clearly diminished by relaxation. If, for an isolated square Co_4 cluster, a Hamiltonian including only nearest-neighbor d-electron interactions is considered, the energy spectrum is easily analyzed in terms of orbitals or the corresponding spherical functions. Namely, for the z-axis normal to the square plane, the (x^2-y^2,xy) orbitals (orbital moment eigenvalues $m_l=\pm 2$) with hopping matrix elements that comprise also a strong $dd\sigma$ interaction form a wide spectrum. The (xz,yz) pair $(m_l=\pm 1)$ with mainly $dd\pi$ interactions forms bonding and antibonding groups of levels, and $3z^2-r^2(m_l=0)$ orbitals with rather weak interatomic interactions form a group of essentially nonbonding states. The minority-spin LDOS at E_F conserves partially this character even when the island is embedded in Cu; see Fig. 5. In that figure we do not display the $m_l=\pm 2$ components that form a rather uniform background with poorly pronounced peaks

TABLE III. A comparison of magnetic properties of supported and embedded Co_9 clusters in a fully relaxed geometry. The notation as in Tables I and II.

	Supported Co_9				Immersed Co_9			
Atom	L_Z^m	L_X^m	$\Delta E(X,Z)$	M	L_Z^m	L_X^m	$\Delta E(X,Z)$	M
1	0.09	0.18	−1.13	1.78	0.10	0.19	−0.70	1.76
2	0.13	0.19	−1.05	1.70	0.13	0.19	−0.73	1.70
2*	0.13	0.25	−1.26	1.70	0.13	0.17	−0.55	1.70
3	0.18	0.39	−2.60	1.71	0.18	0.28	−0.95	1.65
Atom	L_Z^m	L_{X+Y}^m	$\Delta E(X+Y,Z)$	M	L_Z^m	L_{X+Y}^m	$\Delta E(X+Y,Z)$	M
1	0.09	0.21	−1.06	1.78	0.10	0.19	−0.65	1.76
2	0.13	0.20	−1.15	1.70	0.13	0.18	−0.52	1.70
3	0.18	0.37	−2.38	1.71	0.18	0.25	−0.79	1.65
3*	0.18	0.35	−2.71	1.71	0.18	0.26	−0.91	1.65

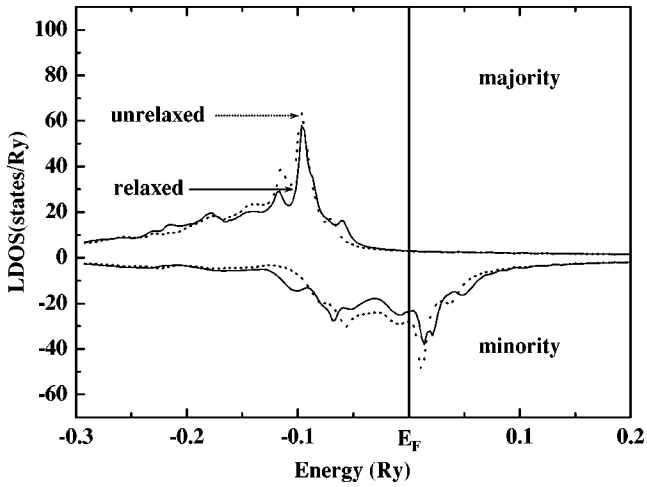

FIG. 4. The LDOS on the Co_4 clusters embedded in the Cu(001) surface

away from E_F. The remaining components form marked peaks above ($m_l = \pm 1$) and below ($m_l = 0$) E_F; the former peak is well sensitive to the geometry relaxation. For the quantization axis in the Co_4 plane, however, we observe a drastic reduction of LDOS with $m_l = \pm 2$ near E_F caused by relaxation. This may explain the large drop in the MAE value for the relaxed cluster.

