Self-consistent density-functional calculations of the geometries, electronic structures, and magnetic moments of Ni-Al clusters

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We report *ab initio* molecular dynamics simulations of Ni_2, Al_2, Ni_{13}, Al_{13}, and $Ni_{12}Al$ clusters using SIESTA, a fully self-consistent density-functional method that employs linear combinations of atomic orbitals as basis sets, standard norm-conserving pseudopotentials and a generalized-gradient approximation to exchange and correlation. Our results for the pure Ni and Al clusters, which are compared with those obtained by other recent *ab initio* calculations, are in good agreement with available experimental data. For the binary cluster $Ni_{12}Al$ our calculations show that a distorted icosahedral configuration with the Al atom at the cluster surface is more stable than that with the Al atom located at the central site, a result that clarifies discrepancies between the results of different semiempirical treatments. [S0163-1829(99)15227-5]

I. INTRODUCTION

Computer simulations have become a powerful tool for describing the properties of materials in general, in particular those of mesoscale systems such as clusters of metal atoms. Semiempirical many-body potentials, such as those based on the embedded atom model[1–4] (EAM) or the second-moment approximation to the tight-binding method (TBM-SMA;[5] the so-called Gupta-like potential[6]), lead to simple computational schemes with which it is possible to study the behavior of quite large clusters (see, e.g., Refs 7–10 and those cited therein). *Ab initio* methods, on the other hand, are computationally very demanding, and are generally limited to clusters with very few atoms (see, e.g., Refs. 11–13). The difficulties are particularly great for clusters of transition-metal atoms (CTMA's), due to the problem of treating the compact *d* orbitals.

Although the EAM is based[14] on density-functional theory (DFT),[15] its practical implementation adopts a semiempirical approach in which the embedding function and core-core interaction (the two contributions to the EAM expression for the energy) are fitted to available experimental data. The various EAM versions that have been proposed differ in the forms of the EAM functions involved and in the method used for their parameterization. The Voter and Chen (VC) version,[4] which uses diatomic data as well as bulk properties in the fitting procedure, has been used to describe the properties of free pure and mixed clusters of metal atoms[7,8] and those of CTMA's supported on metal surfaces.[16,17] The TBM-SMA has also been applied extensively to the study of clusters.[7,9,10,18,19] Although the physical rationales of the EAM and TBM-SMA are quite different, their governing equations are formally equivalent. The principal advantage of the TBM-SMA is that it gives an explicit

expression for the energy (whereas in the EAM the embedding function must be constructed numerically), which facilitates its use in molecular-dynamics (MD) simulations.

Not surprisingly, cluster calculations based on different semiempirical methods often lead to predictions that differ not only quantitatively but also qualitatively. For instance, recent MD simulations of $Ni_{13-x}Al_x$ clusters using the VC EAM placed the Al ''impurity'' of $Ni_{12}Al$ at the surface of an icosahedron with a slight distortion due to the size difference between Ni and Al,[8] whereas TBM-SMA MD calculations place it at the central site.[9] Accurate predictions of how the atoms are distributed in a bimetallic cluster (in particular, of which atoms are segregated on the cluster surface) are of importance for both theoretical and technological reasons due to the use of this kind of cluster as catalysts.[20,21]

Regarding *ab initio* computer simulation methods, great efforts have been devoted over the last few years to the development of schemes allowing description of the structure and electronic properties of large clusters. The pioneering work in this area was that of Car and Parrinello (CP),[22] which combined DFT with MD methods. A major limitation of this and most other *ab initio* techniques is that the computational cost scales as N^3, where N is the number of atoms. However, a number of methods have recently been developed with $O(N)$ scaling, i.e., with computational demands scaling linearly with system size (see Ref. 23 and those cited therein). In particular, Ordejón *et al.*[24,25] have developed an $O(N)$ self-consistent DFT program, SIESTA, that uses linear combinations of atomic orbitals (LCAO's) as basis sets. It has recently been applied to Au clusters,[26] but has not hitherto been used to study the magnetism of CTMA's, an effect that results from the delicate interplay of several factors, including cluster symmetry, *d*-shell filling,

bond lengths, coordination numbers, and the number of atoms in the cluster.

The aim of the work described in this paper was threefold. First, we wished to use SIESTA to obtain the structures and binding energies of some pure Ni and Al clusters for comparison with both available experimental information and with the results obtained from other *ab initio* DFT calculations. Second, we wanted to analyze the structure of the binary cluster $Ni_{12}Al$ in order to shed light on the discrepancies between the VC EAM and TBM-SMA predictions[8,9] (note that since both these semiempirical methods predict a difference of less than 1 eV between the binding energies of the surface Al and centered Al configurations, very accurate calculations are required to settle the dispute). Finally, we wanted to calculate the magnetic moment of each cluster studied, magnetic moments not being calculable by either the EAM or the TBM-SMA, at least in their standard forms.

