Structure and magnetic properties of small Fe clusters supported on the Ni(001) surface

E. Martínez,[1] R. C. Longo,[2] R. Robles,[3] A. Vega,[1] and L. J. Gallego[2]
[1]*Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, E-47011 Valladolid, Spain*
[2]*Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago de Compostela, E-15782 Santiago de Compostela, Spain*
[3]*Department of Physics, Uppsala University, SE-75121 Uppsala, Sweden*
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Using the modified embedded atom model in conjunction with a self-consistent tight-binding method, we calculated the structures and magnetic properties of small Fe_n clusters ($n=2-9$) supported on the Ni(001) surface. The structures are predicted to be two-dimensional islands, and the average spin magnetic moment per *d* hole is found hardly to vary with *n*. This latter finding contrasts with conclusions recently drawn on the basis of x-ray magnetic circular dichroism results. The magnetic moments of the individual Fe atoms in each cluster tended to increase with decreasing coordination number, and noncollinear tight-binding calculations showed all systems to be ferromagnetic. Cluster magnetism was hardly affected by Fe-Ni hybridization.

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I. INTRODUCTION

The magnetic properties of clusters and thin or ultrathin films of transition metal atoms on metal surfaces have attracted much research in recent years due to significant advances in both experimental and theoretical techniques. Experimental research in this field has been particularly stimulated by the introduction of spin-polarized scanning tunnelling microscopy and spectroscopy. The magnetic moments of metal-supported nanostructures can also be extracted from x-ray magnetic circular dichroism (XMCD) spectra.

Following Edmonds *et al.*[1,2] XMCD studies of graphite-supported Fe nanoclusters with an average cluster size of a few hundred atoms, Lau *et al.*[3] have used the same technique to study the size dependence of the magnetic properties of Fe_n clusters ($n=2-9$) that were deposited on ultrathin Ni films grown on a Cu(001) surface. In the absence of any information on the geometric structures of these clusters, it was suggested that the observed size dependence of their spin and orbital magnetic moments, and of the ratio of the two, might be due to geometric differences between clusters with odd and even numbers of atoms.

Motivated by Lau *et al.* call for further experimental and theoretical investigations to elucidate their findings,[3] in the work described here we investigated the lowest-energy structures and spin magnetic moments of Ni(001)-supported Fe_n clusters ($n=2-9$). Since current first-principles methods are too slow to be applicable to these complex systems, structures were identified by minimization of total energies using the semiempirical modified embedded atom method (MEAM) as recently extended by Baskes and co-workers[4,5] (see also Ref. 6), and spin magnetic moments were then calculated using a self-consistent tight-binding (TB) method that adequately describes the electronic structures of a variety of transition metal systems, including free clusters,[7] supported and embedded clusters,[6,8–10] and surfaces and multilayers.[11] A very similar hybrid approach has been successful in previous studies of free[7] and embedded[6,9,10] clusters. To parametrize the TB model, we fitted it to *ab initio* results for a full Fe monolayer supported on the Ni(001) surface [FeML/Ni(001)], a system that is also of interest in its own right [structural data for epitaxially grown Fe films on Ni(001) have been obtained by means of photoelectron diffraction (PD); Ref. 12].

The remainder of this paper is organized as follows. The methodology and computational details, together with some preliminary structural results on Ni(001) and FeML/Ni(001), are given in Sec. II. In Sec. III we present and discuss our main structural and magnetic results, and in Sec. IV we summarize our conclusions.

II. METHODOLOGY AND COMPUTATIONAL DETAILS

The MEAM is an extension of the embedded atom model (EAM), which was developed by Daw and Baskes[13,14] from the Stott and Zaremba quasiatom approach[15] and has proved useful for investigation of bulk, surface and cluster properties of fcc transition metals (see, e.g., Refs. 16–20). In the EAM, the total energy of a system is the sum of an energy due to two-body interactions and the "embedding energy", i.e., the energy necessary to embed each atom into a background electron density that is the sum of distance-dependent contributions from neighboring atoms. Although both the embedding energy and the pair interaction can be calculated from first principles,[16,21] in practice they are obtained empirically by fitting the model to fundamental solid state properties (and also, in some cases, to other data judged to be relevant for ensuring transferability of the model[17,22]). The MEAM extends the EAM by introducing angular dependence into the contributions to the background electron density; this broadens the scope of the model beyond fcc transition metals, allowing calculation of the physical properties of many materials with bcc, hcp, and diamond cubic structure. In this work, the lowest-energy structures of the Fe/Ni(001) systems studied were computed using an even more recent member of this family of models, the second-nearest-neighbor MEAM (2NN MEAM),[4,5] which was developed to