It is important to note that small ferromagnetic clusters and adatoms above Ag(001) or Au(001) surfaces have been treated theoretically in papers.[8,41] The comparison can be made with results for Co in the second reference. Similarly as in the present study, the authors get preferred in-plane

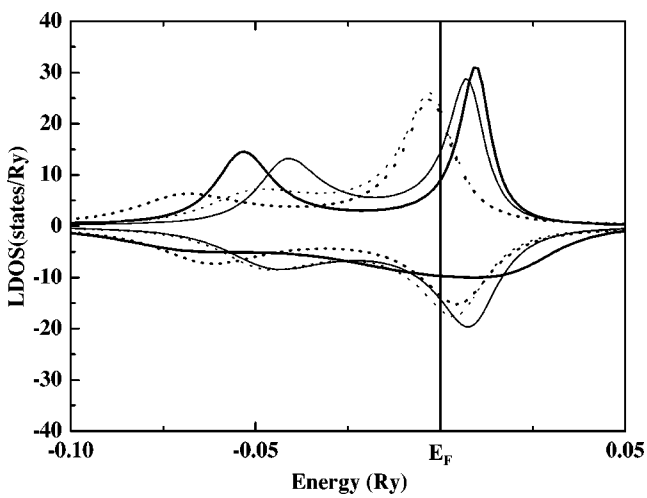

FIG. 5. Decomposition of the tight-binding LDOS of minority-spin d-electrons in the Co_4 cluster embedded in the Cu(001) substrate into components with different magnetic orbital moments Positive LDOS corresponds to the quantization axis along the surface normal; full (dotted) lines are associated with orbital-moment eigenvalue $m_l = 1$ ($m_l = 0$). Negative LDOS correspond to the quantization axis X; full (dotted) lines mean $m_l = 1$ ($m_l = 2$). Heavy (normal) lines show LDOS for the relaxed (ideal) cluster. Spin-orbit coupling is not included and, hence, results are the same for m_l and $-m_l$, respectively.

magnetization for clusters containing at least two Co atoms. Their MAE and orbital-moment values are generally much higher than ours because of embedding of clusters into the noble-metal surface as well as because of different interatomic distances and another position of the copper d-electron band.[10] The recent calculation[42] ascribes a magnetic orbital moment of 0.11 μ_B (0.27 μ_B when orbital-polarization is included) to Co impurity in Cu which is well below the value for single Co in the surface (Table II). Embedding into the surface removes any tendency of a single Co atom to prefer the perpendicular magnetization that might be present when it is deposited *upon* the surface.[8,10,41]

Now we would like to comment on the approximate relation between the MAE (denoted below as ΔE^{orb}) and the magnetic orbital-moment change ΔL^m proposed by Bruno.[43,44] From the 2nd order perturbation theory one can obtain

$$\Delta E^{orb} \approx -0.25 \xi \Delta L^m. \tag{7}$$

In the derivation of Eq. (7) one supposes that the interaction between minority- and majority-spin electrons can be neglected. In the paper[45] it has been argued that Eq. (7) should refer rather to global system MAE and magnetic orbital moment than to their local values associated with particular atoms. Note that an inaccuracy of ~ 0.01 μ_B in ΔL^m introduces an error of more than 0.1 meV in ΔE^{orb}. Our analysis shows that the relation (7) is correct with accuracy about 20–40%; the exception is Co_4 where ΔE^{orb} is about twice as large as the calculated MAE. We ascribe the inaccuracy of Eq. (7) mainly to large LDOS at E_F for all the clusters considered which can make the 2nd order perturbation theory not fully adequate. We have yet illustrated this situation for the case of Co_4. To see whether the spin-orbit interaction between electrons with unlike spins cannot change the situation, we have made some tests with the SOC operator acting solely upon minority electrons. The tests show that accuracy of Eq. (7) remains the same and thus corroborate our idea about quasidegenerate states at E_F that are not treated accurately enough by the 2nd order perturbation theory.

