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Density-functional calculations of the structures, binding energies, and magnetic moments of Fe clusters with 2 to 17 atoms

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We report *ab initio* calculations of Fe_n clusters up to $n=17$. We used a density-functional method that employs linear combinations of numerical atomic orbitals as basis sets, nonlocal norm-conserving pseudopotentials, and the local spin density approximation for exchange and correlation. Our results for $n\leqslant 7$ generally agree quite well with those obtained in previous density-functional studies. The structural predictions for $n>7$ are also generally in keeping with information inferred from chemical probe and time-of-flight mass spectrometry experiments. The origin of the discrepancies arising in some cases is discussed.

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I. INTRODUCTION

The properties of Fe_n clusters have been investigated experimentally by several means, including chemical probes,[1–3] photoionization studies,[4,5] collision-induced dissociation experiments,[6] Stern-Gerlach measurements,[7–10] photoelectron spectroscopy,[11] and time-of-flight (TOF) mass spectrometry.[12] These studies reveal a strong size dependence of the properties of this kind of cluster, which can be attributed to changes in geometrical structure as n increases. In particular, the large reactivity variations observed in experiments with H_2, D_2O, and NH_3 adsorbates on Fe_n clusters ($n\leqslant 23$) were attributed by Parks *et al.*[1] to structural changes occurring as n increased from 13 to 14, 14 to 15, 18 to 19, and 22 to 23. Although cluster structures cannot be determined with certainty on the basis of adsorbate-binding data, Parks *et al.*[1] put forward possible geometries for these clusters. In particular, they suggested that the most likely structure for Fe_{15} is the bcc rhombic dodecahedron, and that possible candidates for the structure of Fe_{13} are the fcc cubooctahedron, the bcc rhombic dodecahedron with two missing apical atoms, and the icosahedron. By analyzing the TOF mass spectra of ionized Fe clusters, Sakurai *et al.*[12] have recently shown that Fe_{13} and Fe_{15} are ''magic number'' clusters (i.e., they are particularly stable), and have suggested that their ground state structures are the icosahedron and the bcc rhombic dodecahedron, respectively.

On the theoretical side, several *ab initio* studies have been performed to predict the geometries and electronic structures of Fe_n clusters, although due to their complicated nature (especially the presence of partially filled d orbitals) calculations have hitherto been restricted to clusters with $n\leqslant 7$. For instance, Chen *et al.*[13] investigated the properties of Fe_n clusters ($n\leqslant 4$) using an all-electron, linear combination of Gaussian atomic orbitals method based on density-functional theory (DFT) with the local spin density approximation (LSDA) to exchange and correlation; Castro and Salahub[14] used a similar all-electron DFT method, with local and nonlocal exchange-correlation potentials, to analyze the properties of neutral and charged iron clusters (Fe_n, $Fe_n{}^+$, and $Fe_n{}^-$) up to $n=5$; Ballone and Jones[15] performed LSDA DFT calculations based on the Car-Parrinello (CP) method,[16] with a basis set of plane waves and pseudopotentials constructed along the lines prescribed by Troullier and Martins,[17] to predict the structures and magnetic moments of Fe_n clusters with up to seven atoms; and, more recently, Oda *et al.*[18] have studied the properties of Fe_n ($n\leqslant 5$) using an approach that combines a generalized, noncollinear LSDA with the CP technique. Calculations for Fe_n clusters with $n>7$ have hitherto only been performed using less accurate approaches, such as the tight-binding method with adjustable parameters (see, e.g., Refs. 19 and 20).

The size limit on previous *ab initio* studies has prevented their being confronted with experimental information so as to obtain a better understanding of the properties of this kind of cluster, which is of interest not only for basic physics but also for technological reasons due to its use in the recording industry and nanotechnologies.[21] With this in mind, we decided to perform an extensive study of the structures, binding energies, and magnetic moments of Fe_n clusters up to $n=17$ using a fully self-consistent DFT-based method with numerical atomic orbitals as basis sets,[22–25] nonlocal norm-conserving Troullier-Martins pseudopotentials,[17] and the LSDA for exchange and correlation.[26]

The essential technical 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.