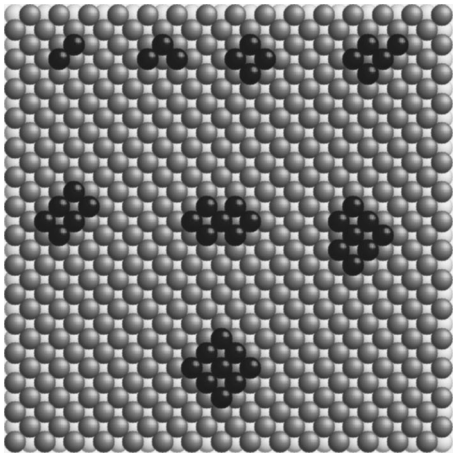

FIG. 1. Predicted lowest-energy structures of Fe_n clusters ($n=2-9$) supported on the Ni(001) surface. Dark spheres represent Fe atoms, gray spheres top-layer Ni atoms, and white spheres second-layer Ni atoms.

overcome the inability of the original, first-nearest-neighbor MEAM (the 1NN MEAM)[23] to deal with bcc transition metals such as Fe. Details of the 1NN and 2NN MEAMs, which can be applied to both pure elements and binary systems, can be found elsewhere.[4–6,23] In this work, the parameters required by the 2NN MEAM for the bcc transition metal Fe were taken from Ref. 5, and the parameters required for the fcc metal Ni were those obtained by Baskes[23] using the 1NN MEAM.

The Ni(001) surface was modeled by the top (001) layer of a 15-layer slab of Ni atoms that had 450 atoms per layer and periodic boundary conditions in the [100] and [010] directions. The atoms in the slab were initially arranged as in bulk Ni, but before addition of the Fe adatoms (adsorbed atoms) its top 11 layers were relaxed to the minimum energy configuration using a conjugated gradient procedure.[24] The bottom four layers remained fixed throughout all simulations described in this paper. Before relaxation, the interlayer spacing of the slab in the [001] direction was $d=a/2$, where $a=3.52$ Å is the bulk lattice constant of Ni.[25] Initial relaxation (without Fe adatoms) decreased the first interlayer space by 1.02% and increased the second by 0.02%, values which agree with those obtained in Ref. 20 using the EAM potential proposed by Voter and Chen,[22] which is particularly suitable for Ni systems. The finding that the first interlayer space of Ni(001) is contracted is consistent with the results obtained by ion shadowing and blocking measurements by Frenken *et al.*,[26] who reported a contraction of (3.2 ± 0.5)%, and with those obtained more recently, using PD measurements, by Gazzadi *et al.*,[12] who found a contraction of (0.57 ± 0.5)%, although expansion was observed in earlier studies using low-energy electron diffraction (LEED) and spin-polarized LEED.[27,28]

To compute the lowest-energy structures of Fe_n clusters on the Ni(001) surface we chose several starting configurations for each value of n and, for each configuration, calculated the minimum energy of the cluster+substrate system using a quenched molecular dynamics minimization technique,[29] thus allowing further, post-adsorption, relaxation of the slab. The set of starting configurations included linear chains oriented in the [110] direction, one-dimensional angular arrangements, two-dimensional islands and, for $n>4$, three-dimensional (3D) structures. In these calculations, the atoms of one- and two-dimensional structures, and the bottom-layer atoms of 3D structures, were initially placed at adsorption sites a distance d (1.76 Å) above the uppermost (001) layer of the relaxed Ni substrate.