Finally, we note that very recently it has been reported that for Co chains at steps on the Pt(111) surface, spin and orbital moments can become noncollinear[46] even if all spins are parallel. For geometries considered in our work, such a situation cannot occur because of high C_{4v} symmetry of the atomic arrangement. For example, let us consider in-plane orientation of spins and let us suppose that the magnetic orbital moment has a nonzero Z component, the same on all atoms connected by rotations around the central symmetry axis. By applying the time-reversal operation, all X, Y, Z components of spin and orbital magnetic moments change sign. Now, performing the $(C_4)^2$ rotation, we change the sign of X and Y components. Hence, the solution must remain unchanged when the sign of the Z-component of any vector changes. In other situations, reflection planes are also to be invoked.

IV. CONCLUSIONS

Our studies lead to the conclusion that mesoscopic strain relaxations in the Co islands embedded in the Cu substrate

have a strong effect on the magnetic properties at the interface. The size-dependent mesoscopic mismatch is the driving force of the strain relaxations in the island and the substrate. We have shown that the MAE of the embedded clusters is significantly reduced compared to those in supported clusters. The interaction with the substrate atoms and the atomic relaxations drastically reduce the MAE of edge atoms of embedded clusters which play a major role for supported clusters. Atomic relaxations are also found to reduce the orbital magnetic moments of embedded clusters. For all clusters, including a single Co atom, in-plane magnetization is energetically preferred over the perpendicular one. We have found a strong enhancement of the spin magnetic moments in embedded Co clusters compared to a single Co atom in the Cu(001) surface. We believe that our results are of fundamental value to understand how the magnetic properties of nanostructures change due to the interface intermixing. We have used for our studies a particular system, Co islands in the Cu(001) surface, which has been believed not to exhibit a strong strain relaxation. However, our results clearly demonstrate that due to the mesoscopic mismatch, strain relaxations and their impact on magnetic properties could be stronger than expected. It would be of great interest to study the effect of mesoscopic relaxations on magnetic properties for a system having a large macroscopic mismatch, for example Fe islands on W or Pd substrates. We expect that in such cases the impact of relaxations on magnetism can be crucial. Such studies are in progress now.

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*Electronic address: stepanyu@mpi-halle. de

[1] P. Gambardella, S. Rusponi, M. Veronese, S. S. Dhesi, C. Grazioli, A. Dallmeyer, I. Cabria, R. Zeller, P. H. Dederichs, K. Kern, C. Carbone, and H. Brune, Science **300**, 1130 (2003).

[2] T. Jamneala, V. Madhavan, and M. F. Crommie, Phys. Rev. Lett. **87**, 256804 (2001); V. Madhavan, T. Jamneala, K. Nagaoka, W. Chen, Je-Luen Li, Steven G. Louie, and M. F. Crommie, Phys. Rev. B **66**, 212411 (2003).

[3] F. Silly, M. Pivetta, M. Ternes, F. Patthey, J. P. Pelz, and W.-D. Schneider, Phys. Rev. Lett. **92**, 016101 (2004).

[4] S. Rusponi, T. Cren, N. Weiss, M. Epple, P. Buluschek, L. Claude, and H. Brune, Nat. Mater. **2**, 546 (2003); W. Kuch, *ibid.* **2**, 505 (2003).

[5] P. Gambardella, A. Dellmeyer, K. Maiti, M. C. Malagoli, W. Eberhardt, K. Kern, and C. Carbone, Nature (London) **416**, 301 (2002).

[6] V. S. Stepanyuk, A. N. Baranov, D. V. Tsivlin, W. Hergert, P. Bruno, N. Knorr, M. A. Schneider, and K. Kern, Phys. Rev. B **68**, 205410 (2003); V. S. Stepanyuk, L. Niebergall, R. C. Longo, W. Hergert, and P. Bruno, *ibid.* **70**, 075414 (2004).

[7] J. Dorantes-Dávila and G. M. Pastor, Phys. Rev. Lett. **81**, 208 (1998).

[8] B. Lazarovits, L. Szunyough, and P. Weinberger, Phys. Rev. B **65**, 104441 (2002).

