

Effect of atomic relaxations on magnetic properties of adatoms and small clustersŠ. Pick,¹ V. S. Stepanyuk,^{2,*} A. N. Baranov,³ W. Hergert,³ and P. Bruno²¹*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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Performing *ab initio* and tight-binding calculations we demonstrate the effect of atomic relaxations on the magnetic properties of Co adatoms and Co clusters on the Cu(001) surface. Atomic relaxations decrease the spin and orbital magnetic moments and drastically affect the magnetic anisotropy of the Co adatom. We show that due to relaxations the in-plane magnetization of the Co adatom is stabilized.

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Supported magnetic clusters are considered to be one of the candidates for the development of new high-density magnetic storage media. Their electronic and magnetic properties are governed by size and quantum effects,¹ which become very important as the size of the cluster approaches atomic dimensions.

Advances in scanning tunneling microscopy (STM) make it possible to investigate individual magnetic atoms and small magnetic clusters on metal surfaces. For example, STM experiments performed with single magnetic adatoms, dimers, and small magnetic clusters² raise the possibility of a direct study of the magnetism at the atomic scale. Using x-ray magnetic circular dichroism (XMCD) Gambardella *et al.*³ have shown that the magnetic properties of Co clusters containing 1 to 40 atoms, grown on Pt(111), change drastically with the cluster size, even if the latter is changed only by one single atom.

There are quite a number of theoretical studies of the magnetic properties of supported clusters.^{1,4,5} As a general result, it is found that the spin moments of small clusters are enhanced compared to the moments of the monolayers and bulk materials being driven by the reduced coordination. Even magnetic nanostructures can be made from materials that are nonmagnetic in bulk.⁶

Possible technological applications of supported magnetic clusters are connected with the magnetic anisotropy energy (MAE), which determines the orientation of the magnetization of the cluster with respect to the surface. Large MAE barriers can stabilize the magnetization direction in the cluster and a stable magnetic bit can be made. For example, a giant MAE for monoatomic cobalt chains on Pt(111) found in the experiments of Gambardella *et al.*⁷ indicates that not more than a few hundred cobalt atoms might be needed in tailor-made structures for constructing a stable magnetic bit at room temperature. Recently Dorantes-Dávila and Pastor performing tight-binding calculations have concluded that the MAE of 3*d* transition-metal wires is an order of magnitude larger than in two-dimensional thin films.⁸

Ab initio calculations have predicted very large MAE and orbital moments for 3*d*, 5*d* adatoms and 3*d* clusters on Ag(001).^{3,5,9} One of the central issues in physics of new nanoscale magnetic structures is the interplay between magnetism and atomic structure. The interaction between mag-

netic adatoms and the surface leads to atomic relaxations at the interface. Strain relaxations in small clusters may lead to pronounced structural changes in the substrate and shape of clusters.¹⁰ The following fundamental question arises: What is the effect of atomic relaxations on the magnetic moment and MAE for adatoms and small supported clusters? We believe that the answer of this question is of great importance for our understanding of magnetism in nanostructures at the atomic scale.

In this paper we address this problem by calculating magnetic properties of the Co adatom and the Co₉ cluster on the Cu(100) surface. To the best of our knowledge, this will be the first study of the effect of atomic relaxations on magnetic properties of adatoms and supported clusters.

The relaxation of a single Co adatom on Cu(001) has been performed using density functional theory in the local spin density approximation and the Korringa-Kohn-Rostoker (KKR) Green's function method for impurities and clusters on metal surfaces.^{4,6,11} We treat the ideal surface as a two-dimensional perturbation of the bulk. The Green's function of the ideal surface and the Green's function of adatoms on the surface are calculated using multiple-scattering theory. The forces acting on adatoms are determined by means of an ionic version of the Hellmann-Feynman theorem¹¹ in the full potential approximation. Details of the method and several of its applications can be found elsewhere.^{4,6,11}

First, we calculate the effect of relaxations on the spin moment of the Co adatom using the KKR Green's function method. Figure 1 shows the calculated spin moments for the different position of the adatom near the surface. In a fully relaxed geometry (13.5% of relaxations) the spin moment is reduced by 7% compared to the moment for the unrelaxed position near the surface. The effect of the substrate is mainly determined by the hybridization of the *sp* Cu states with the *d* states of the Co adatom.