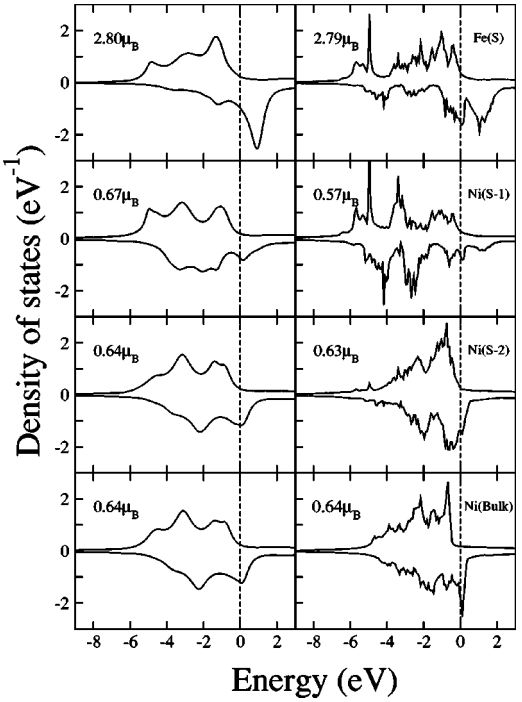

FIG. 2. LDOS in the top three layers of the system formed by an Fe monolayer supported on the Ni(001) surface, and in deeper layers of this system ("Bulk"), as calculated using the self-consistent TB model (left-hand panel) and the TB-LMTO method (right-hand panel). The magnetic moments shown are the spin magnetic moments per atom in these layers. The vertical dashed lines at 0 eV indicate the Fermi level.

As indicated above, apart from the supported Fe_n clusters

TABLE I. Computed energies $E=(E_{cs}-E_s)-n(E_{as}-E_s)$ (see text) of the linear (l) and minimum-energy island (i), angular (a), and three-dimensional (3D) configurations of Fe_n clusters on the Ni(001) surface ($n=2-9$), in eV.

n	i	a	l	3D
2	−0.367			
3	−0.762		−0.758	
4	−1.456	−1.162	−1.149	
5	−1.878	−1.564	−1.540	−0.282
6	−2.588	−1.956	−1.931	−0.707
7	−3.029	−2.347	−2.322	−1.424
8	−3.751	−2.738	−2.713	−0.752
9	−4.478	−3.129	−3.104	−1.193

TABLE II. Average spin magnetic moments per atom (μ, in μ_B), and numbers of d holes per atom (n_h), of Ni(001)-supported Fe_n clusters.

n	2	3	4	5	6	7	8	9
μ	3.13	3.05	2.93	2.94	2.89	2.88	2.86	2.84
n_h	3.49	3.45	3.40	3.40	3.38	3.38	3.37	3.37

we also considered, basically for the purposes of TB parametrization, a full Fe monolayer on the Ni(001) surface [FeML/Ni(001)], calculating the interlayer distances in this system using the same energy minimization procedure as for the Fe_n/Ni(001) systems. The predicted Fe-Ni interlayer distance, 1.84 Å, agrees very well with the value 1.85 ± 0.03 Å obtained by Gazzadi *et al.*[12] by means of PD measurements.

For the geometries obtained as described above, the spin-polarized electronic structures of the Fe_n/Ni(001) systems were determined by self-consistently solving a TB Hamiltonian for the *s*, *p*, and *d* valence electrons in a mean field approximation,[6] using the recursion method[30] and the global neutrality condition. As in our recent study of Fe clusters at the nonmagnetic Al(001) surface,[6] the homonuclear hoppings and the exchange integrals J_{dd}(Fe) and J_{dd}(Ni) of the TB model were obtained by fitting the model to TB linear muffin-tin orbital (TB-LMTO)[31] results for a related system, in this case FeML/Ni(001). This fit allows both the influence of the surface and possible hybridization between Fe and Ni atoms to be taken implicitly into account. In fitting the TB model to the TB-LMTO data, the TB hopping parameters were obtained by the method described by Andersen and Jepsen for bulk solids,[31] here adapted for a semi-infinite system. The values of J_{dd}(Fe) and J_{dd}(Ni) were then varied to minimize overall discrepancy between the TB and TB-LMTO values for the local magnetic moments in the supported Fe monolayer, the Ni interface layer, and the bulklike Ni layers (for this last, the inner, bulklike layers of the TB calculation were compared with the central bulklike Ni layer in the TB-LMTO supercell); the optimized values were $J_{dd}(\mathrm{Fe}) = 0.88$ eV and $J_{dd}(\mathrm{Ni}) = 1.36$ eV. In order to study the possibility of noncollinear magnetic configurations, which can be important in low-dimensional transition-metal systems, we also performed calculations using the appropriately modified TB scheme described in a recent paper on the noncollinear magnetism of Cr films on a stepped Fe substrate.[32] Spin-orbit coupling was not included in our calculations.

