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Metamagnetic states of 3d nanostructures on the Cu(001) surface

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Abstract

Different magnetic states for a given real structure are known for bulk metals and alloys and also for free transition metal clusters. We have calculated the magnetic properties of small 3d transition metal clusters on the Cu(001) surface by means of an ab initio KKR Green's function method. It is shown that multiple magnetic states exist in these nanostructures. High spin and low spin ferromagnetic states as well as antiferromagnetic states occur. The energy differences between the different states are calculated.

Keywords: Metamagnetism; Transition metal nanostructures; Supported clusters; Green's function – KKR

The existence of different magnetic states like high spin ferromagnetic (HSF), low spin ferromagnetic (LSF) and antiferromagnetic (AF) is well known for bulk systems. In a series of papers Moruzzi et al. investigated the volume dependence of the magnetic and electronic properties of 3d transition metals and transition metal compounds [1–4]. They have investigated the transition from a non-magnetic to a ferromagnetic state for V and Mn [3]. V and Mn show a transition from a non-magnetic to a LSF state if the Wigner–Seitz radius is increased. For a certain range of the Wigner–Seitz radius ($3.47 \leq r_{WS} \leq 3.52$ a.u.) bcc V can be either in the LSF or in the HSF state. The system can be driven from one state to the other by an external field. The equilibrium value of r_{WS} is 2.79 a.u. Changes of the lattice constant of more than 20% are necessary to reach this region of coexistence of the LSF and HSF state.

A theoretical investigation of Zhou et al. [5] shows that up to five different magnetic states are found for γ-Fe. (LSF, HSF, AF, and two ferrimagnetic states). Different theoretical investigations have shown, that energy differences between the magnetic states can be of the order of 1 meV. In such a case magnetic fluctuations can be excited by temperature changes or external fields. Magneto-volume effects play also an important role in the theory of the Invar effect [6].

Lee and Callaway [7] have studied the electronic and magnetic properties of free V and Cr clusters. They found that for some atomic spacings as many as four or five magnetic states exists for a V_9 or Cr_9 cluster. The typical low and high spin moments are 0.33 μ_B and 2.78 μ_B for the V_9 cluster.

Recently, a lot of experimental work is concentrated on the growth of ordered nanostructures on metal surfaces. A preferential growth of special nanostructures can be achieved [8]. Metallic nanostructures, pseudomorphically grown on a metallic substrate can show considerable changes of the lattice constant compared to the bulk value. Therefore, the lattice spacing in the supported 3d transition metal clusters can be changed between less than 1% and approximately 15% if different noble metal substrates like Cu, Ag, Au are used.

Ab initio calculations for 3d, 4d and 5d adatoms and supported clusters on different substrates suggest, that a rich variety of magnetic nanostructures exist, which are built also from non-magnetic metals [9]. The aim of the paper is to show, that 3d nanostructures on Cu(001) can show a large variety of magnetic states like it is known for bulk systems and free clusters and that the energy differences between different states can be so small that magnetic fluctuations occur.

The calculational method used is described here only

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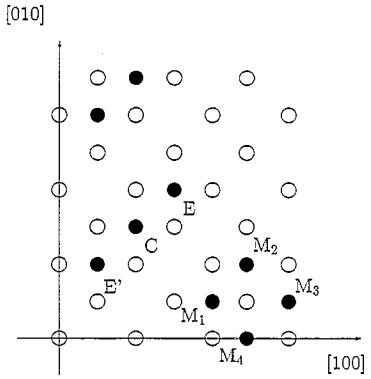

Fig. 1. Metallic nanostructures (dimer, trimer and tetramer) on the fcc (001) surface.

briefly, since details can be found elsewhere [10]. The calculations are carried out with the Korringa–Kohn–Rostocker (KKR) Green's function method. The method is based on density functional theory in the local spin density approximation (LSDA). The Green's function of the bulk system is transformed into a Wannier–Bloch representation. The atomic potentials of seven layers are removed to create two practically uncoupled half-crystals. The Green's function of the ideal surface is used as the reference Green's function to calculate the electronic properties of supported clusters. Exchange and correlation effects are included in LSDA applying the potential of Vosko et al. [11]. The full charge density is taken into account using a multipole expansion up to $l = 6$. The potentials are assumed to be spherically symmetric inside the Wigner–Seitz spheres. Our calculations show that the spherical approximation is not important for the magnetic properties [13].