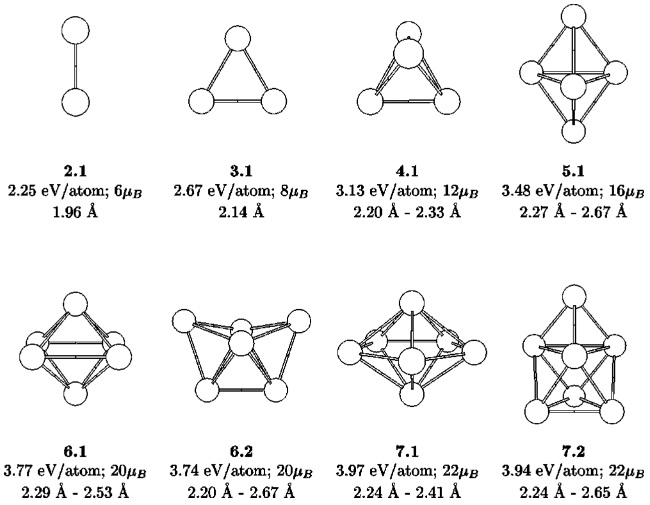
II. DETAILS OF THE COMPUTATIONAL PROCEDURE

The computational method used in this paper has been described in detail elsewhere.[22–25] It consists in DFT calculations using numerical atomic orbitals as basis sets to solve the single-particle Kohn-Sham equations. Implemented in the program SIESTA, it has recently been applied to several systems, including C nanostructures (fullerenes and nanotubes), metallic nanostructures, biomolecules, surfaces, and disordered systems (for reviews, see Refs. 27 and 28).

In these calculations we used a triple-ζ basis with double-ζ polarization functions. This means that the basis contains three orbitals with different radial forms to describe the $4s$ shell and three orbitals for each of the angular functions of the $3d$ shell, and the $4s$ shell is polarized by the inclusion of a double set of p orbitals. The triple-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.[25] In order to achieve linear scaling in the calculations of the matrix elements, the method uses orbitals that have a finite spatial range, defined by limiting the orbital confinement energy (the difference between the atomic eigenvalues of the confined and free orbitals);[25] in this work we used a value of 0.0006 Ry, which yields orbitals with confinement radii shorter than 10 bohrs.

The core electrons were represented by nonlocal, norm-conserving Troullier-Martins pseudopotentials[17] factorized in the Kleinman-Bylander form,[29] which were generated by relativistic atomic calculations and included nonlinear core corrections to account for the significant overlap of the core charge with the $3d$ orbitals of Fe.[30] The importance of generating a pseudopotential using an atomic configuration that mimics the enviroment in which it has to be placed as closely as possible has been pointed out by Troullier and Martins.[17] Here we generated the ionic Fe pseudopotential using the valence configuration $3d^7 4s^1$, because, although the configuration of the free atom in its ground state is $3d^6 4s^2$, studies of small Fe clusters performed by Vega *et al.*[31] using an spd-band model Hamiltonian in the unrestricted Hartree-Fock approximation suggest that the orbital occupations for Fe_2 resemble the $3d^7 4s^1$ configuration more closely than the ground-state configuration. The pseudopotential radii employed in our calculations for the *s*, *p*, and *d* orbitals were 2.00 bohrs. Pseudopotentials generated in this way have recently been used by Izquierdo *et al.*[32] in a study of several iron-based systems.

Our calculations were performed within the LSDA,[26] using a supercell geometry with an 18 Å × 18 Å × 18 Å unit cell (large enough for interaction between clusters in neighboring cells to be negligible), and to define the finite real space grid for numerical integration[22–24] we used a 100 Ry cutoff, which determined a distance of 1/6 Å between neighboring grid points. In order to improve grid-cutoff convergence, a sampling process was performed for quantities that are sensitive to the breaking of translational symmetry by the grid, such as the total energy and atomic forces; after achieving self-consistency, these quantities were also computed using three more grids that were displaced with respect to the original one in a fcc arrangement. The results were then averaged, yielding numerical integrals with an accuracy comparable to that of a uniform grid defined with a cutoff larger than 200 Ry.



