Structures of 13-atom clusters of fcc transition metals by *ab initio* and semiempirical calculations

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We report the results of *ab initio* calculations of the structures and magnetic moments of Ni_{13}, Pd_{13}, Pt_{13}, Cu_{13}, Ag_{13}, and Au_{13} that were performed using a density-functional method that employs linear combinations of pseudoatomic orbitals as basis sets (SIESTA). Our structural results for Pt_{13}, Cu_{13}, Ag_{13}, and Au_{13} show that a buckled biplanar structure (BBP) is more stable than the icosahedral configuration, in keeping with results obtained recently by Chang and Chou [Phys. Rev. Lett. **93**, 133401 (2004)] using the Vienna *ab initio* simulation package with a plane-wave basis. However, for Ni_{13} and Pd_{13} we found that the icosahedral structure is more stable than BBP. For all these clusters, two semiempirical methods based on spherically symmetric potentials both found the icosahedral structure to be the more stable, while the modified embedded atom model method, which uses a direction-dependent potential, found BBP to be the more stable structure. When low-energy structures found in recent *ab initio* studies of Pt_{13}, Cu_{13}, and Au_{13} other than Chang and Chou were optimized with SIESTA, those reported for Pt_{13} and Cu_{13} were found to be less stable than BBP, but the two-dimensional planar configuration reported for Au_{13} proved to be more stable than BBP.

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I. INTRODUCTION

Accurate determination of the geometrical structures of clusters of transition metal (TM) atoms is of prime importance given the structure dependence of their optical, magnetic, and chemical properties. However, experimental structure determinations are not always unequivocal, particularly in the case of the chemical probe method,[1–5] in which the adsorption of molecules onto the cluster surface can modify the configuration of the bare cluster. Theoretical methods of structure determination fall into two broad classes: *ab initio* calculations, which are generally based on density-functional theory (DFT); and semiempirical methods involving many-body potentials, such as those based on the embedded atom model (EAM)[6] or on the second-moment approximation of the tight-binding method (TBM-SMA),[7,8] the so-called Gupta-like potential.[9] *Ab initio* methods are in principle more accurate than semiempirical methods, but are computationally extremely demanding; although global exploration of potential energy surfaces (PES) has been performed using *ab initio* techniques (Aprà *et al.*,[10] for example, have used DFT calculations with the basin-hopping algorithm[11,12] to find the global energy minimum of Au_{20}), the computational power required is not universally available. It is accordingly common practice to perform *ab initio* calculations of minimum-energy geometry starting from configurations that have been postulated on symmetry grounds or located by extensive exploration of the PES using a semiempirical method; for example, Aprà *et al.*[10] supplemented their global DFT calculations with local DFT optimizations of this kind. Chang and Chou[13] recently performed local DFT optimization to investigate the geometries of 13-atom clusters of all TMs in the 4*d* series and a selection of those belonging to the 3*d* and 5*d* series (Ti, Co, Cu, Hf, Ir, Pt, and Au). These calculations were carried out using the Vienna *ab initio* simulation package (VASP) (Refs. 14 and 15) with a plane-wave basis, Vanderbilt-type ultrasoft pseudopotentials,[16,17] and the spin-polarized generalized gradient approximation to exchange and correlation (GGA).[18,19]

With the exception of Au, all the metals examined by Chang and Chou[13] that have *d* shells that are more than one-half full were found to have a C_{2v}-symmetric "buckled biplanar" isomer (BBP; see Fig. 1) that was of lower energy than the close-packed icosahedral or cuboctahedral structures that have been predicted by studies employing semiempirical methods or other DFT approaches (see references cited in Ref. 13). They attributed the adoption of this geometry to enhanced *s-d* hybridization, and its nondetection in previous *ab initio* studies to incomplete PES exploration. In the case of theoretical studies employing semiempirical approaches, it is well known that the use of spherically symmetric potentials favors icosahedral geometries.