III. RESULTS AND DISCUSSION

Table I lists the so-called "binding energies" E of the linear and minimum-energy angular, island and 3D structures of Fe_n clusters ($n = 2-9$) on the Ni(001) surface [$E = (E_{cs} - E_s) - n(E_{as} - E_s)$, where E_s is the energy of the relaxed slab, E_{cs} that of the relaxed cluster+slab system, and E_{as} that of the relaxed system comprising the slab plus a single adatom; the true binding energy ("the energy required to dissociate [the adsorbed cluster] into isolated adatoms")[19] is of course $-E$]. Figure 1 shows the predicted absolute lowest-energy structures, which in agreement with the Lau *et al.* expectations[3] are all two-dimensional islands that are much more stable than any alternative linear, angular or 3D arrangements. With the exception of Fe_7, these structures exhibit a well-defined "growth" pattern, each new atom being placed so as to maximize the number of first-neighbor bonds in the cluster (and in the case of ties, the number of second-neighbor bonds); and the seven-atom cluster complying with this rule (the structure that is "intermediate" between those of Fe_6 and Fe_8) is in fact only 0.006 eV less stable than the configuration actually calculated for Fe_7.

Figure 2 shows the local densities of states (LDOS) and spin magnetic moments in various layers of FeML/Ni(001) as calculated using the TB and TB-LMTO methods. The TB method reproduces quite well both the spin magnetic moment in each layer and the main peaks of the TB-LMTO LDOS, which is an indication of the quality of the TB parametrization. It is worth noting that the LDOS of the supported Fe monolayer reflects a situation that is quite different from that of the bcc Fe surface.[33] The fcc Ni substrate and the surface effect together lead to occupied states being almost entirely occupied by majority-spin electrons, i.e., to magnetic near saturation, with each Fe atom having a spin magnetic moment of $2.79\mu_B$ (μ_B being the Bohr magneton). This value is considerably larger than that found by TB-LMTO calculations for the interior of bulk bcc Fe, $2.41\mu_B$.[6] Note also that the second Ni layer has an LDOS and spin magnetic moment per atom that already resemble those of bulk fcc Ni, for which the spin magnetic moment per atom afforded by TB-LMTO calculations is $0.64\mu_B$.

Table II lists, for each supported Fe_n cluster, the calculated average values per atom of the spin magnetic moment μ (in μ_B) and of the number of d holes n_h; and Fig. 3 shows the n dependence of the ratio μ/n_h as calculated in this work and as reported by Lau *et al.*[3] The calculated values of μ/n_h hardly vary with n because the same is true of both μ and n_h, which in the case of μ is attributable to all these clusters being close to magnetic saturation, and in the case of n_h to their all having island structures that, with the above-noted minor exception of Fe_7, grow with n in accordance with a well-defined pattern. In the case of Fe_2, the cluster for which our results differ most from those of Lau *et al.*, these authors suggested that the experimental value probably included a significant contribution by a spin magnetic dipole term that cannot be distinguished separately by XMCD experiments (and cannot be calculated by the computational methods employed in this work). Although for most of the other clusters our calculated values of μ/n_h agree with Lau *et al.* experimental data to within the reported experimental error, it

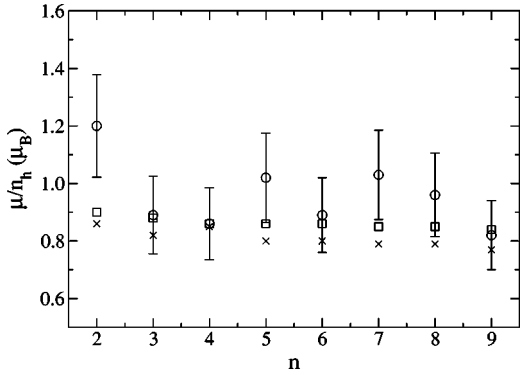

FIG. 3. Calculated spin magnetic moments per *d* hole of Ni(001)-supported Fe_n clusters (squares), together with the experimental results of Lau *et al.* (Ref. 3) (circles with error bars). Also shown are the values computed while imposing an artificial interfacial contraction of 20% (crosses).

seems likely that dipole contributions may also be significant for some of the clusters for which our results differ most widely from Lau *et al.*, such as the unsymmetrical cluster Fe_5 or the "growth-rule infringer" Fe_7.

Although we determined the spin magnetic moments of individual inequivalent atoms in all the Fe_n/Ni(001) systems studied, for the sake of brevity we present here only the results for Fe_5/Ni(001), in which all the Fe atoms are inequivalent (see Fig. 1). Table III lists the spin magnetic moment of each Fe atom together with those of some inequivalent Ni atoms in the neighborhood of the cluster (see Fig. 4). As in free Fe_5,[34] the Fe atoms couple ferromagnetically to each other and to Ni atoms (within the "parallel or antiparallel" constraint imposed by the TB method used at this stage), and the magnitude of their spin magnetic moments decreases as their coordination number increases; and, following the same trend, all these moments are considerably larger than in either bulk bcc Fe or FeML/Ni(001). Those of the Ni atoms in the neighborhood of the cluster are slightly smaller than in the interior of bulk Ni and about 30% smaller than at the surface of bulk Ni.