[9] B. Nonas, I. Cabria, R. Zeller, P. H. Dederichs, T. Huhne, and H. Ebert, Phys. Rev. Lett. **86**, 2146 (2001).

[10] Š. Pick, V. S. Stepanyuk, A. N. Baranov, W. Hergert, and P. Bruno, Phys. Rev. B **68**, 104410 (2003).

[11] J. Fassbender, R. Allenspach, and U. Dürig, Surf. Sci. **383**, L742 (1997); K. E. Johnson, D. D. Chambliss, R. J. Wilson, and S. Chiang, *ibid.* **313**, L811 (1994).

[12] C. G. Zimmermann, M. Yeadon, K. Nordlund, J. M. Gibson, and R. S. Averback, Phys. Rev. Lett. **83**, 1163 (1999); S. Padovani, F. Scheurer, and J. P. Bucher, Europhys. Lett. **45**, 327 (1999).

[13] F. Nouvertne, U. May, M. Bamming, A. Rampe. U. Korte, G. Günterrodt, R. Pentcheva, and M. Scheffler, Phys. Rev. B **60**, 14 382 (1999). V. S. Stepanyuk and W. Hergert, *ibid.* **62**, 7542 (2000); V. S. Stepanyuk, D. V. Tsivline, D. I. Bazhanov, W. Hergert, and A. A. Katsnelson, *ibid.* **63**, 235406 (2001); R. C. Longo, V. S. Stepanyuk, W. Hergert, A. Vega, L. J. Gallego, and J. Kirschner, *ibid.* **69**, 073406 (2004).

[14] O. Kurnosikov, J. T. Kohlhepp, and W. J. M. de Jonge, Europhys. Lett. **64**, 77 (2003).

[15] N. Quaas, W. Wenderoth, A. Weismann, R. G. Ulbrich, and K. Schönhammer, Phys. Rev. B **69**, 201103 (2004).

[16] N. Knorr, M. A. Schneider, L. Diekhöner, P. Wahl, and K. Kern, Phys. Rev. Lett. **88**, 096804 (2002).

[17] A. B. Klautau and S. Frota-Pessôa, Surf. Sci. **497**, 385 (2002).

[18] V. S. Stepanyuk, A. N. Baranov, D. I. Bazhanov, W. Hergert, and A. A. Katsnelson, Surf. Sci. **482-485**, 1045 (2001).

[19] R. Robles, R. C. Longo, A. Vega, C. Rey, V. S. Stepanyuk, and L. J. Gallego, Phys. Rev. B **66**, 064410 (2002).

[20] X. Chuanyun, Y. Jinlong, D. Kaiming, and W. Kelin, Phys. Rev. B **55**, 3677 (1997).

[21] Y. Xie and J. A. Blackman, Phys. Rev. B **66**, 155417 (2002).

[22] J. A. Gomez and D. Guenzburger, Phys. Rev. B **63**, 134404 (2001).

[23] R. N. Nogueira and H. M. Petrilli, Phys. Rev. B **63**, 012405 (2001).

[24] K. Wildberger, V. S. Stepanyuk, P. Lang, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **75**, 509 (1995); N. Papanikolaou, R. Zeller, P. H. Dederichs, and N. Stefanou, Phys. Rev. B **55**, 4157 (1997).

[25] N. A. Levanov, V. S. Stepanyuk, W. Hergert, D. I. Bazhanov, P. H. Dederichs, A. Katsnelson, and C. Massobrio, Phys. Rev. B **61**, 2230 (2000).

[26] I. J. Robertson, V. Heine, and M. C. Payne, Phys. Rev. Lett. **70**, 1944 (1993); F. Ercolessi and J. B. Adams, Europhys. Lett. **26**, 583 (1994); I. R. Robertson, D. I. Thomson, V. Heine and M. C. Payne, J. Phys.: Condens. Matter **6**, 9963 (1994); Y. Mishin, D. Farkas, M. J. Mehl, and D. A. Papaconstantopoulos, Phys. Rev. B **59**, 3393 (1999); D. W. Brenner, Phys. Status Solidi B **217**,

23 (2000).