We believe that an efficient tool to study the MAE and orbital magnetism for adatoms and supported clusters in a fully relaxed geometry could be based on the tight-binding approximation,¹² because such calculations are still out of the possibilities of *ab initio* methods.

We employ the tight binding electronic Hamiltonian with parameters chosen to fit the KKR local densities of electronic states (LDOS) and the local magnetic moments of Co over-

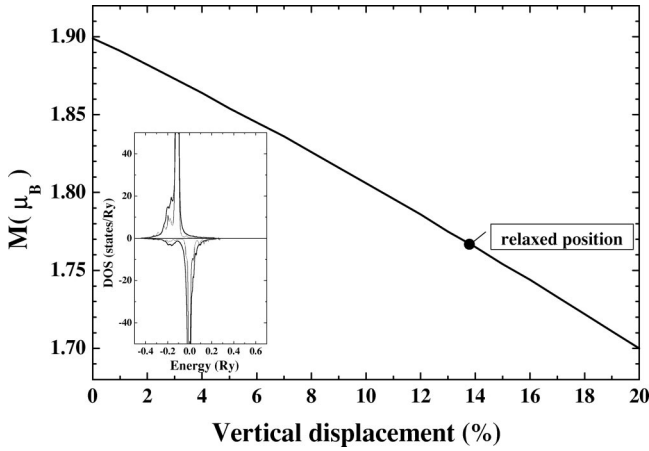


FIG. 1. The dependence of the spin magnetic moment of the Co adatom on the distance from the Cu substrate. The relaxed position of the adatom is indicated: 0% corresponds to Co at a Cu interlayer separation above the Cu surface. The magnetic moments per atom are given in Bohr magnetons. Inset: *ab initio* (thick line) and TB (thin line) results for the *d* component of the LDOS of the Co adatom for unrelaxed position.

layer and small Co clusters on Cu(001). In particular, the Slater-Koster parameters from Ref. 13 yield a very satisfactory LDOS. The Co-Cu hopping matrix elements are approximated using the geometric mean of the two elemental-metal values. For distance scaling, the usual “canonical” form is supposed.^{12,14} (Note that the Co parameters of Ref. 13 are derived for the Co-Co distance that lies roughly half way between those for unrelaxed and relaxed clusters, respectively.) Charges on the Co adatom and Co atoms in the Co cluster are fitted to reproduce KKR results. We introduce empty spheres at neighboring sites of the single Co adatom because the LDOS peak on the Co adatom is too sharp.^{15,16}

It has been found for free-standing monolayers that a rather reduced number of moments is sufficient¹⁷ to evaluate MAE correctly by the recursion-method technique. Here, the convergence turns out to be much worse due to two factors: (1) for massive systems, more moments than for ultrathin films are to be used, and, which is probably yet more important, (2) sharp LDOS peaks at E_F for Co atoms with low coordination need a much more serious attention. The inclusion of *s* electrons also slows down the convergence. We perform the final accurate self-consistent adjustment and MAE and orbital-moment evaluation with 600 moments (300 levels of the continued fraction). (The Coulomb integrals are adjusted to get the prescribed local charge occupation for the perpendicular magnetization orientation that makes more atoms equivalent.) Naturally, such a calculation is possible only when the Cu crystal is approximated by a cluster.¹⁸ We use a six-layer Cu(001) slab with $(2N \times 2N)$ atoms in each layer, $N=9$ or 24.

