NON-COLLINEAR MAGNETISM IN THE Fe_3 MICROCLUSTER: FREE-STANDING VS SUPPORTED ENVIRONMENTS

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The possibility of a non-collinear magnetic configuration of the Fe_3 microcluster supported on the Ni (001) surface has been investigated. The morphology of the supported cluster has been calculated by means of the modified embedded atom model with quenched molecular dynamics simulations, and the electronic structure for the most stable geometrical configuration has been studied using a self-consistent non-collinear *spd* tight-binding method parameterised to *ab-initio* tight-binding linear muffin tin orbital results. Our predictions are compared with previous results for the free-standing Fe_3 microcluster. The influence of the substrate in both the structure and the magnetic properties, particularly the onset of non-collinear magnetism, is discussed in detail.

Keywords: Electronic structure; magnetic properties; supported clusters.

1. Introduction

In recent years, several studies have been reported about the magnetic properties of Fe nanoclusters. The main part of these works have focused in the free-standing situation. On the experimental side, we can quote the Stern-Gerlach measurements of Cox *et al.*[1] and Billas *et al.*[2,3] These experiments only provide some information about the mean magnetic moment, but the local distribution of magnetic moments within the cluster remains unknown. From the theoretical point of view, there have also been several studies about free-standing Fe nanoclusters. Some of them have addressed the problem using parametrised models, like Hubbard-like tight-binding (TB) Hamiltonians.[4–6] Other authors have used DFT based calculations, using pseudopotential[7,8] or all-electron approximations.[9,10] All these works were restricted to a global spin-quantisation axis. This approximation is justified by the collinear magnetic order that many materials exhibit. However, sometimes this approximation is not enough since the most stable configuration corresponds to a non-collinear magnetic arrangement. This is specially important for Mn or Cr clusters,[11–13] but can also play an important role in the study of Fe clusters. Recently, some works have appeared where the possibility of a non-collinear magnetic order in these systems has been investigated.[11–15] All of them are based on DFT approaches and study very

small clusters containing between 2 and 7 atoms. Oda *et al.*[14] and Hobbs *et al.*[11] have found different non-collinear solutions for the 3-atoms Fe cluster, although they are metastable. These authors, as well as Fujima[12] and Postnikov *et al.*,[15] have found the ground state solution for the 5-atoms Fe cluster to be non-collinear. For the 7-atoms Fe cluster, Fujima[13] has found a non-collinear arrangement for certain interatomic distances. All these calculations agree qualitatively, but differs significantly.

For supported Fe clusters the situation is different and only a few works have been reported so far. In a recent work, Lau *et al.*[16] have used X-Ray Magnetic Circular Dichroism to measure the magnetic moments of size selected Fe clusters deposited on the (001) surface of Ni. These authors have determined the spin and orbital moments of small clusters ($2 \leq n \leq 9$), suggesting two-dimensional configurations where the Fe atoms follow a pseudomorphic arrangement on the Ni surface. Motivated by this study, we investigate the morphology and magnetic properties of the 3-atoms Fe cluster on Ni(001). Our aim is to study the lowest-energy structure, the average magnetic moment and the local magnetic moment distribution in the cluster and the surrounding atoms. We will compare our results with those obtained in the free-standing situation and with the experimental results. The influence of the substrate will be discussed in detail and we will consider the possibility of a non-collinear configuration.

In Sect. 2 we will discuss the theoretical model and the approximations which have been used. In Sect. 3 we will present and discuss our results, and in Sect. 4 we will summarise our main conclusions.

2. Theoretical model

In the present paper we will follow a similar strategy to that employed in our recent study of Fe clusters at the Al (001) surface.[17] First, we will determine the lowest-energy structure of the Fe_3 cluster supported on the Ni (001) surface by using the modified embedded atom method (MEAM).[18–20] The parameters for the fcc metal Ni were taken from Ref. 18 and had been obtained using the earlier, first-nearest-neighbour MEAM. For Fe we used the parameters reported in Ref. 20 for the second-nearest-neighbour MEAM potential of this metal. The Ni (001) surface was modelled by the top (001) layer of a 15-layer slab of atoms with its bottom 4 layers fixed and periodic boundary conditions along the [100] and [010] directions. Each layer comprised 450-Ni atoms. The atoms in the slab were initially arranged as in bulk Ni, but before addition of the Fe atoms its top 11 layers were relaxed to the minimum-energy configuration using a quenched molecular-dynamics minimisation technique.[21] This initial relaxation of the slab (without Fe atoms) reduced the top interlayer distance by 1.02% (and hardly altered the second interlayer distance), which is consistent with the observed inward relaxation of $(0.57 \pm 0.5)\%$ for this surface.[22] The lowest-energy structure of the Fe cluster supported on the Ni (001) surface was determined by considering several initial configurations of various shapes

above the top layer of the relaxed Ni slab, and, for each configuration, calculating the minimum energy of the Fe_3/Ni(001) system, as obtained by fully relaxing the cluster+substrate (bar the bottom 4 layers of the slab).