2.1 2.25 eV/atom; 6μ_B 1.96 Å

3.1 2.67 eV/atom; 8μ_B 2.14 Å

4.1 3.13 eV/atom; 12μ_B 2.20 Å - 2.33 Å

5.1 3.48 eV/atom; 16μ_B 2.27 Å - 2.67 Å

6.1 3.77 eV/atom; 20μ_B 2.29 Å - 2.53 Å

6.2 3.74 eV/atom; 20μ_B 2.20 Å - 2.67 Å

7.1 3.97 eV/atom; 22μ_B 2.24 Å - 2.41 Å

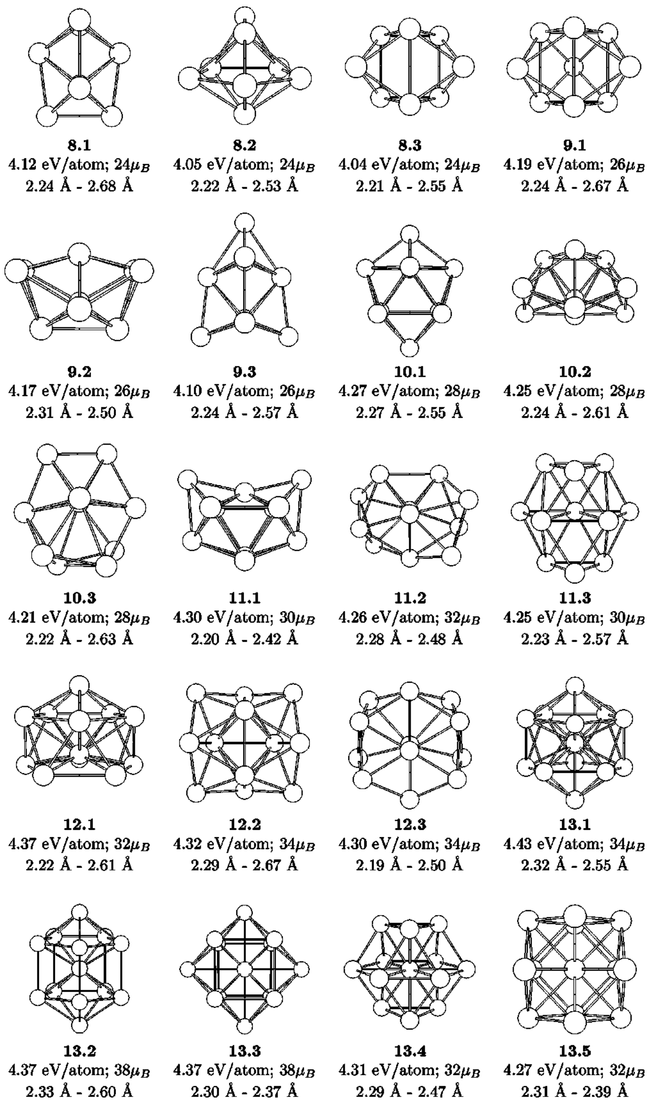
7.2 3.94 eV/atom; 22μ_B 2.24 Å - 2.65 Å

FIG. 1. Some of the isomers found for Fe_n clusters ($2 \leqslant n \leqslant 7$), with their binding energies, total magnetic moments, and nearest-neighbor distances. Isomer $n.m$ is the mth least energetic isomer with n atoms (among isomers with the same configuration, only that with the greatest binding energy is counted).

The lowest-energy structures of the Fe_n clusters were obtained by choosing various initial configurations for each value of n and relaxing them using a conjugated gradient method.[33] The set of starting configurations included stable isomers found in other *ab initio* studies of iron clusters,[13–15,18] and, for the biggest clusters, in investigations of transition metal clusters using semiempirical potentials.[34,35] For each kind of geometry, several configurations with different interatomic distances were used. In all, more than 200 configurations were relaxed to ensure thorough exploration of the potential energy surfaces of the clusters. The forces on ions were computed using a variant of the Hellmann-Feynman theorem which includes Pulay-like corrections to account for the fact that the basis sets are not complete and move with the atoms.[22,24] The clusters were allowed to relax until the interatomic forces were smaller than 0.005 eV/Å .