Details of the computational method used in this paper are given in Sec. II. In Sec. III, we present and discuss our results, and in Sec. IV we summarize our main conclusions.

II. DETAILS OF THE COMPUTATIONAL PROCEDURE

As indicated above, SIESTA performs *ab initio* DFT calculations using numerical atomic orbitals as basis sets.[24,25] Due to the requirements of high accuracy noted above, we use double-ζ bases with polarization functions. For Ni, this means that the basis contains two orbitals with different radial forms to describe the $4s$ shell and two orbitals for each of the angular functions of the $3d$ shell, and that the $4s$ shell is polarized by the inclusion of a single set of p orbitals. For Al, we have two orbitals for the $3s$ and each of the $3p$ functions, and the latter are polarized with a single set of d functions. The double-ζ orbitals are defined in the split-valence spirit, and the polarization functions are obtained perturbatively by applying a small electric field to the free atom.[27] In order to achieve $O(N)$ scaling in the calculation of the matrix elements, SIESTA uses orbitals which have a finite range in real space. The finite range is defined by limiting the orbital confinement energy (the difference between the atomic eigenvalues of the confined and free orbitals) to 0.001 Ry.[27]

The core electrons were eliminated from the calculations, and their effect was accounted for by the inclusion of nonlocal, norm-conserving Troullier-Martins pseudopotentials.[28] These were generated by means of nonrelativistic, spin-polarized atomic calculations. The reference valence configuration used was $4s^1(\uparrow)\ 4s^0(\downarrow)\ 3d^5(\uparrow)\ 3d^4(\downarrow)$ for Ni, and $3s^1(\uparrow)\ 3s^1(\downarrow)\ 3p^1(\uparrow)\ 3p^0(\downarrow)$ for Al (arrows indicate up and down spins), and the pseudopotential radii used were 2.05 bohr for Ni and 2.28 bohr for Al. Due to the significant overlap of the core charge with the $3d$ orbitals of Ni, it was found necessary to include nonlinear core corrections (NLCC) in the description of these atoms. A radius of $r_c = 0.8$ bohr was used to define the NLCC charge density.[29] For a given configuration of the ion cores, the valence electrons were treated selfconsistently within DFT, using the Perdew-Burke-Ernzerhof form of the generalized gradient approximation for the exchange-correlation potential.[30]

In all cluster calculations we considered a supercell geometry with an $18 \times 18 \times 19$ Å unit cell (large enough for

TABLE I. Comparison of the theoretical values of the binding energies E_b and bond lengths R of Ni_2 and Al_2, as obtained by SIESTA calculations in this paper, with the experimental data reported in Refs. 32–34.

	E_b (eV/atom)		R (Å)	
	Theoretical	Expt.	Theoretical	Expt.
Ni_2	1.199	1.04	2.17	2.20
Al_2	0.904	0.80	2.54	2.47

interaction between the clusters in neighboring cells to be negligible) and used a 100 Ry energy cutoff to define the finite real-space grid for the numerical integrals.[24,25]

To obtain the cluster structures we carried out MD simulations using the velocity Verlet algorithm.[31] The forces on ions were computed using a variant of the Hellman-Feynman theorem, which includes Pulay-like corrections to account for the fact that the basis sets are not complete and move with the atoms.[24,25] A quenching technique was used in which at each MD step the velocity components of atoms going uphill (i.e., atoms being decelerated by the forces upon them) were set to zero, while atoms going downhill where allowed to obey Newtonian dynamics. The clusters were allowed to relax until the interatomic forces were smaller than 0.001 eV/Å. The binding energies reported below were calculated by subtracting the sum of the energies for the individual atoms (computed using the same basis sets and cell size as in the cluster calculations) from the cluster energy.