To investigate the possibility that supported Fe clusters might, like free Fe_3 and Fe_5,[35] exhibit noncollinear magnetism, we performed a set of noncollinear TB calculations. The configurations so calculated were in all cases ferromagnetic. The difference with respect to free Fe_3 and Fe_5 is attributable to the atoms of our supported clusters being essentially constrained to occupy the points of the Ni lattice, and to their magnetic coupling with the strongly ferromagnetic Ni substrate.

A priori, the Ni substrate, being ferromagnetic and having few *d* holes, should not appreciably modify the magnetic behavior of the supported Fe clusters through hybridization.

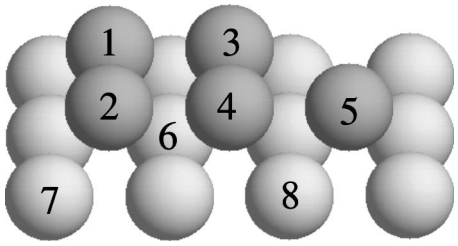

FIG. 4. Predicted lowest-energy structure of Fe_5 on the Ni(001) surface. Darker spheres represent Fe atoms, pale spheres Ni atoms (only a portion of the Ni substrate is shown). Numbers on the Fe atoms, all of which are inequivalent, and on some inequivalent Ni atoms in the neighborhood of the cluster, are used to refer to these atoms in Table III.

To support this prediction, we performed a set of TB calculations in which we imposed an Fe-Ni interlayer distance about 20% shorter than that calculated in the work described above. We found that this constraint only slightly reduced the calculated spin magnetic moments (see Fig. 3); this contrasts with the behavior of Fe_n clusters at the Al(001) surface,[6] where the strong hybridization between the Fe *d* states and the Al *sp* states "kills" the spin magnetic moments of Fe clusters smaller than a certain critical size. In the present case, magnetic properties were largely unchanged in spite of the Fe-Ni distance constraint leading certain clusters to adopt slightly different geometries: Fe_3 became a linear chain, Fe_7 like Fe_6 but with an additional atom at one corner, and Fe_8 a two-by-four rectangle.

IV. SUMMARY AND CONCLUSIONS

In this paper we used the MEAM to compute the lowest-energy structures of small Fe_n clusters supported on the Ni(001) surface ($n=2-9$), and a self-consistent TB method to determine their spin magnetic moments. The results were compared with those provided recently by the Lau *et al.* XMCD measurements.[3] As expected by Lau *et al.*, we found the cluster structures to be two-dimensional islands, but we did not find the odd-even alternation in cluster geometry type that Lau *et al.* tentatively postulated in order to explain the observed irregular variation of μ/n_h with cluster size. Though generally agreeing with the Lau *et al.* experimental values to within experimental error, our predicted values of the ratio μ/n_h hardly varied at all with cluster size, all these clusters having virtually the same number of *d* holes (because of their similar structures) and Fe atoms that are all close to spin-magnetic saturation. The variation in μ/n_h observed by Lau *et al.* may in some cases be due to the

TABLE III. Spin magnetic moments (in μ_B) calculated in this work for some inequivalent atoms of the Fe_5/Ni(001) system (see Fig. 4), together with the TB-calculated values for atoms at the surface (*S*) and in the interior (*B*) of bulk Ni.

	1	2	3	4	5	6	7	8	Ni (*S*)	Ni (*B*)
μ	2.93	2.92	2.91	2.82	3.11	0.48	0.59	0.59	0.92	0.64

influence of cluster geometry on the spin magnetic dipole term included in their estimates. Noncollinear TB calculations confirmed that the Fe atoms were ferromagnetically coupled both to each other and to the Ni substrate. Finally, it was shown that the Ni substrate does not appreciably modify the magnetic behavior of the supported Fe clusters through hybridization.

Note added in proof. Our attention has recently been drawn to a paper by Mavropoulos, Lounis, Zeller, and Blügel,[36] in which they describe a study of the electronic structure of 1-9–atom Fe clusters on Ni(001) that used a different methodology from that employed in the present paper. Their computed spin magnetic moments agree quite well with those obtained here.

ACKNOWLEDGMENTS

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