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Transition metal magnetic nanostructures on metal surfaces

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Abstract

Ab initio calculations of the electronic and magnetic properties of metallic nanostructures on (001) surfaces of Cu and Ag are presented. The LDA approximation of the density functional theory and the KKR–Green's function method are used. It is shown that 3d, 4d and 5d small clusters can be magnetic on metal surfaces. The effect of intermixing with the substrate on the magnetic properties is investigated for Fe clusters on Cu(001). The influence of the geometry and the size of the clusters on the magnetic properties of 4d clusters is shown. Sizeable magnetic moments for 5d clusters are found on the Ag surface.

Keywords: KKR-GF method; Supported clusters; Transition metal nanostructures

1. Introduction

Clusters of atoms show physical and chemical properties which are different from those of bulk crystals and atoms [1]. In particular, the properties strongly depend on the size and geometry of the clusters. The magnetic properties especially are completely changed [2]. While a metal may be non-magnetic in the bulk phase, small clusters of its atoms may exhibit magnetism [3]. The magnetic properties of clusters can be useful for technological applications, such as high-density magnetic recording devices or catalysis [4,5].

Many theoretical [1,2,6] and experimental [7] investigations of magnetic properties of free clusters have been carried out. Most of the possible applications of magnetic clusters are connected with surfaces. The possibility of producing small supported clusters on metal surfaces [8] has opened new research fields in surface science. We have recently developed a new method for ab initio calculations of supported clusters [9] and have shown the possibility of 4d magnetism on metal surfaces [10]. The first experimental confirmation of the magnetism of 4d adatoms on noble metal surfaces has been reported recently [11].

In this paper we present the results of ab initio calculations of magnetic properties of 3d, 4d, and 5d supported clusters. The (001) surfaces of Cu and Ag are investigated.

2. Method of calculation

Our calculations are based on density functional theory and the Korringa–Kohn–Rostocker

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(KKR) method. A Green's function formulation is used [9].

By removing the atomic potentials of a few (5–7) monolayers, we create two half-crystals which, due to the work function barrier, are practically not coupled. We treat the surface as a two-dimensional perturbation of the bulk and apply multiple scattering theory to obtain the Green's function of the surface by using the Dyson equation. The Green's function of the ideal surface is used as the reference system in the Dyson equation for the calculation of clusters on surfaces.

Exchange and correlation effects are included using the local spin density approximation with the exchange-correlation potential of Vosko et al. [12].

The full charge density is taken into accout by a multipole expansion up to $l=6$. The potentials are assumed to be spherically symmetrical within the Wigner–Seitz spheres. Technical details of our calculations can be found elsewhere [9,10].

3. Results and discussion

Noble metal substrates like Ag(001), Au(001), and Cu(001) have been used for a long time to investigate, either theoretically or experimentally, the magnetic properties of supported metallic layers. Because there has, until now, been a disagreement between theoretical predictions and experimental results, it is necessary to study in detail the influences of intermixture, defects a.s.o. on the magnetic properties of the supported metallic structures.

Fig. 1 shows our results for the magnetic moments of 3d adatoms, dimers, trimers, and plain square islands of four atoms as well as results for monolayers [13] on the Cu(001) surface. Only ferromagnetic solutions are presented here. Recently we have shown that 3d clusters on the Cu(001) surface have many magnetic solutions and magnetic fluctuations are possible [14]. Among the 3d series the largest local moments are obtained at the center of the series. The magnetic moments of 3d clusters at the beginning of the series are strongly suppressed and the monolayers have no ferromagnetic solutions. The more or less

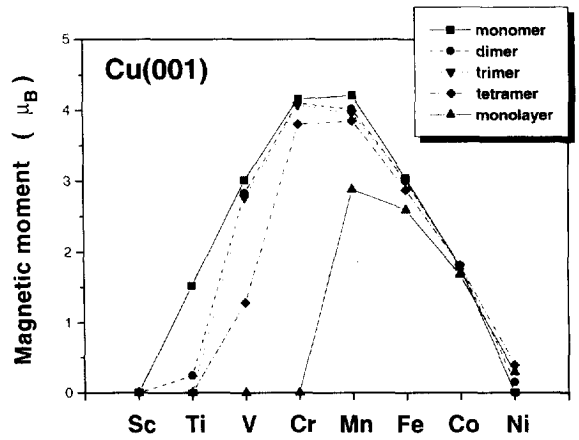

Fig. 1. Magnetic moments of nanostructures of 3d transition metals on Cu(001).

equal moments obtained for Fe, Co, and Ni for adatoms, clusters and monolayers are basically a consequence of the fact that in all these cases the majority band is practically filled. Therefore, the real structure of the clusters should not strongly influence the magnetic properties of supported structures prepared from transition metals from the end of the 3d series. The Ni adatom is non-magnetic, whereas dimers, islands and monolayers have a magnetic moment ($\approx 0.4\ \mu_B$). We have also made calculations for the Ni trimer. Our results indicate that this cluster is non-magnetic, i.e. the changes in the magnetic moment of Ni clusters are not monotonic with increasing cluster size.