III. RESULTS AND DISCUSSION

Figures 1, 2, and 3 show the structures, binding energies E_b (i.e., the sign-reversed total energies per atom relative to the isolated spherical ^5D Fe atom), total magnetic moments μ (in units of the Bohr magneton μ_B), and nearest-neighbor distances (NND's) of some of the lowest-energy isomers found in our calculations for Fe_n clusters with $n=2–7$, $n=8–13$, and $n=14–17$, respectively (when the same geometry is shared by more than one isomer with different



8.1 4.12 eV/atom; 24μ_B 2.24 Å - 2.68 Å

8.2 4.05 eV/atom; 24μ_B 2.22 Å - 2.53 Å

8.3 4.04 eV/atom; 24μ_B 2.21 Å - 2.55 Å

9.1 4.19 eV/atom; 26μ_B 2.24 Å - 2.67 Å

9.2 4.17 eV/atom; 26μ_B 2.31 Å - 2.50 Å

9.3 4.10 eV/atom; 26μ_B 2.24 Å - 2.57 Å

10.1 4.27 eV/atom; 28μ_B 2.27 Å - 2.55 Å

10.2 4.25 eV/atom; 28μ_B 2.24 Å - 2.61 Å

10.3 4.21 eV/atom; 28μ_B 2.22 Å - 2.63 Å

11.1 4.30 eV/atom; 30μ_B 2.20 Å - 2.42 Å

11.2 4.26 eV/atom; 32μ_B 2.28 Å - 2.48 Å

11.3 4.25 eV/atom; 30μ_B 2.23 Å - 2.57 Å

12.1 4.37 eV/atom; 32μ_B 2.22 Å - 2.61 Å

12.2 4.32 eV/atom; 34μ_B 2.29 Å - 2.67 Å

12.3 4.30 eV/atom; 34μ_B 2.19 Å - 2.50 Å

13.1 4.43 eV/atom; 34μ_B 2.32 Å - 2.55 Å

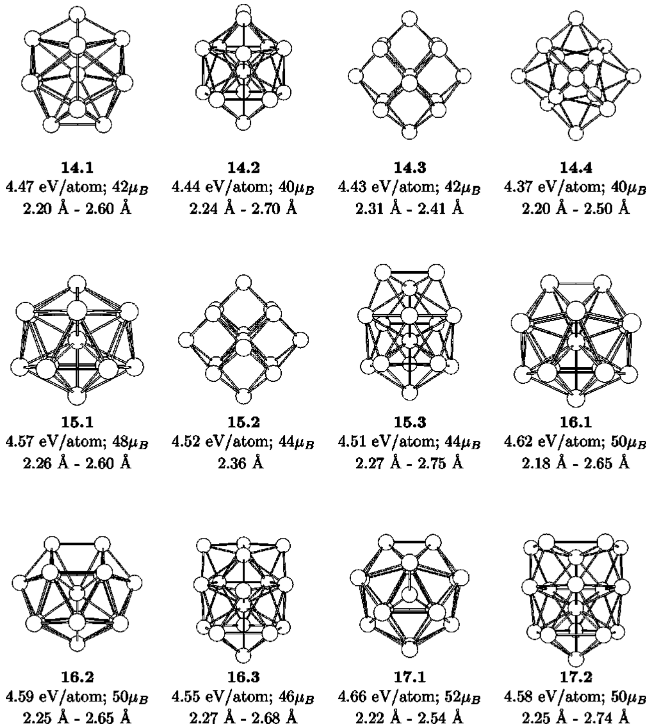
13.2 4.37 eV/atom; 38μ_B 2.33 Å - 2.60 Å

13.3 4.37 eV/atom; 38μ_B 2.30 Å - 2.37 Å

13.4 4.31 eV/atom; 32μ_B 2.29 Å - 2.47 Å

13.5 4.27 eV/atom; 32μ_B 2.31 Å - 2.39 Å

FIG. 2. As for Fig. 1, but for $8 \leqslant n \leqslant 13$.