III. RESULTS AND DISCUSSION

As a first test of our computational method, we performed calculations for Ni_2 and Al_2, for which experimental data are available for comparison. Table I shows that the computed binding energies E_b and bond lengths R of these dimers are in good agreement with the reported experimental data.[32–34] The calculated total spin for both Ni_2 and Al_2 is $S=1$ (amounting to a magnetic moment μ of $1\mu_B$/atom, where μ_B is the Bohr magneton), which for Ni_2 is consistent with matrix isolation measurements.[35]

Of the various *ab initio* studies for Ni and Al clusters that have been carried out (see Refs. 13 and 36 and those cited therein), we mention here only the most recent. Reuse and Khanna[13] investigated the geometries, electronic structures and magnetic moments of Ni_n clusters ($n=2$–$6, 8, 13$), within the framework of DFT, using an LCAO molecular-orbital approach.[37] The molecular orbitals were constructed from Gaussian functions centered at the atomic sites, the exchange correlation energy was treated using the local-spin density (LSD) approximation,[38] and the inner cores were replaced by norm-conserving nonlocal pseudopotentials of the form proposed by Bachelet *et al.*[39] For Ni_2, Reuse and Khanna found the ground state to have $E_b = 1.61$ eV/atom, $R=2.0$ Å, and $S=1$; the E_b and R values agree with the experimental data less well than ours (Table I). Recent DFT calculations in the LSD approximation on Al clusters by Akola *et al.*[36] using the MD method of Barnett and Landman[40] give for the ground state of Al_2 the values $E_b = 0.98$ eV/atom, $R=2.46$ Å, and $S=1$, in good agreement

TABLE II. Computed values of the binding energy (E_b), mean center-to-vertex (R_{c-v}) and vertex-to-vertex (R_{v-v}) bond lengths, and total spins (S) and magnetic moments (in parentheses) of Ni_{13} and Al_{13} and of the binary cluster $Ni_{12}Al$ with the Al atom at the cluster surface [$Ni_{12}Al(s)$] or the cluster center [$Ni_{12}Al(c)$]. For $Ni_{12}Al(s)$, the first R_{c-v} value is the average distance between the central Ni atom and the Ni surface atoms and the second is the distance between the central Ni atom and the Al atom, while the first R_{v-v} value is the average distance between the Ni surface atoms and the second is the average distance between the Al atom and its neighboring surface atoms.

	E_b (eV/atom)	R_{c-v} (Å)	R_{v-v} (Å)	S
Ni_{13}	2.757	2.41±0.03	2.53±0.03	4 (0.62 μ_B/atom)
Al_{13}	2.616	2.72±0.02	2.86±0.02	1/2 (0.08 μ_B/atom)
$Ni_{12}Al(s)$	2.786	2.42±0.04	2.56±0.04	7/2 (0.54 μ_B/atom)
		2.52	2.61±0.04	
$Ni_{12}Al(c)$	2.746	2.42±0.03	2.54±0.03	5/2 (0.39 μ_B/atom)

with both our *ab initio* results and the experimental data.

Calculations for Ni_{13} and Al_{13} were also performed, taking as starting geometries those obtained by Rey *et al.*[8] These authors used the VC EAM potential to obtain minimum energy structures of $Ni_{n-x}Al_x$ clusters ($n = 13$, 19, and 55) by performing a thorough simulated annealing search, finding 100–200 local minima for each cluster. For both Ni_{13} and Al_{13}, the most stable structure found was an undistorted icosahedron; the prediction of icosahedral geometries is in keeping with previous *ab initio* calculations[13,36,41,42] and, in the case of Ni_{13}, with the conclusions inferred from chemical probe experiments.[43] Relaxation of these undistorted icosahedral structures with our DFT method slightly distorted both icosahedra, Ni_{13} especially. This distortion has also been predicted by other authors, both for Al[41] and for Ni,[44] as a Jahn-Teller effect. Table II shows the calculated binding energies, mean center-to-vertex and vertex-to-vertex bond lengths, total spins, and magnetic moments of Ni_{13} and Al_{13}. The binding energy we obtain for Ni_{13}, 2.757 eV/atom, must be more reasonable than Reuse and Khanna's value (4.26 eV) given that the experimental cohesive energy of bulk fcc Ni is only 4.45 eV (Ref. 4). Moreover, Reuse and Khanna obtained their result without allowing for the Jahn-Teller distorsion, which would increase it even further. Regarding Al_{13}, our predicted binding energy, 2.616 eV/atom, is in good agreement with the value measured by Ray *et al.*[45]

TABLE III. Mulliken population analyses for Ni_{13} and Al_{13} and for the binary cluster $Ni_{12}Al$ with the Al atom at the cluster surface [$Ni_{12}Al(s)$] or the cluster center [$Ni_{12}Al(c)$]. For the surface atoms, charges shown are averages over all surface atoms [for $Ni_{12}Al(s)$ the first value for each orbital is the average contribution of an Ni surface atom, the second that of the Al atom]. Arrows indicate up (↑) and down (↓) spins.