The physics we study is controlled by LDOS in some neighborhood of E_F , and, in particular, by a prominent peak that lies in the upper part of the cobalt minority-spin *d* band. Fitting the *d*-electron occupation and magnetic moments enables us to pin this peak at the right energy position at Fermi level. In Fig. 1 (inset) we show the LDOS of the Co adatom

for the unrelaxed position above the Cu surface. The vertical relaxation of the Co adatom leads to stronger hybridization with the substrate and slightly shifts the minority LDOS to lower energy. The *ab initio* calculation shows that this shift is about 0.1 eV for a fully relaxed position of the Co adatom. The TB model predicts the same tendency with slightly smaller shift of the *d* band (0.05 eV).

The MAE is expressed as difference of electronic band energies evaluated for two different magnetization orientations.¹² The local band energy reads $E_{\text{band}}(E_F) = \int^{E_F} E \rho(E) dE$. (ρ is the Co *d*-electron LDOS; for the sake of simplicity we omit the site index.) If the local charge differs by δq from the correct value, the corrections up to the second order are

$$\delta E_{\text{band}}(E_F) = E_F \delta q + 0.5 [\rho(E_F)]^{-1} \delta q^2. \quad (1)$$

The term linear in δq in Eq. (1) represents the content¹⁹ of the force theorem. To our knowledge, the effect of similar second order corrections to the MAE of magnetic adatoms and clusters has not been investigated. In principle, other second-order corrections (SOC's) can contribute to the energy difference such as the double-counting corrections. The latter terms arise due to a *real* charge redistribution. Analysis of these terms²⁰ gives no reason to expect that they are essential in our case. On the other hand, δq in Eq. (1) is not the *real* charge but an *error* coming from the frozen-potential approximation. If there are sharp LDOS peaks at E_F , the correction at second order can become essential and has to be considered then. Naturally, when it is too large the result might become problematic. However, since it is based on sound principles, such a correction bears information on the accuracy of the calculation and should give at least an idea of the MAE behavior. (For example, for the single Co adatom considered below, δq can exceed the value 0.1.)

We also utilize the first order correction to the calculated orbital-moment value L :

$$\delta L = \rho_L(E_F) [\rho(E_F)]^{-1} \delta q. \quad (2)$$

In Eq. (2), $\rho_L(E) = \sum_m m \rho_m(E)$ is the local density of orbital-moment states with partial densities of states ρ_m evaluated for orbital-moment eigenstates $|m\rangle$.

To evaluate the MAE, the intraatomic SOC is represented by the operator $\xi \mathbf{L} \cdot \mathbf{s}$, where ξ is the SOC parameter. In the present paper we do not introduce the orbital-polarization corrections because their accuracy for adatoms and supported clusters with nearly localized magnetic moments is uncertain.⁹ Our calculations show that for $\xi=0.06$ eV taken from the *ab initio* studies of Nonas *et al.*,⁹ we get the MAE of -0.51 meV per Co atom in Co monolayer on Cu(100) which compares well with the first-principles²¹ value -0.38 meV/atom (a negative MAE indicates that in-plane magnetization is more stable). The moderate discrepancy between our results and the *ab initio* studies is due to model simplifications of the TB model rather than the value of ξ . One can fit the TB results to *ab initio* calculations using a ξ value of about 0.05 eV. However, the SOC parameter in this case would fall out of the range of values accepted in the literature. Moreover, our studies show than main results discussed

TABLE I. Magnetic orbital moments and the magnetic anisotropy energy of a single Co adatom on the Cu(001) surface; L_Z^m and L_X^m are the orbital moments for magnetization along the normal Z and in-plane X direction; the electronic part of the magnetic anisotropy energy ΔE (meV) is presented. Values obtained without the quadratic corrections to ΔE and without linear corrections to L^m are shown in parentheses.

	Unrelaxed geometry	Relaxed geometry
L_Z^m	1.06 (1.06)	0.77 (0.77)
L_X^m	1.04 (0.97)	0.80 (0.75)
ΔE	1.70 (0.67)	-0.37 (-1.01)

later in this paper are not seriously affected by the small variation of ξ between 0.05 and 0.06 eV (generally, orbital moments scale linearly with ξ and the MAE dependence is between linear and quadratic one).