14.1 4.47 eV/atom; 42μ_B 2.20 Å - 2.60 Å

14.2 4.44 eV/atom; 40μ_B 2.24 Å - 2.70 Å

14.3 4.43 eV/atom; 42μ_B 2.31 Å - 2.41 Å

14.4 4.37 eV/atom; 40μ_B 2.20 Å - 2.50 Å

15.1 4.57 eV/atom; 48μ_B 2.26 Å - 2.60 Å

15.2 4.52 eV/atom; 44μ_B 2.36 Å

15.3 4.51 eV/atom; 44μ_B 2.27 Å - 2.75 Å

16.1 4.62 eV/atom; 50μ_B 2.18 Å - 2.65 Å

16.2 4.59 eV/atom; 50μ_B 2.25 Å - 2.65 Å

16.3 4.55 eV/atom; 46μ_B 2.27 Å - 2.68 Å

17.1 4.66 eV/atom; 52μ_B 2.22 Å - 2.54 Å

17.2 4.58 eV/atom; 50μ_B 2.25 Å - 2.74 Å

FIG. 3. As for Fig. 1, but for $14 \leqslant n \leqslant 17$.

NND's, only the most stable isomer is shown). The isomers are labeled with two indices: the first represents the number of atoms in the cluster and the second ranks the isomers in decreasing order of binding energy. Table I lists, for each minimum energy isomer in the range $n = 8-17$ (for which no previous DFT calculations have been performed), the magnetic moment and charge of the inner atom (when it exists), and the mean values of these quantities among the external atoms (full lists of the magnetic moments and charges of all atoms are available from the authors on request). In Figs. 4 and 5 we compare the binding energies and average magnetic moments per atom, $\bar{\mu}$, of the ground-state structures obtained in this paper with the results of previous LSDA-based DFT calculations for $n \leqslant 7$ (see Refs. 13–15 and 18; in the case of $\bar{\mu}$, only two previous results differ from ours).

As in previous DFT studies,[13–15,18] our computed binding energy for Fe_2, 2.25 eV/atom, is larger than the experimental value, 0.65 eV/atom.[36] This overestimation of binding energies is typical of LSDA calculations (mainly due to the error in the atomic energy), and is not resolved totally by using nonlocal approximations to exchange and correlation.[14,32] The predicted value of the average magnetic moment per atom for this cluster, $3\mu_B$, is in keeping with the results obtained in previous DFT calculations,[13–15,18] and agrees quite well with the experimental value of $(3.3 \pm 0.5)\mu_B$ reported in Ref. 7. Our Fe-Fe distance, 1.96 Å , is consistent with the experimental values obtained in argon[37] and neon[38] matrices, 1.87 and 2.02 Å , respectively. As a test of the computational procedure employed, we also calculated the bond length and average magnetic moment per atom for Fe_2 taking the semicore p shell into account in constructing the Fe pseudopotential. The results obtained, 1.98 Å and $3\mu_B$,

TABLE I. Calculated magnetic moments and charges (in units of the charge of the electron, e) of the inner atom (when it exists) and the external atoms of the minimum energy isomers of Fe_n clusters with 8 to 17 atoms (for the external atoms, means are given with standard deviations in parentheses).

	Magnetic moment (μ_B)		Charge (e)	
Isomer	Inner atom	External atoms	Inner atom	External atoms
8.1		3.00 (0.02)		8.00 (0.14)
9.1		2.89 (0.03)		8.00 (0.10)
10.1		2.80 (0.04)		8.00 (0.06)
11.1		2.73 (0.26)		8.00 (0.28)
12.1	1.20	2.80 (0.05)	7.03	8.09 (0.17)
13.1	−0.24	2.85 (0.02)	6.47	8.13 (0.01)
14.1	2.45	3.04 (0.09)	6.45	8.12 (0.04)
15.1	3.12	3.21 (0.01)	6.42	8.11 (0.01)
16.1	3.12	3.12 (0.03)	6.31	8.11 (0.05)
17.1	3.01	3.06 (0.01)	6.11	8.12 (0.06)

