Magnetism of the Fe_9 microcluster supported on Ni(001)

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Abstract

The morphology and the spin-polarized electronic structure of the Fe_9 cluster supported on the (001) surface of Ni is investigated by combining the Modified Embedded Atom Model (MEAM) with quenched Molecular Dynamics (MD) and a selfconsistent non-collinear spd Tight-Binding (TB) method parameterized to ab-initio Tight-Binding Linear Muffin Tin Orbitals (TB-LMTO) results. Two-dimensional geometry and overall ferromagnetic couplings are found in agreement with a recent experiment. We analyze the local magnetic moments and Fe-Ni hibridization effects as a function of the interfacial relaxation.

Key words: magnetism, supported nanostructures, transition metal system
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1. Introduction

Although many theoretical studies concerning the magnetic properties of nanostructures have been reported so far, the magnetic characterization at the atomic scale has been an experimental challenge for many years. Recently, important advances have taken place in the experimental techniques, opening the possibility of confirming many theoretical predictions as well as of exploring a great variety of novel nanostructured materials. Perhaps the most exciting advance in this context is the Spin-Polarized Scanning Tunneling Microscopy (SP-STM) and Spectroscopy (SP-STS)[1]. Also X-Ray Magnetic Circular Dichroism (XMCD) allows at present to measure quite locally the magnetic moments of supported nanoparticles[2]. Among the wide scenario of magnetic nanostructures, supported clusters deserve particular attention due to their technological interest and to the fact that being many free standing clusters widely investigated from a theoretical point of view, one can compare with them the forthcoming results of the supported ones, thus improving the understanding of mechanisms that play a relevant role in the magnetic behavior (electron hybridization, geometry, relaxation effects).

Recently, Lau et al.[2] have been able to measure, using XMCD, the magnetic moments of size selected iron clusters smaller than ten atoms deposited on Ni(001). The interpretation of their

measurements allows these authors to propose two-dimensional configurations for the Fe clusters, whose atoms should be located on the nickel sites following a pseudomorphic arrangement. Motivated by this experimental study, in the present work we investigate the morphology and the magnetic properties (resulting from the spin-polarization) of the 9-atoms iron cluster supported on the (001) surface of Ni. Several questions will be addressed like the magnitude of the average magnetic moment, compared to the bulk and the corresponding free-standing cluster, and the local magnetic moments distribution within the system (including the substrate); the influence of the Fe-Ni hybridization on both the geometries and the magnetic moments; and the effects of the interfacial relaxation on the overall behavior.

The computational procedure of the present work was twofold. First, we wished to determine the ground-state structure of the Fe cluster on top of the (001) surface of Ni by combining the MEAM[3–5] with quenched MD. We computed the lowest-energy structures by considering numerous starting configurations on top of the Ni surface and, for each configuration, calculating the minimum energy of the cluster+substrate system using a quenched MD minimization technique[6]. Second, we wanted to determine the magnetic properties of the whole system. For this latter purpose, using the cluster geometries and interatomic distances obtained as described above, the spin-polarized electronic structure of the substrate+cluster system was determined by self-consistently solving a TB Hamiltonian for the s, p and d valence electrons in a mean field approximation[**?**] and global neutrality using the recursion method[7]. As in our recent study of Fe clusters supported in Al surfaces,[12] the parameters of the TB model (homonuclear hoppings and the exchange integrals) were obtained by fitting them to TB-LMTO[8] results for a single system, in this case the Fe monolayer on top of the Ni (001) surface. This fit allows to take implicitly into account both the influence of the surface and hybridization between Fe and Ni atoms, Fe clusters having been found in the experiment[2] to be on top of the (001) surface of Ni. The interlayer distances in the Fe overlayer on Ni(001) used for the fit were determined using the same geometrical optimization procedure as for the substrate+cluster systems.

Our structural calculations showed that the most stable Fe_9 cluster on top of the (001) surface of Ni was a two-dimensional close-packed island. In figure 1 we illustrate this configuration indicating the inequivalent sites within the iron cluster at the underlying Ni atoms. Notice that the iron atoms are located on top of nickel sites following a pseudomorphic arrangement. Therefore, our results concerning the morphology of the system are consistent with the experiments of Lau *et al.*[2] and can be understood in terms of the geometrical environment if we take into account that on the Ni surface the broken bonds favour the planar structures to a large extent. In contrast, free-standing iron clusters have been found to adopt more compact tree-dimensional structures[9]. In particular, for the free-standing Fe_9 cluster it has been predicted a tricapped trigonal prism structure as the ground state. According to the pseudomorphic arangement of the iron cluster, the lateral interatomic distances nearly correspond to those of the Ni substrate. However, a slight interfacial Fe-Ni outwards relaxation of about 4% in average exists with respect to Ni-Ni distances. This outwards relaxation is similar to the one found in the Fe overlayer on Ni(001) (the system considered for the TB fit) and it is consistent with the estimation based on the constant-atomic-volumes approximation as well as with Low Energy Electron Diffrancion experiments by Lu *et al.*[10] and Photoelectron Diffraction measurements by Gazzadi *et al.*[11] for Fe/Ni(001) films.