[27] Transferability means that the interatomic potentials should be able to describe with a good accuracy structures not included in a fitting data base. In our scheme a fully *ab initio* KKR results for binding energies of different clusters not included in a fitting data base and energetics of surface impurities are compared with calculations performed with the interatomic potentials. We have also shown, see Ref. 30, that the interatomic potentials constructed for Co on Cu(001) can be also used for Co on Cu(111). We emphasize that in the present work the data base used includes the *ab initio* HF forces acting on adatoms at the different distances from the surface, see Ref. 10. This allows us to correctly describe atomic relaxations near the surface.

[28] V. S. Stepanyuk, A. L. Klavsyuk, L. Neibergall, A. M. Saletsky, W. Hergert, and P. Bruno, cond-mat/0405674, to be published in Phase Transitions.

[29] V. S. Stepanyuk, D. I. Bazhanov, A. N. Baranov, W. Hergert, P. H. Dederichs, and J. Kirschner, Phys. Rev. B **62**, 15398 (2000).

[30] D. V. Tsivlin, V. S. Stepanyuk, W. Hergert, and J. Kirschner, Phys. Rev. B **68**, 205411 (2003).

[31] V. S. Stepanyuk, D. I. Bazhanov, W. Hergert, and J. Kirschner, Phys. Rev. B **63**, 153406 (2001).

[32] R. Longo, V. S. Stepanyuk, W. Hergert, A. Vega, L. J. Gallego, and J. Kirschner, Phys. Rev. B **69**, 073406 (2004).

[33] R. Haydock, Solid State Phys. **35**, 215 (1980).

[34] Š. Pick, J. Dorantes-Dávila, G. M. Pastor, and H. Dreyssé, Phys. Rev. B **50**, 993 (1994).

[35] O. V. Lysenko, V. S. Stepanyuk, W. Hergert, and J. Kirschner, Phys. Rev. Lett. **89**, 126102 (2002).

[36] V. S. Stepanyuk, D. V. Tsivlin, D. Sander, W. Hergert, and J. Kirschner, Thin Solid Films **428**, 1 (2003).

[37] D. Sander, S. Ouazi, V. S. Stepanyuk, D. I. Bazhanov, and J. Kirschner, Surf. Sci. **512**, 281 (2002).

[38] A. Bogicevic, Phys. Rev. Lett. **82**, 5301 (1999).

[39] The magnitude of the MAE oscillates with the cluster size. This behavior reflects the strong dependence of magnetic properties on cluster size and geometry; see, for example, J. T. Lau, A. Föhlisch, R. Nietubyc, M. Reif, and W. Wurth, Phys. Rev. Lett. **89**, 057201 (2002); Y. Xie and J. A. Blackman, J. Phys.: Condens. Matter **15**, L615 (2003) and Ref. 7.

[40] P. Lang, V. S. Stepanyuk, K. Wildberger, R. Zeller, and P. H. Dederichs, Solid State Commun. **92**, 755 (1994).

[41] I. Cabria, B. Nonas, R. Zeller, and P. H. Dederichs, Phys. Rev. B **65**, 054414 (2002).

[42] S. Frota-Pessôa, Phys. Rev. B **69**, 104401 (2004). This paper together with the study Y. Xie and J. A. Blackman, *ibid.* **69**, 172407 (2004) do not exclude the possibility that the addition of an orbital-polarization term with reduced Racah coefficient might improve the results. All calculated values obtained in the present work would be undoubtedly enhanced by such a correction without changing qualitative conclusions.

[43] P. Bruno, Phys. Rev. B **39**, 865 (1989).

[44] G. van der Laan, J. Phys.: Condens. Matter **10**, 3239 (1998).

[45] Š. Pick, Solid State Commun. **127**, 531 (2003).

[46] A. B. Shick, F. Máca, and P. M. Openeer, Phys. Rev. B **69**, 212410 (2004).