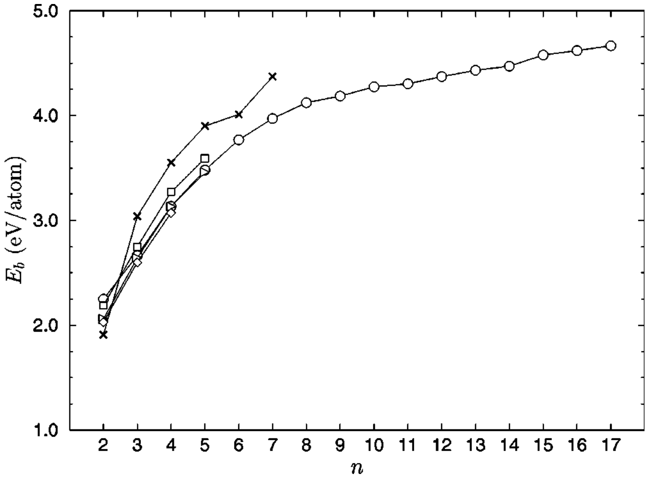


FIG. 4. Binding energies for the ground-state structures of Fe_n clusters ($2\leq n\leq 17$) as computed in the present work (○). For comparison, the results obtained by Chen *et al.* (Ref. 13) (◇), Castro and Salahub (Ref. 14) (□), Ballone and Jones (Ref. 15) (×), and Oda *et al.* (Ref. 18) (▷) are also shown.

are identical or very close to those obtained using the single valence $3d^7 4s^1$ configuration, showing that the inclusion of the p shell is not necessary.

For Fe_3 we found the ground state to be an equilateral triangle with $\bar{\mu}=2.67\mu_B$, in keeping with previous DFT calculations.[13–15,18] This value of the average magnetic moment per atom is close to the experimental $(2.7\pm 0.3)\mu_B$.[7] The computed bond lengths in this cluster, 2.14 Å , are in good agreement with the results of other DFT calculations (2.04 Å , Ref. 13; 2.10 Å , Ref. 14; 2.14 Å , Ref. 15; and 2.11 Å , Ref. 18). The previously published DFT calculations also agree in predicting that the most stable isomer of Fe_4 is a regular[13,14] or distorted[15,18] tetrahedron with $\bar{\mu}=3\mu_B$; in the present study we found the most stable structure of Fe_4 to be a distorted tetrahedron with D_{2d} symmetry, likewise with $\bar{\mu}=3\mu_B$. For Fe_5 our predicted ground-state structure is a trigonal bipyramid (in keeping with previous calculations[14,15,18]) with $\bar{\mu}=3.20\mu_B$, the same value as was reported by Castro and Salahub[14] and greater than those obtained in the other two theoretical studies ($2.8\mu_B$, Ref. 15; $2.91\mu_B$, Ref. 18).

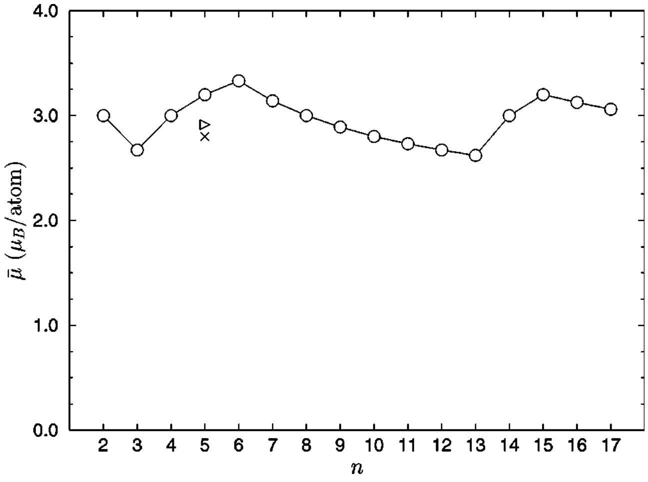


FIG. 5. Calculated average magnetic moments per atom for the ground-state geometries of Fe_n clusters ($2\leq n\leq 17$). Within the range $n=2-7$, our results agree with those obtained in previous LSDA-based DFT calculations (Refs. 13–15,18), except for the values reported by Ballone and Jones (Ref. 15) and by Oda *et al.* (Ref. 18) for Fe_5 (× and ▷, respectively).