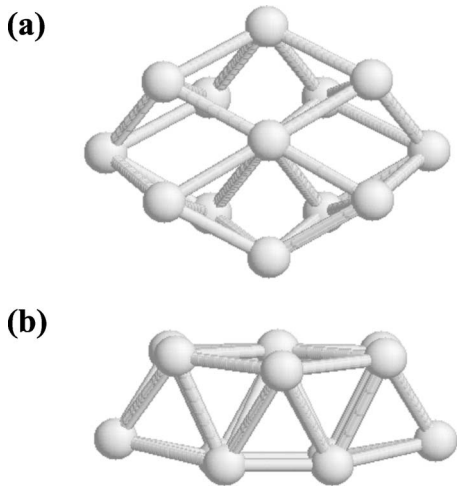

FIG. 1. Top (a) and side (b) views of the buckled biplanar (BBP) structure. Note that both the seven-atom centered-hexagonal top layer and the six-atom bottom layer (a square with two flanking atoms) deviate slightly from planar.

Using the same computational approach as Chang and Chou to study the 13-atom cluster of the 4*d* TM rhodium, Bae *et al.*[20,21] have subsequently identified structures with even lower energies than the BBP configuration, one a cage-like structure[20] and the other a capped simple cubic configuration.[21] These results, and others that are mentioned below, raise the question of how many late TMs really have BBP ground structures.

Here we report the results of a study of 13-atom clusters of selected late 3*d*, 4*d*, and 5*d* TMs (Ni, Pd, Pt, Cu, Ag, and Au) that was carried out with the following objectives: (a) to determine whether BBP structures were also more stable than icosahedral structures when calculated by a DFT-based method different from that used by Chang and Chou; (b) to examine whether three commonly used semiempirical methods, with standard parametrizations, were able to order the stabilities of the icosahedral and BBP structures of these TM clusters correctly; and (c) to determine whether the DFT-based method used in this work does or does not support the claims of other structures that have been put forward as possible ground structures for the TM clusters studied.

II. COMPUTATIONAL METHODS

DFT calculations were performed using SIESTA,[22] which employs linear combinations of numerical pseudoatomic orbitals as basis sets to solve the standard Kohn-Sham equations. The SIESTA method has been applied to a large variety of systems, including free and supported clusters, nanotubes, biological molecules, amorphous semiconductors, and ferroelectric films (for a review, see Ref. 23). For the exchange and correlation potential we used the Perdew-Burke-Ernzerhof form of the GGA.[24] Atomic cores were replaced by nonlocal, norm-conserving scalar-relativistic Troullier-Martins pseudopotentials,[25] which were generated using the valence configuration of the free atoms in their ground states.[26–28] Valence states were described using triple-ζ doubly polarized basis sets. In the calculations the clusters were placed at the center of a supercell of size $20\times20\times30$ Å, large enough (a) for interactions between the cluster and its replicas in neighboring cells to be negligible, and (b) for it to suffice to consider only the Γ point ($k=0$) when integrating over the Brillouin zone. An energy cutoff of 150 Ry was used to define the finite real-space grid for numerical integrals. Cluster structures were optimized by quenching molecular dynamics simulations using the velocity Verlet algorithm,[29] the forces being computed using a variant of the Hellman-Feynman theorem that includes Pulay-type corrections.[22] In each case, the starting configuration was of the kind used by Chang and Chou[13] [objective (a)] or some other authors [objective (c)]. The clusters were allowed to relax until the interatomic forces were smaller than 0.001 eV/Å.