It has been reported [15] that the intermixing of Fe with Cu is possible for the Fe/Cu(001) system. The question arises, whether intermixing at the Fe–Cu interface can strongly influence the Fe moment. To study this effect in more detail, we have investigated it for plain square islands of Fe on Cu. Different mixed configurations of Fe and Cu have been studied. The adatom position (cluster in the first vacuum layer) and the terrace position (cluster in the topmost layer of the substrate) of the clusters are considered as well (cf. Table 1). Our results show that the magnetic moment of Fe in small clusters is not influenced strongly by the Cu atoms.

Another widely used substrate is Ag(001). Due to the large extent of the 4d and 5d wavefunctions, the magnetic moments of clusters of these atoms

Table 1
Moment of Fe atoms in Fe clusters on Cu(001)

Cluster	Position	μ (μ_B)
Fe_1	Adatom	3.09
Fe_1	Terrace	2.90
Fe_4	Adatom	2.91
Fe_4	Terrace	2.80
Fe_2Cu_2	Adatom	2.96

are more strongly influenced by surfaces. Fig. 2 shows the magnetic moments of small 4d clusters of four atoms for two geometries: linear chains and plain square islands. One can see that the "geometrical effect" is dramatic for Mo and Tc and has little effect for Ru and Rh. The d wavefunctions of the clusters at the end of the d series are well localized on the surfaces and therefore the changes in the geometry of clusters are not so important. Our results also show that clusters with lower symmetry can have larger moments than clusters with higher symmetry.

The size dependence of the average magnetic moment of Rh clusters is shown in Fig. 3. The results obtained demonstrate clearly the non-monotonic behaviour of the magnetic moments with increasing cluster size.

Results for 5d clusters on Ag(001) together with results for monolayers [16] are presented in Fig. 4. Moments are strongly suppressed by interactions between atoms in clusters and with the substrate.

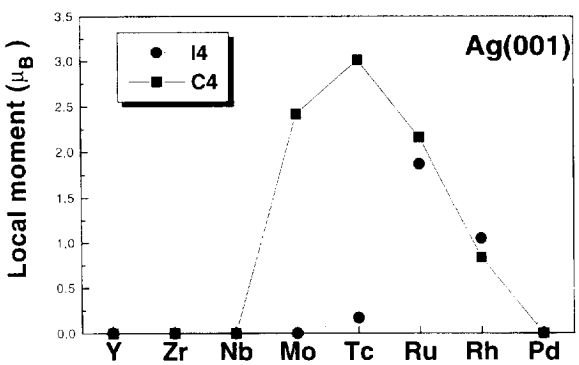

Fig. 2. Magnetic moments of linear chains of four atoms (C4) and plain square islands (I4) of 4d transition metals on Ag(001).

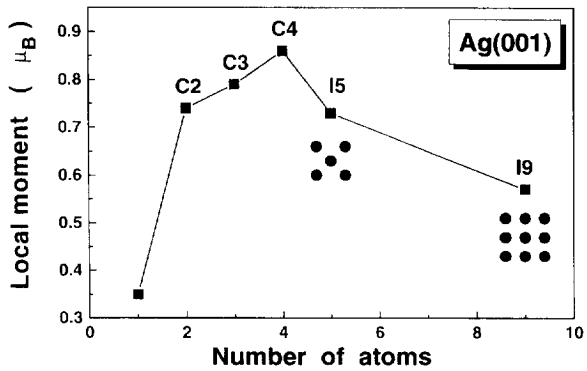

Fig. 3. Size dependence of the magnetic moment of small Rh clusters on Ag(001). Linear chains of 2, 3, and 4 atoms (C2, C3, C4) and plain islands of 5 and 9 atoms (I5, I9) are considered.

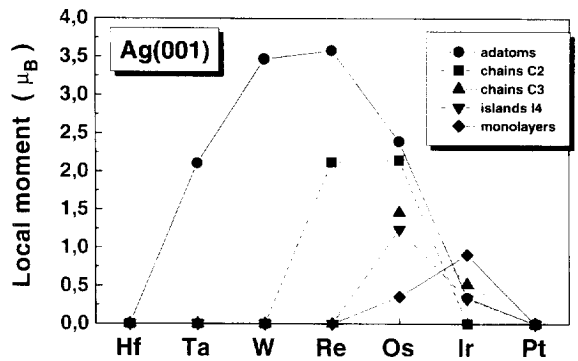

Fig. 4. Magnetic moments of small clustes of 5d transition metals on the Ag(001) surface.

Only Os and Ir are magnetic for clusters with more than two atoms.

4. Conclusions

We have shown that many 3d, 4d, and 5d small clusters are magnetic on the noble metal surfaces. The intermixing of Fe and Cu cannot seriously influence the magnetic properties of small Fe clusters. The magnetic moments of supported clusters changes non-monotonically with the cluster size. The clusters with higher symmetry do not always have larger magnetic moments than the low-symmetry clusters.

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