Our results for Fe_6 and Fe_7 can be compared only with those obtained by Ballone and Jones,[15] who performed what has hitherto been the most extensive DFT study of Fe_n clusters. Our calculations predict that the ground state of Fe_6 is a compressed octahedron with $\bar{\mu}=3.33\mu_B$, and that of Fe_7 a pentagonal bipyramid with $\bar{\mu}=3.14\mu_B$. These results agree with Ballone and Jones' findings, except that their predicted minimum energy structure for Fe_6 was a capped trigonal bipyramid (structure 6.2 in Fig. 1). It should be noted, however, that in both Ballone and Jones' calculations and ours the capped trigonal bipyramid and the octahedron are almost isoenergetic (in our case, the energy difference between these two structures is only 0.03 eV/atom, and in Ballone and Jones' study 0.02 eV/atom).

We now discuss our results for Fe_n clusters in the size range $n=8-17$, for which no previous DFT calculations have been performed. The predicted ground-state structures of Fe_8, Fe_9, and Fe_{10} are a bidisphenoid, a tricapped trigonal prism, and a bicapped square antiprism, respectively (structures 8.1, 9.1, and 10.1 in Fig. 2). Not far in energy from these ground-state structures are isomers 8.2, 9.2, and 10.2, which follow an icosahedral growth pattern by adding Fe atoms to the triangular faces of the pentagonal bipyramid Fe_7.

Our calculations predict that Fe_{11}, Fe_{12}, and Fe_{13} have ground-state structures based on icosahedral packing (see Fig. 2). In particular, Fe_{13} has an icosahedral configuration with bond lengths in the range 2.32 Å–2.55 Å and $\bar{\mu}=2.62\mu_B$. A similar icosahedral ground-state structure for Fe_{13}, with bond lengths between 2.23 Å and 2.69 Å and $\bar{\mu}=2.77\mu_B$, has been predicted by Andriotis and Menon[19] using a tight-binding molecular dynamics method. Isomers 13.2, 13.3, 13.4, and 13.5 have truncated decahedral, bcc, hcp, and fcc structures, respectively. As mentioned above, icosahedral, bcc, and fcc structures were suggested as the most probable by Parks *et al.*[1] on the basis of their chemical probe results.

Fe_{14} and Fe_{15} are predicted to have the nonicosahedral symmetries C_{2v} and D_{6h}, respectively (see Fig. 3). Hence our calculations are consistent with Parks *et al.*'s[1] conclusion that structural changes occur in Fe_n clusters between $n=13$ and $n=14$ and between $n=14$ and $n=15$ (note that the structural change occurring between $n=13$ and $n=14$ is accompanied by a marked change in the average magnetic moment per atom; Fig. 5). However, Parks *et al.* suggested, as a possible structure for Fe_{14}, a central tetrahedron with an atom capping each face and six further atoms added between the latter four. This is the structure of isomer 14.4 in Fig. 3, which has an energy 0.10 eV/atom above that of the com-

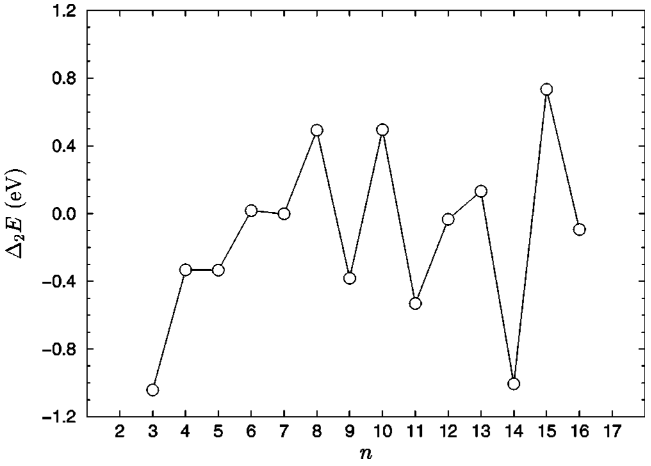


FIG. 6. Calculated second finite difference of the total minimum energy of Fe_n clusters as a function of cluster size.

puted ground-state configuration of this cluster. On the other hand, the geometry suggested as most likely for Fe_{15} by Parks *et al.*, the bcc rhombic dodecahedron, is that of isomer 15.2, which is only 0.05 eV/atom above the computed ground-state configuration.

Finally, for Fe_{16} and Fe_{17} our calculations predict ground-state structures following a growth pattern based on the geometry of Fe_{15} (see Fig. 3).