For the orbital magnetic moments when the magnetization is along the normal direction Z or in-plane direction X we find $L_Z^m = 0.15\mu_B$ (cf. $0.12\mu_B$ in Ref. 22), $L_X^m = 0.20\mu_B$. Our results for the MAE and orbital moments of the Co adatom in the unrelaxed and relaxed positions are presented in Table I.

Calculations of the MAE reveal that for the unrelaxed position above the surface, out-of plane magnetization for the Co adatom is more stable. Table I shows that the quadratic correction to the MAE strongly affects the MAE. Therefore, the calculation of the MAE as simply the difference of the (first-order in δq) band energies may not give reliable numerical answers, as previously noted in Ref. 9. Note also that in the pioneering work on MAE calculation²³ the assumption of small LDOS perturbation has been stressed which is not generally valid in our case. The second order corrections are aimed at better handling this source of inaccuracy. We have verified for a few systems that the second order corrections are negligible for “regular” geometries when all surface atoms have full surface coordination. Hence, the physical picture will be seen to be unchanged so these results should be adequate for our purposes.

For the unrelaxed position we get values of L^m that are very large for magnetization along the normal and in plane directions. One can see that the first order correction to the orbital moment has only a minor impact on the calculated moments.

Compared to recent *ab initio* calculations for adatoms on the ideal surfaces, our orbital moments lie between the values presented in Refs. 3 for Co on Pt(111) and those typical for magnetic impurities in alkali-metal films.²⁴

The relaxation of the vertical position of the adatom by 14% shortens the first NN Co-Cu separation from 2.56 to 2.39 Å and has a drastic effect on MAE. The results presented in Table I show that the huge stability of the perpendicular magnetization of the single Co adatom in the unrelaxed geometry is drastically affected by atomic relaxations. We find that the relaxation of the Co adatom leads to in-plane magnetization. One can see that the quadratic correction significantly changes the MAE stabilizing in-plane magnetization. We believe that although the exact MAE value is

sensitive to the details of the model, the fact that relaxation strongly reduces the perpendicular MAE and probably switches the magnetization to an in-plane direction has a more general character.

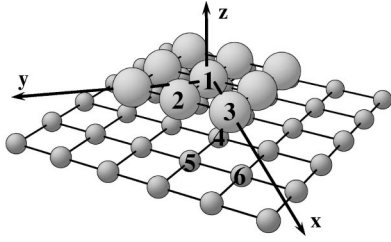
We have analyzed the second moments of Co-Cu interactions originating from d electrons. For the unrelaxed geometry, the adatom orbitals split into pairs (xz , yz) with large second moments, and (xy , $x^2 - y^2$) with small second moments. Hence, the LDOS for each of these pairs will be similar, and for an appropriate position of E_F a large stabilization in the perpendicular magnetization occurs due to the SOC for $L_Z = \pm 1$ states (first pair) or $L_Z = \pm 2$ states (second pair). In the relaxed geometry, second moments for particular orbitals are essentially less different. This means that in the LDOS, all orbitals are well mixed and the SOC can also become effective for parallel magnetization. It seems that the effect is controlled by the change of the Hamiltonian matrix elements with the bond-angle variation rather than by the Co-Cu distance reduction, since the latter effect is counterbalanced by self-consistency (pinning of the LDOS peak at E_F).

Now we turn to the discussion of results for Co clusters on Cu(001). It is known that there are two main factors that determine the magnetic moments in low-dimensional systems: the coordination number and the interatomic distances. The decreasing coordination number tends to enhance the moments, but on the other hand, the decreasing interatomic distance tends to reduce the moment. The study of magnetic properties of adatoms, clusters, and monolayers in the ideal geometry allows one to resolve the effect of dimensionality on the magnetic properties. The comparison of magnetic properties of the unrelaxed and relaxed structures reveals the effect of the interatomic distances.