Icosahedral and BBP structures of the clusters studied were also optimized using three semiempirical model potentials: the TBM-SMA,[7–9] the version of the EAM proposed by Voter and Chen (VC-EAM),[30] and the modified EAM (MEAM) as recently extended by Baskes and co-workers to take second-nearest neighbors into account.[31,32] All three methods have been used to analyze the structures and other properties of TM clusters (see, e.g., Refs. 33–47). It is perhaps worth noting that although the physical rationales of the TBM-SMA and the EAM are quite different, their governing equations are formally equivalent and have in common that the interaction between the atoms depends upon their local environment. The MEAM is an extension of the EAM that includes angular forces. Complete details of the TBM-SMA, VC-EAM, and MEAM as used in this work can be found elsewhere.[7–9,30–32] The parameters required by the TBM-SMA for the TMs studied were taken from Ref. 8 and had been obtained by fitting the model to the experimental values of the bulk properties of each metal; the parameters required by the MEAM were taken from a recent paper by Baskes and co-workers,[32] and had likewise been obtained by fitting to bulk properties; and the parameters required by the VC-EAM (obtained by fitting to both diatomic and bulk data) were taken from Ref. 30 for Ni and for the remaining metals from previous work on the structural and dynamical behavior of these clusters[37] (these VC-EAM parameters are available upon request).

TABLE I. Total energies (eV) of BBP structures of Ni_{13}, Pd_{13}, Pt_{13}, Cu_{13}, Ag_{13}, and Au_{13} relative to those of their icosahedral structures, as computed by various methods in this work (SIESTA, TBM-SMA, VC-EAM, MEAM) or by Chang and Chou (Ref. 13) (VASP).

	SIESTA	VASP	TBM-SMA	VC-EAM	MEAM
Ni_{13}	2.48		1.57	2.04	−0.04
Pd_{13}	0.13	−0.02	0.67	1.86	−0.22
Pt_{13}	−1.43	−1.56	0.60	1.43	−2.56
Cu_{13}	−0.39	−0.53	1.22	1.30	−0.05
Ag_{13}	−0.75	−0.84	0.78	0.95	−0.52
Au_{13}	−1.96	−1.78	0.24	1.03	−2.46

III. RESULTS

For each cluster studied, Table I lists the total energy of the BBP structure relative to the icosahedral structure as reported by Chang and Chou[13] and as obtained in this work using SIESTA, the TBM-SMA, the VC-EAM and the MEAM. Like Chang and Chou,[13] our DFT BBP structures have C_{2v} symmetry (see Fig. 1), and our DFT icosahedral structures deviate little from ideal icosahedra. The magnetic moments computed for these structures with SIESTA are listed in Table II together with the values reported by Chang and Chou[13] for Pd_{13} and Ag_{13}.

Our SIESTA results agree with the Chang and Chou[13] VASP results in predicting that the BBP structure is more stable than the icosahedral structure for Pt_{13}, Cu_{13}, Ag_{13}, and Au_{13}. However, for Ni_{13} (which Chang and Chou did not study), and for Pd_{13}, our SIESTA calculations predict that the icosahedral structure is the more stable. In the case of Ni_{13}, the SIESTA prediction is almost certainly correct, an icosahedral structure having been inferred from N_2 adsorption experiments (unlike some other adsorbates, N_2 does not appear to

TABLE II. Spin magnetic moments of the BBP and icosahedral structures of Ni_{13}, Pd_{13}, Pt_{13}, Cu_{13}, Ag_{13}, and Au_{13}, in units of the Bohr magneton μ_B, as obtained in this work by SIESTA calculations. Also shown are the values obtained by Chang and Chou for some of these clusters using VASP (Ref. 13).

	Icosahedral		BBP	
	SIESTA	VASP	SIESTA	VASP
Ni_{13}	8		10	
Pd_{13}	8	8	4	4
Pt_{13}	2		8	
Cu_{13}	5		1	
Ag_{13}	5	5	1	1
Au_{13}	5		1	

cause gross alteration of cluster structure).[3] In the case of Pd_{13}, icosahedral structures have also been found in other *ab initio* studies.[48–51]

For all the clusters studied, both the TBM-SMA and the VC-EAM found icosahedral structures to be more stable than BBP, while the MEAM found the contrary. The TBM-SMA and VC-EAM results are expected for the reason noted in the Introduction: a spherically symmetric potential must favor the more symmetric structure. Given the SIESTA results (and others commented on below), it is therefore doubtful whether, as has been claimed,[51] the use of phenomenological potentials allows reliable calculation of the symmetry of the minimum-energy configurations of TM clusters. Furthermore, even if the potential does not disfavor the correct symmetry, other aspects of structure are known to depend critically on the parametrization of the potential.[36,37]