Afterwards, we used the obtained structure and interlayer distances to determine the magnetic and electronic properties of the whole system (Fe_3 + Ni substrate). For that purpose we have self-consistently solved an *spd* TB Hamiltonian in mean field and global neutrality approximations. In order to consider the possibility of a non-collinear configuration, we allow the spin-quantisation axis to change from site to site. The Hamiltonian was solved in the real space by using the recursion method.[23] An explanation of our model can be found in Ref. 24. The parameters of the TB model were determined as follows. The homonuclear hoppings and the exchange integral were obtained by fitting them to TB linear muffin-tin orbital (TB-LMTO)[25] results for an Fe monolayer on top of the Ni (001) surface. This fit allows to take implicitly into account both the influence of the surface and the hybridisation between Fe and Ni atoms, Fe clusters having been found in the experiment[16] to be on top of the Ni (001) surface. The interlayer distances in the Fe overlayer on Ni(001) used for the fit were determined using the same geometrical optimisation procedure as for the cluster+substrate system. The Coulomb integrals were taken from a previous work.[4] The bare energy levels and the crystal field parameters are unique for each material and were determined from a series of TB-LMTO calculations for Fe and Ni systems with different coordinations (for more details, see Ref. 24).

3. Results and discussion

Our MEAM calculations showed that the lowest-energy structure of Fe_3 on Ni(001) is an isosceles triangle. The Fe atoms are situated on hollow Ni sites following a pseudomorphic arrangement. In Fig. 1a we show this configuration, indicating some inequivalent sites on Fe and surrounding Ni. The interatomic distances are

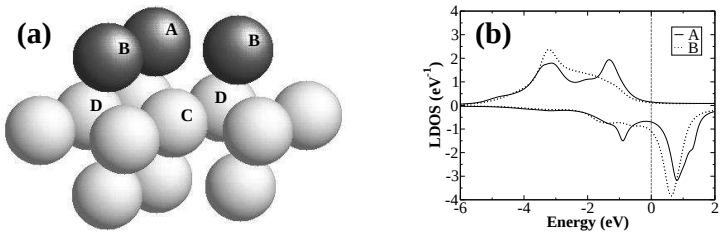

Fig. 1. **(a)** Structural configuration of the most stable Fe_3 cluster on top of the Ni (001) surface. Black (grey) balls represent Fe (Ni) atoms. Inequivalent sites of Fe and some Ni atoms are indicated with different letters. Ni atoms other than first- and second-nearest Fe neighbours have been removed for clarity. **(b)** Local density of states for the two inequivalent sites of Fe_3. The vertical dotted line at 0 eV indicates the Fermi level.

almost the same as the ones that can be found in FCC Ni. The distance between atoms of type A and B is 2.49 Å, which is the first-nearest-neighbour distance

in FCC Ni. The distance between both atoms of type B is 3.44 Å, 2% smaller than the second-neighbour-distance (3.52 Å). There is also a slight interfacial Fe-Ni outward relaxation of about 4% in average with respect to the Ni-Ni distances. This outward relaxation is similar to that found in the Fe overlayer on Ni(001) (the system considered for the TB fit), and is consistent with the estimation based on the constant-atomic-volume approximation as well as with low energy electron diffraction experiments by Lu *et al.*[26] and photoelectron diffraction measurements by Gazzadi *et al.*[22] for Fe/Ni(001) films.

For free-standing Fe clusters the situation is different. In this case there is no constriction imposed by the environment and the trimer is free to adopt any possible geometry. In the literature several alternatives have been found: equilateral and isosceles triangles and linear chains. However, all authors find the equilateral triangle to be the most stable configuration. The interatomic distance is 2.04 Å for Chen *et al.*;[9] 2.10 Å for Castro *et al.*,[10] Andriotis *et al.*[6] and Hobbs *et al.*[11] (when using the local-density approximation (LDA)); 2.11 Å for Oda *et al.*;[14] 2.14 Å for Ballone *et al.*[7] and Diéguez *et al.*;[8] and, finally, 2.22 Å for Hobbs *et al.*[11] (when using the generalised gradient approximation (GGA)).