		Ni_{13}	Al_{13}	$Ni_{12}Al(s)$	$Ni_{12}Al(c)$
Central atom					
	$s\uparrow$	0.122	0.122	0.154	0.611
	$s\downarrow$	0.125	0.118	0.143	0.608
	$p\uparrow$	0.125	0.227	0.268	0.010
	$p\downarrow$	0.082	0.116	0.245	0.001
	$d\uparrow$	4.507	0.405	4.398	0.138
	$d\downarrow$	4.430	0.402	4.527	0.173
	Total	9.391	1.390	9.735	1.541
Surface atoms					
	$s\uparrow$	0.332±0.004	0.648±0.006	0.350±0.015	0.324±0.005
				0.733	
	$s\downarrow$	0.358±0.004	0.641±0.001	0.355±0.008	0.355±0.004
				0.686	
	$p\uparrow$	0.180±0.004	0.771±0.011	0.213±0.005	0.192±0.006
				0.438	
	$p\downarrow$	0.218±0.006	0.711±0.021	0.216±0.014	0.230±0.004
				0.420	
	$d\uparrow$	4.842±0.004	0.186±0.002	4.809±0.025	4.754±0.009
				0.000	
	$d\downarrow$	4.121±0.006	0.178±0.001	4.161±0.041	4.267±0.013
				0.000	
	Total/atom	10.051	3.134	10.090	10.122
				2.277	

by means of photodissociation experiments, 2.481 eV/atom. For this cluster, the binding energy obtained by Akola *et al.*[36] using the LSD approximation is about 2.94 eV/atom, while the local-density approximation value recently calculated by Kumar[42] is 2.89 eV/atom. The computed magnetic moments of Ni_{13} and Al_{13} (Table II) show that only the former is, in fact, a magnetic cluster, our prediction for its magnetic moment being the same as that obtained by Reuse and Khanna.[13]

Mulliken population analysis of Ni_{13} and Al_{13} (Table III) reveals that in each case the charge on the central atom is less than that on an isolated atom of the same species ($10e$ for Ni and $3e$ for Al, where e is the charge of the electron). In Cheng *et al.*'s DFT studies of the electronic structure of Al clusters, the central atom of Al_{13} was predicted as being negatively charged.[46] This discrepancy may be due to the fact that Cheng *et al.*'s calculations were performed using the discrete variational $X\alpha$ scheme (a less accurate approach than that used in our work), but also may be related to the arbitrariness of the Mulliken charges definition, specially for relatively large bases. The results listed in Table III also show that for both Ni_{13} and Al_{13} the spin-up and spin-down contributions to the Mulliken population are generally very similar for all orbitals except the d orbitals of the surface atoms of Ni_{13}. It is the contribution of these orbitals that originates the large magnetic moment of this cluster.

Figure 1 (upper panel) shows the computed densities of states (DOS) of Ni_{13} and Al_{13}, which were obtained from the corresponding Khon-Sham one-electron eigenvalues. For Al_{13} there is a substantial gap (0.44 eV) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which is consistent with the high-ionization potential of this cluster.[47] For Ni_{13} the HOMO-LUMO gap is a mere 0.03 eV.