For the above optimized geometrical configuration, we have obtained an average magnetic moment per atom in the supported Fe_9 cluster of $2.84\mu_B$. The experiments of Lau *et al.*[2] provide the average spin-polarization divided by the number of d-holes (about $0.81 \pm 0.4\mu_B/n_h$ for the Fe_9 cluster). Since the average number of d-holes obtained in our calculations for this cluster size is $3.37n_h$, we have a quite good agreement with the experiment, with only a 4% difference. Let us now analyze the magnetic moments distribution within the cluster-substrate system. In Table 1 we report the magnetic moments at the inequivalent sites of the iron cluster and Ni sites at the interface. Over-

all ferromagnetic couplings are found in the whole system, that is both within the cluster and at the Fe-Ni interface, in good agreement with the experimental observations[2]. In the Fe atoms, local magnetic moments considerably larger than in the bulk and close to the magnetic saturation limit are obtained; this trend is consistent with the noticeable surface effect and is typical in free-standing iron clusters[9]. Also, like in free-standing Fe clusters, the less coordinated sites display the largest magnetic moments. The Ni substrate a priori should not modify appreciably through hybridization the magnetic behavior of the supported Fe cluster due to its ferromagnetic character and the few d-holes available to be polarized in Ni. In order to confirm this assesment we performed a new set of TB calculations but considering now an artificial strong inwards interfacial relaxation of about 20% (values in parentheses in figure 1) and we obtained only a slight reduction of the magnetic moments. The weak Fe-Ni hybridization is also reflected in the density of states of the Fe_9 cluster, plotted in figure 2 (upper panel) for both interfacial relaxations. Both DOS ehibit a similar structure, although with a smaller spin-splitting in the case of the 20% relaxed case, consistent with the slight reduction of the Fe magnetic moment as compared with the real situation. Theses trends contrast with those found for Fe_N clusters on Al(001)[12], where the strong Fe-Al hybridization kills the magnetic moment of small iron clusters, being neccessary for them to reach a critical size in order to exhibit weak magnetic moments, and prove again the strong influence of the chemical environment on the magnetic behavior. In the lower panel of figure 2 we plot the density of states at the Fe overlayer on the Ni (001) substrate. It is noticeable that the main peaks are already present in the DOS of the supported Fe_9 cluster.

Once analyzed in detail the behavior of a typical iron cluster supported on the Ni (001) surface, the next step will be to investigate how the structural and electronic properties, in particular the magnetism, evolve as a function of the cluster size, and to compare with the experimental results of Lau et al.[2] as well as with available results for iron clusters both free-standing and supported in other substrates. This systematical study, which is under work, will be published in the near future.

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References

References

[1] O. Pietzsch, A. Kubetzka, R. Wiesendanger, Science 292 (2001) 2053.

[2] J. T. Lau, A. Föhlisch, W. Wurth, Phys. Rev. Lett. 89 (2002) 057201.

[3] M. I. Baskes, Phys. Rev. B 46 (1992) 2727.

[4] B.-J. Lee, M. I. Baskes, Phys. Rev. B 62 (2000) 8564.

[5] B.-J. Lee, M. I. Baskes, Y. K. Cho, Phys. Rev. B 64 (2001) 184102.

[6] G.J. Ackland, R. Thetford, Phil. Mag. A 56 (1987) 15.

[7] R. Haydock, Solid State Physics, Vol. 35, Academic, New York, 1980, p. 215.

[8] O. K. Andersen, O. Jepsen, Phys. Rev. Lett. 53 (1984) 2571.

[9] O. Diéguez, M.M.G. Alemany, L. Gallego, Phys. Rev. B 63 (2001) 205407.

[10] S.H. Lu, Z.Q. Wang, P. Marcus, Surf. Sci. 221 (1989) 35.

[11] G.C. Gazzadi, P. Luches, S. Nannarone, Phys. Rev. B 61 (2000) 2246.

[12] R. Robles, R.C. Longo, Phys. Rev. B 69 (2004) 115427.

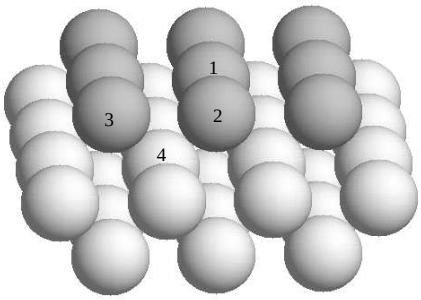

Fig. 1. Structural configuration of the lowest energy Fe_9 cluster on top of the Ni(001) surface. The inequivalent sites within the iron cluster are indicated together with the underlying Ni sites. The magnetic moments at those inequivalent sites are reported in Table 1.

Table 1
Magnetic moments at the inequivalent sites showed in Fig. 1. Values in parentheses correspond to an artificial inward interfacial relaxation of 20%.

	1	2	3	4
$\mu(\mu_B)$	2.72	2.91	2.81	0.50
	(2.49)	(2.81)	(2.66)	(0.47)

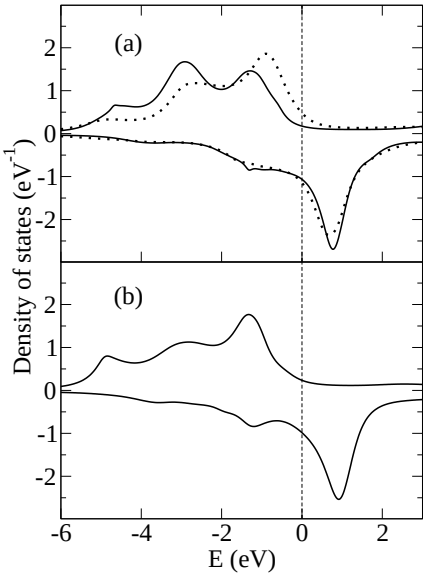

Fig. 2. (a) Average density of electronic states of the Fe_9 cluster on top of the (001) surface of Ni (full line) compared with the result when considering an artificial inward interfacial relaxation of 20%. (dotted line). (b) Density of states per iron atom of the Fe overlayer on Ni(001).