For Pt_{13}, Cu_{13}, and Au_{13} (for all of which BBP was found to be more stable than an icosahedral structure both in this work and by Chang and Chou[13]), structures other than BBP or the icosahedron have been put forward as possible minimum-energy structures in a number of other recent *ab initio* studies (for a review, see Ref. 52). For Pt_{13}, VASP/GGA calculations have pointed to a capped three-layer structure,[53] but when optimized using SIESTA this structure has an energy 0.184 eV greater than that of BBP. For Cu_{13}, VASP/GGA calculations[54] have pointed to a "disordered" or "amorphous" ground structure, but when optimized using SIESTA this structure has an energy 0.616 eV greater than that of BBP [SIESTA/GGA calculations by Fernández *et al.*[27] found a possible icosahedral ground state, but in view of the breadth of their study they did not use spin polarization (SP) in their calculations]. Finally, for Au_{13}, SIESTA/GGA calculations without SP have afforded a nonicosahedral, non-BBP three-dimensional ground structure,[27] while a two-dimensional configuration was the lowest-energy structure found in both the Chang and Chou work with VASP/GGA[13] and in a high-level *ab initio* study including coupled clusters and single and double excitations.[55] Optimization of the two-dimensional geometry with SIESTA corroborated that it is more stable than BBP (by 0.413 eV; it was also calculated to have a magnetic moment of $1\mu_B$); and a similar calculation for the three-dimensional structure obtained by SIESTA/GGA without SP (Ref. 27) showed that although it is more stable than BBP, it is 0.376 eV less stable than the planar structure.

The propensity of Au clusters to adopt planar structures has been shown to be due to the relativistic contraction of the Au 6*s* orbital; this contraction leads to substantial overlapping and hybridization with the 5*d* orbitals, which greatly increases the contribution of the latter to bonding with neighboring atoms.[55–57] Strong directional effects due to *d*-*d* interactions have also been found in Pt clusters,[58] whereas in Cu and Ag clusters, which have smaller relativistic effects and larger *s*-*d* energy differences, bonding is mainly due to the *s* electron.[55,59] This explains why, in this study and the study by Chang and Chou,[13] the DFT energy of the preferred, lower-symmetry BBP structure differs much more from that of the high-symmetry icosahedral structure for Au_{13} and Pt_{13} than for Cu_{13} and Ag_{13} (see Table I).

IV. SUMMARY AND CONCLUSIONS

When optimized by means of the DFT package SIESTA using the GGA and SP, the BBP isomers of Pt_{13}, Cu_{13}, Ag_{13}, and Au_{13} are all found to be more stable than the corresponding icosahedral isomers, whereas the reverse holds for Ni_{13} and Pd_{13}. Comparison of the result for Pd_{13} with that obtained by Chang and Chou[13] highlights the fact that different DFT methods can sometimes lead to predictions that differ qualitatively as well as quantitatively, even when performed at similar levels of sophistication (in this case the use of GGA with SP). With the parameters described above under Computational Methods, the MEAM predicts a BBP structure for all six of these TM clusters, while the VC-EAM and TBM-SMA both predict icosahedral structures for all six. SIESTA/GGA/SP optimization of other reported low-energy isomers of Pt_{13}, Cu_{13}, and Au_{13} confirms that BBP is the most stable isomer yet calculated for Pt_{13} and Cu_{13}, and that the most stable isomer of Au_{13} yet calculated is planar.

We conclude that, as is generally recognized but has recently been questioned,[51] the structures of small TM clusters that are predicted by semiempirical methods are not necessarily in qualitative agreement with those predicted by *ab initio* calculations; and that there are probably more exceptions than Chang and Chou[13] supposed to their suggestion that for almost all 13-atom late TM clusters a BBP structure is more stable than previously reported configurations.

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