With the above results in support of the reliability of our computational scheme, we next focused on the $Ni_{12}Al$ cluster. Using the VC EAM potential, Rey *et al.*[8] predicted that the lowest-energy configuration of this cluster is a slightly distorted icosahedron. DFT relaxation of their coordinates for two different configurations, in one of which the Al atom is at the center and in the other at the surface of the cluster, showed that a distorted icosahedral configuration with the Al atom at the cluster surface [denoted $Ni_{12}Al(s)$ in Table II] is 0.52 eV more stable and has a larger magnetic moment than the configuration with the Al atom at the central site [$Ni_{12}Al(c)$]. The sign of the energy difference is in keeping with the EAM results of Rey *et al.*,[8] rather than with Jellinek and Krissinel's TBM-SMA results.[9] In principle, the strong tendency of the bulk alloy to form ordered compounds[48] might suggest that the Al atom would prefer the cluster center, which would increase the number of Al-Ni bonds. However, if the larger Al atom were placed at the center of the icosahedron, the cluster would undergo a slight expansion; this would raise the energy of the Ni-Ni bonds, especially in view of the tendency in metallic systems for surface interatomic distances to contract in order to compensate for lower coordination.[49] Thus, it is the atomic size mismatch that appears to be the origin of the higher stability of the $Ni_{12}Al(s)$ configuration, an effect that is reflected in its appreciable DOS at energies close to -3.5 eV, which is unmatched by $Ni_{12}Al(c)$ (Fig. 1, lower panel). Mulliken population analysis
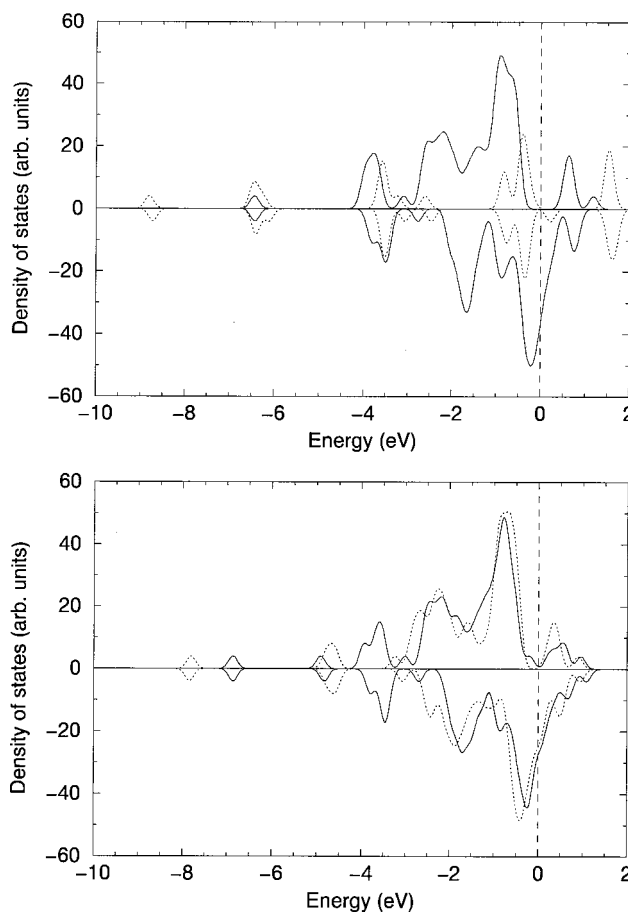

FIG. 1. Upper panel: density of states of Ni_{13} (full line) and Al_{13} (dashed line). Lower panel: density of states for $Ni_{12}Al(s)$ (full line) and $Ni_{12}Al(c)$ (dashed line). The curves were obtained using a Gaussian broadening of 0.1 eV for the discrete electron level spectrum. Positive and negative values represent spin-up and spin-down contributions, respectively. The Fermi energy is shifted to zero.

(Table III) shows that the central Ni of $Ni_{12}Al(s)$ is slightly more negatively charged than that of Ni_{13}. Hence, the replacement of a surface Ni of Ni_{13} by an Al atom is associated with a transfer of charge to the central Ni atom, which is consistent with the fact that Ni has greater electronic affinity than Al.[50]

In spite of the qualitative agreement between the *ab initio* results for $Ni_{12}Al$ obtained in this paper and the VC EAM findings of Ref. 8, there are significant differences between the results of the two methods as regards the structures and energies predicted for this and the other clusters. Specifically, the VC EAM binding energies for Ni_{13}, Al_{13}, $Ni_{12}Al(s)$, and $Ni_{12}Al(c)$ are 3.174, 2.472, 3.185, and 3.129 eV/atom,[8] somewhat different from the *ab initio* results of Table II. Moreover, the icosahedral VC EAM structures for Ni_{13} and Al_{13} fail to exhibit the slight distortions predicted by the *ab initio* calculations, which derive from electronic structure. Hence, although the VC EAM can be considered as a useful guide for qualitative description of the structural features of clusters of metal atoms, quantitative description requires more accurate, *ab initio* calculations. For this latter purpose, the self-consistent DFT technique employed in this paper has proved to be both accurate and efficient.

IV. SUMMARY AND CONCLUSIONS

In this paper, we performed self-consistent DFT calculations to investigate the binding energies, electronic structures and magnetism of Ni_2, Al_2, Ni_{13}, Al_{13}, and $Ni_{12}Al$ clusters. Our predictions for the pure clusters are in good agreement with available experimental data, and in general are better than those obtained in other recent DFT studies of these clusters. For the binary cluster $Ni_{12}Al$ we found that a distorted icosahedral configuration with the Al atom at the cluster surface is more stable than a configuration with the Al atom located at the central site, a result that clarifies the discrepancy between the results of recent studies that used the semi-empirical VC EAM (Ref. 8) and TBM-SMA (Ref. 9) potentials.

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