First, we concentrate on the effect of the dimensionality. We perform calculations for the Co_9 cluster (2D) in the unrelaxed geometry and compare the results with the Co adatom (0D). Our KKR Green’s function calculations for spin moments of a Co_9 cluster are presented in Fig. 3. We find that the spin moments of atoms of the cluster are close to moments of the Co adatom (see Fig. 1) and the Co monolayer ($1.7 m_B$). This is because the majority state of Co is practically filled. The increase of the coordination number of the central atom in the Co_9 cluster compared to the Co adatom broadens the d states and slightly enhances the moment. It was shown that at the end of the d series the d - d interaction in transition metal nanostructures can enhance the moments.²⁵

We find that the orbital magnetic moments of the atoms in the cluster are drastically reduced compared to the orbital moments of the single Co adatom (see Table I). The orbital moment decreases with the atom coordination being minimal for the central atom in the cluster. For all atoms in the cluster we find that in-plane magnetization is energetically favorable with the maximal MAE for the corner atoms of the cluster. Figure 3 shows that the quadratic corrections to the MAE are most important for such an atom.

Our results for the MAE and orbital moments are in the line with the recent theoretical study⁵ of Co_9 at Ag(001). The fact that our MAE values are a bit smaller is quite natural



№	Unrelaxed geometry			Relaxed geometry		
	coordinates (Å)			coordinates (Å)		
	x	y	z	x	y	z
1	0	0	0	0	0	-0.127
2	1.8075	1.8075	0	1.703	1.703	-0.092
3	3.615	0	0	3.409	0	-0.068
4	1.8075	0	-1.8075	1.788	0	-1.922
5	3.615	1.8075	-1.8075	3.603	1.816	-1.809
6	5.4225	0	-1.8075	5.383	0	-1.779

FIG. 2. Atomic relaxations in the Co_9 island and in the Cu substrate; lattice constant $a_0 = 3.615 \text{ \AA}$. The positions of atoms in unrelaxed and relaxed positions are presented in the table.

since the d band of silver lies well below E_F and has a lesser effect on the cobalt d electrons.

The equilibrium structure of the plane square Co_9 island on the Cu(001) surface is determined by computing the forces at each atomic site and relaxing the geometry of islands and the substrate atoms. We use the quasi-*ab initio* molecular dynamics method,^{10,26} which is based on the tight-binding approximation for many body potentials. Accurate first principle spin-polarized calculations of cluster-substrate properties and *ab initio* forces are performed to construct the many-body interatomic potentials at the Co/Cu(001) interface. It has been shown that surface and bulk properties are well described by this method.^{10,26}

Our results reveal that the Co_9 island and the surface layers are not flat anymore in the relaxed geometry (see Fig. 2). The island assumes a “platelike” shape. The edge atoms in the Co island are placed highest. However, they do not have the largest spin moments. Similar to the calculation in the unrelaxed geometry we find that the central atom of the cluster has the largest moment (see Fig. 3). In the relaxed geometry spin moments are reduced by about $0.09m_B$. Orbital moments are also strongly affected by relaxation. For example, the orbital moment L_X^m of the central (see Fig. 3) is reduced by 30%. This effect is caused by the strong reduction of all first NN Co-Co distances to about 2.41 \AA (2.56 \AA for the unrelaxed structure). The stability in-plane magnetization is reduced by relaxations for the central atom and for atom 2, while it is enhanced for the corner atom and for atom 2^* . For all atoms in the cluster the MAE is found to be considerably larger than the MAE of the single Co adatom in the relaxed position (see Table I). The relative stability of atoms 2 and 2^* for the X orientation of the magnetization is changed as one goes from the unrelaxed to relaxed cluster. It can resemble the switch of in-plane magnetization at Co steps.²⁷

For both unrelaxed and relaxed Co_9 cluster, the magnetization along X is slightly more stable than along $X+Y$.