As indicated in Sec. 2, in our calculation we considered the possibility of a non-collinear magnetic order. We have investigated such possibility by starting our calculation with several initial non-collinear arrangements. However, none of them converged to a non-collinear solution, leading to the same collinear one in all cases. This can easily be understood: Fe and Ni are metals with a strong tendency to exhibit ferromagnetic couplings, as can be seen in the present work (Table 1) and in the experimental observations;[16] therefore, no magnetic frustration can appear in these case, in contrast to what occurs for antiferromagnetic clusters, such as those of Cr or Mn.[11–13] The non-collinear studies of free-standing Fe clusters[11,14,15] show that for Fe_3 the non-collinear arrangements, when found, are metastable, being the collinear situation the lowest-energy state. Only for Fe_5 and Fe_7, these studies and those of Fujima[12,13] found a non-collinear ground-state solution. However, they found a tridimensional structure (a bipyramid) to be the most stable geometry, very different to the planar structures found for Fe_5 and Fe_7 on Ni(001).[27] For both free-standing clusters the non-collinear arrangement has been related to the antiferromagnetic coupling between the apical atoms in the bipyramid. We believe than for supported Fe clusters on the Ni (001) surface the ferromagnetic coupling with the substrate would certainly be stronger than any antiferromagnetic coupling within the clusters. Therefore, any non-collinear state would be blocked. Actually, in our case a non-collinear state can not be found even as a metastable one. Nevertheless, we found interesting to investigate the possibility of a non-collinear solution in some Fe cluster supported on Ni(001) since, to our knowledge, such calculation had not been done so far.

Let us now to analyse the collinear solution. In Table 1 we show the local magnetic moments of the inequivalent sites of Fe_3. From these values we obtain an

Table 1. Local magnetic moments (in μ_B) and d and total occupations of some selected inequivalent sites of the Fe_3/Ni(001) system (those shown by letters in Fig. 1a).

	$\mu(\mu_B)$	N_d	N
A	2.93	6.60	7.36
B	3.11	6.52	7.18
C	0.52	8.70	10.21
D	0.56	8.71	10.06

average magnetic moment per atom of $3.05\mu_B$. The experiments of Lau *et al.*[16] provide the average spin-polarisation divided by the number of d holes n_h. For Fe_3 the value is about $(0.89 \pm 0.40)\mu_B/n_h$. In Table 1 we show the number of d electrons on each site, from where we can obtain that the average number of d holes for Fe_3 is 3.45. Taking this value into account, we found our predicted spin magnetic moment to be in excellent agreement with the experiment (1% of difference). In order to clarify the origin of this magnetic moment and to explore the role of the Ni surface, we can compare with the free-standing situation. In all the theoretical works referred previously the total magnetic moment for the whole cluster was $8\mu_B$, which gives an atomic moment of $2.67\mu_B$. The only exception is the GGA calculation of Hobbs *et al.*,[11] which gave a total moment of $10\mu_B$ and an atomic moment of $2.97\mu_B$. The only experimental information we found is that due to Cox *et al.*,[1] who reported a magnetic moment of $(2.7 \pm 0.3)\mu_B$. In both situations (free-standing and supported), the magnetic moment is increased with respect to the bulk value, which experimentally is $2.21\mu_B$. This enhancement can be related with the lower coordination of the Fe_3 cluster. Following this argument, a higher magnetic moment would be predicted for the free-standing situation. However, the opposite happens. To explain it, two facts must be considered. On the one hand, we have seen that the average distances within the Fe_3 cluster are considerably bigger when supported in the Ni (001) surface, due to the pseudomorphic arrangement. Thus, a higher magnetic moment is favoured. On the other hand, the hybridisation with Ni is not very important due to its ferromagnetic character and to the small number of d-holes which are available to be polarised. In other substrates the effect is much bigger. For example, for small Fe clusters at the Al (001) surface[17] the strong hybridisation between Fe an Al totally suppresses the magnetic moment of Fe_3.

Our method also allow us to obtain the local density of states (LDOS) for each one of the Fe atoms in Fe_3 (Fig. 1b). The behaviour resembles that found in free-standing clusters: the less coordinated atoms (sites B) display narrower and higher peaks and also higher magnetic moments (see Table 1).

4. Conclusions and perspectives

In this paper we have used the MEAM[18–20] to compute the lowest-energy structure of the Fe_3 cluster supported on Ni(001), finding it to be a planar configuration, in

agreement with Lau *et al.*[16] experimental findings. Afterwards, we have used the obtained geometry to determine the electronic structure and magnetic properties of the whole system (Fe_3 + Ni substrate) by self-consistently solving a non-collinear *spd* TB method[24] parametrised to *ab initio* TB-LMTO[25] results. We have explored the possibility of a non-collinear arrangement of the magnetic moments, being unable to find any other solution than the collinear one. For this solution we have found the calculated value for the average spin magnetic moment (divided by the number of *d* holes) to be in excellent agreement with the experimental result of Lau *et al.*[16] Finally, we have compared our results with previous ones for the free-standing Fe_3, discussing the influence of the Ni substrate in the properties of the collinear solution and in the impossibility of finding a non-collinear one.

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