In their CP-based[16] study of Fe_n clusters with $n \leqslant 7$, Ballone and Jones[15] noted the striking similarity of the structures they obtained to those found using simple model potentials. This is also true for $n=8$–17: except for small distortions, the ground-state structures obtained in this work for this size range generally agree with those obtained[35] using the embedded atom model potential proposed by Besson and Morillo.[39] The only exceptions are Fe_9 and Fe_{10}, for which the Besson-Morillo potential predicts geometries based on icosahedral packing that correspond to our isomers 9.2 and 10.2; but the energies of these isomers are very close to those of the corresponding ground-state structures. It is also worth pointing out that the size range over which our calculations predict hollow cluster geometries, $n \leqslant 11$, is only one smaller than the range $n \leqslant 12$ found by Christensen and Cohen[40] using the effective medium theory supplemented with a tight-binding description of *d*-band formation.

Figure 6 shows the second finite difference of the total minimum energy, $\Delta_2 E(n) = E(n+1) + E(n-1) - 2E(n)$, plotted against cluster size *n*. The peaks at $n=8$, 10, 13, and 15 mean that these are our predicted magic numbers within the size range studied. In the TOF mass spectrometry study performed by Sakurai *et al.*[12] with autoionized and postionized Fe clusters, it was clusters with $n=7$, 13, 15, 19, and 23 atoms that were found to have much greater intensities than those with neighboring *n* values (although the peak at $n=7$ was less clear for postionized Fe clusters), and for clusters with these sizes possible structures were suggested (in particular, the pentagonal bipyramid, the icosahedron, and the bcc rhombic dodecahedron were put forward for Fe_7, Fe_{13}, and Fe_{15}, respectively). Thus the observed magic numbers $n=13$ and $n=15$ for ionized Fe clusters agree with our predictions for neutral Fe clusters, but instead of the experimental peak at $n=7$ we found peaks at $n=8$ and $n=10$ (Fig. 6). In principle, this discrepancy might be attributed to possible structural modifications as a consequence of ionization. However, since our structural calculations were performed for $T=0$ K, while in Sakurai *et al.*'s experiments the Fe clusters are heated to high temperature, it is also possible that the differences between the theoretical and experimental results are due to thermal effects. This explanation has recently been proposed by Zhang *et al.*[41] to explain the differences between the predicted magic numbers for neutral C_{60} clusters (see, e.g., Refs. 42 and 43) and those observed for positively charged C_{60} clusters by mass spectrometry.[44] Proper clarification of this issue will require further calculations for ionized Fe clusters and/or simulations to analyze the effect of temperature on the structures of neutral Fe clusters.

IV. SUMMARY AND CONCLUSIONS

In this work we performed self-consistent DFT calculations to obtain the structures, binding energies, and magnetic moments of Fe_n clusters up to $n=17$, a size much larger than those investigated in previous DFT studies. Within the range $n=2$–7, our results generally agree quite well with those of previous DFT calculations. For Fe_n clusters with 8–17 atoms we compare our structural results with the information inferred by Parks *et al.*[1] from chemical probe experiments and by Sakurai *et al.*[12] from TOF mass spectrometry. Our calculations predict that structural changes occur between $n=13$ and $n=14$ and between $n=14$ and $n=15$, in keeping with the variations observed by Parks *et al.* in the chemical reactivity of these clusters with adsorbate molecules. Moreover, the structures predicted for Fe_{13} and Fe_{15} agree with, or are close in energy to, those suggested as most likely by Parks *et al.* on the basis of their adsorbate-binding data. However, the difference between our computed minimum energy structure for Fe_{14} and that proposed by Parks *et al.* suggests that in some cases adsorbates may significantly change cluster structure.

Magic numbers for neutral Fe_n clusters are predicted at $n=8$, 10, 13, and 15. These predictions agree only partially with the mass spectrometry results obtained for ionized Fe clusters by Sakurai *et al.*,[12] who found that $n=7$, 13, and 15 are magic numbers. It seems possible that thermal effects, rather than the ionization of the clusters, may be the origin of the discrepancy.

ACKNOWLEDGMENTS

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