	Ideal geometry			Relaxed geometry		
	L_z^m	L_x^m	$\Delta E(X,Z)$	L_z^m	L_x^m	$\Delta E(X,Z)$
1	0.11 (0.11)	0.25 (0.25)	-1.48 (-1.48)	0.09 (0.09)	0.18 (0.18)	-1.13 (-1.14)
2	0.17 (0.17)	0.24 (0.24)	-1.35 (-1.35)	0.13 (0.13)	0.19 (0.19)	-1.05 (-1.05)
2^*	0.17 (0.17)	0.27 (0.30)	-0.87 (-1.45)	0.13 (0.13)	0.25 (0.28)	-1.26 (-1.77)
3	0.21 (0.21)	0.43 (0.49)	-2.44 (-2.89)	0.18 (0.18)	0.39 (0.44)	-2.60 (-3.03)
Atom	L_z^m	L_{X+Y}^m	$\Delta E(X+Y,Z)$	L_z^m	L_{X+Y}^m	$\Delta E(X+Y,Z)$
1	0.11 (0.11)	0.25 (0.25)	-1.47 (-1.46)	0.09 (0.09)	0.21 (0.18)	-1.06 (-1.06)
2	0.17 (0.17)	0.25 (0.26)	-1.20 (-1.33)	0.13 (0.13)	0.20 (0.23)	-1.15 (-1.33)
3	0.21 (0.21)	0.40 (0.47)	-2.17 (-2.62)	0.18 (0.18)	0.37 (0.43)	-2.38 (-2.32)
3^*	0.21 (0.21)	0.40 (0.46)	-2.30 (-2.91)	0.18 (0.18)	0.35 (0.47)	-2.71 (-2.99)

FIG. 3. Magnetic properties of Co_9 cluster on the Cu(001) surface in unrelaxed and relaxed geometries; spin magnetic moments in Bohr magnetons are shown for each atom in the cluster; orbital magnetic moments and electronic part of the MAE are presented in the table for the normal Z , in-plane X and $X+Y$ directions of the magnetization; the MAE and orbital moments obtained without the quadratic correction to the MAE and without linear corrections to the orbital moments are shown in parentheses. For the unrelaxed cluster, the average MAE is $-1.74(-2.07) \text{ meV/Co atom}$ for X direction; for $X+Y$ direction these values are $-1.69(-1.99) \text{ meV/Co atom}$. For the relaxed cluster, the above energies are $-1.79(-2.10) \text{ meV/Co atom}$ for X direction and $-1.76(-1.98) \text{ meV/Co atom}$ for $X+Y$ direction.

However, MAE contributions from particular atoms have an inhomogeneous distribution and possibility of noncollinear magnetization cannot be ruled out.

One can imagine two opposite mechanisms controlling the MAE of atoms in the cluster: (1) the LDOS is effectively narrower at less coordinated atoms which leads to the local MAE enhancement and (2) the less coordinated atoms possess lower symmetry and should be less sensitive to the magnetization direction. The results of the present calculations and of Ref. 9 show that the first mechanism seems to be more important.

Finally, we comment on the simple approximate relation²⁸ connecting the MAE and the change L^m when the magnetization direction is switched:

$$\Delta E \approx -0.25\xi\Delta L^m. \quad (3)$$

The available comparison varies between qualitative and good agreement, with some failures especially for adatoms.^{9,29}

For example, existing *ab initio* calculations for single ferromagnetic adatoms above Ag(001) (Ref. 9) show a lower accord than for more coordinated structures. Our results (see Table I and Fig. 3) show that Eq. (3) appears to be approximately correct, with an accuracy ranging from 60% to complete accord.

To summarize, we have investigated the effect of atomic relaxation on magnetic properties of Co adatoms and Co₉ clusters on the Cu(001) surface. The tight-binding model with parameters fitted to *ab initio* results has revealed that a strong tendency to perpendicular magnetization of the Co adatom on the ideal surface is totally suppressed by atomic relaxations. The in-plane magnetization for the Co adatom is

obtained in a fully relaxed geometry. We have shown that the spin and orbital moments of the Co adatom and the Co cluster are reduced by relaxations. The magnetic anisotropy energy is found to be the largest for the low-coordinated atoms in the cluster.

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