We have calculated the electronic and magnetic properties of small 3d transition metal clusters on the Cu(001) surfaces. Dimers, trimers and tetramers, as given in Fig. 1,

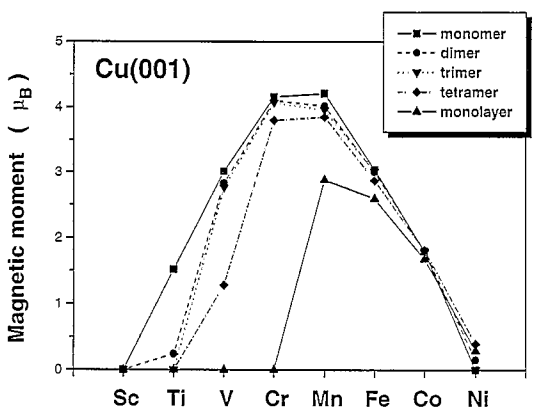

Fig. 2. Magnetic moments of the ferromagnetic state for 3d adatoms, dimers, trimers, and tetramers on Cu(001). The magnetic moments of complete monolayers [12] are given for comparison.

Table 1
Magnetic moments (in μ_B) for the atoms of the trimers V_3 and Mn_3 on Cu(001)

State	V_3			Mn_3		
	M_E	M_C	$M_{E'}$	M_E	M_C	$M_{E'}$
HSF	2.85	2.58	2.85	4.03	3.83	4.03
LSF	2.63	1.41	2.63	4.04	.01	4.04
AF	2.63	−2.02	2.63	3.99	−3.88	3.99
AS	2.62	0.00	−2.62	3.98	0.00	−3.98

are investigated. All atoms occupy ideal lattice sites. No relaxation at the surface is taken into account. In Fig. 2 the magnetic moments of the 3d nanostructures in the ferromagnetic state are given. The magnetic moments for the monolayer are also given for comparison [12]. At the beginning of the 3d series complete monolayers have an AF ground state. The peak of the moment curves is shifted to higher valencies, if comparing the chain structures with the island and the monolayer (cf. Ref. [9]).

While larger clusters might show a non-collinear structure of the magnetic moments, such a situation is not likely for the clusters studied here. Dimers and tetramers have only one non-equivalent site in the paramagnetic state. The trimers have two non-equivalent sites (C – center, E, E′ – edge positions). Ferromagnetic states of the trimers, either low spin (LSF) or high spin (HSF) states, have parallel moments at the sites C and E, E′, but the moments have different sign at C and E, E′ in the antiferromagnetic state (AF). The atoms at the edge positions (E, E′) have the same moment ($M_E = M_{E'}$) for LSF, HSF and AF states. Another possible magnetic state, which is compatible with the chemical symmetry of the system is an antisymmetric (AS) one. The magnetic moment at the central atom of the trimer is zero and the moments at the edge positions have different sign ($M_E = -M_{E'}$).

We concentrate our discussion on the multiplicity of magnetic states to V and Mn. For the single V adatom only a high spin state with a moment of 3.0 μ_B is obtained. For the V_2 dimer we find both a ferromagnetic and an antiferromagnetic state with moments of 2.85 and 2.58 μ_B, respectively. The antiferromagnetic state has the lowest energy being about 0.2 eV/atom lower than the ferromagnetic one.

The magnetic moments for all the different magnetic states of the V and Mn trimers are summarized in Table 1. All the magnetic states have a lower total energy than the paramagnetic state. The AF state is the ground state of the V trimer. The energy difference between the AF and LSF state in V is about 8 meV/atom. The LSF state is more stable than the HSF state. The ground state of the Mn trimer is also the antiferromagnetic state. The energy difference between the ground state and the HSF state is only 2 meV/atom. This energy difference corresponds to a

Table 2
Magnetic moments (in μ_B) for the atoms of the tetramer V_4 on Cu(001)

State	M_1	M_2	M_3	M_4
HSF	1.27	1.27	1.27	1.27
LSF	0.5	0.5	0.5	0.5
AF_1	1.9	−1.9	1.9	−1.9
AF_2	2.14	2.14	−2.14	−2.14

temperature difference of 25 K. A transition between the two states caused by temperature changes or an external field leads to a change of the total moment of the Mn trimer of 7.8 μ_B. Such a strong change of the total moment, controlled by an external parameter opens a new field for an experimental proof of the theoretical results.

Table 2 lists the moments of the square V_4 tetramer. As for the V trimers we find both a high-spin and a low-spin ferromagnetic state. Moreover we find two antiferromagnetic states (AF_1, AF_2) with different symmetry properties. As for the trimer the AF_1 state with antiparallel coupling of nearest neighbors has the lowest energy being about 0.05 eV/per atom lower than for the HSF state, which itself has slightly lower energy than the two other solutions. Analogously to the different magnetic states discussed for the trimer, all four magnetic states of the tetramer do not destroy the chemical point symmetry C_{4v} of this system and thus do not lead to reconstruction.

In summary we have shown, that metamagnetic behaviour exists in supported clusters. It is shown, that the energy differences between different magnetic states can be small, which can lead to a change of the magnetic state of the cluster by an external parameter. The energy differences between different magnetic states will strongly depend on the cluster size. Therefore such ab initio calculations can help to select interesting systems for experimental investigations.

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