

# A density-functional study of small titanium clusters

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The atomic structures and electronic properties of small  $\text{Ti}_N$  ( $N=2-10$ ) clusters have been studied by using the density-functional theory with a local spin density approximation. We find that the inner-shells ( $3s3p$ ) of the titanium atom plays an important role in the formation of the small clusters. We have obtained the ground state of titanium clusters,  $\text{Ti}_7$  is found to be a magic cluster, which is in good agreement with the experimental results. Starting with  $\text{Ti}_8$  cluster some features of the electronic structure of the titanium bulk have been developed. The ionization potentials and magnetic moments for these small titanium clusters are also presented. © 2000 American Institute of Physics. [S0021-9606(00)30544-X]

## I. INTRODUCTION

Over the past two decades, the experimental and theoretical studies of atomic and molecular clusters have been increased significantly. Transition-Metal (TM) clusters are particularly interesting because of their properties and the promising technological application.<sup>1</sup> It also remains a significant purpose in cluster physics to understand when and how electronic states in small clusters are evolved into bands as what in the bulk. Most theoretical studies on the electronic structures of TM clusters have thus far been focused on the small systems on the promise that the studying of the small clusters will help to understand the large systems. However, even the small clusters still pose a tremendous challenge to the first principles calculations and are still not thoroughly understood.

Despite the rapid growth in the research concerning TM clusters, studies on titanium clusters are quite limited. The binding energy of  $\text{Ti}_2$  measured by the experiment<sup>2-5</sup> are from 2.1 to 1.05 eV which was considered as the lowest limit by Haslett *et al.*<sup>3</sup> In 1980, the experimentally measured Raman spectrum of  $\text{Ti}_2$  isolated in an Ar matrix yielded the vibrational frequency  $407.9\text{ cm}^{-1}$  for  $\text{Ti}_2$ .<sup>7</sup> In 1992, Li *et al.*<sup>8</sup> studied the kinetic energy dependence of the collision-induced dissociation (CID) of  $\text{Ti}_N^+$  ( $N=2-22$ ) with Xe by using a guided ion beam mass spectrometer, and found that the dissociation energy  $D^0(\text{Ti}_{N-1}^+ - \text{Ti})$  changed significantly

as a function of the cluster size with local maxima at  $N=7, 13$ , and  $19$ , although they did not clearly point out that these numbers should be the magic numbers of titanium clusters. By size-selected anion photoelectron spectroscopy, Wu *et al.*<sup>9</sup> observed that the  $3d$  states emerged around the eight-atom cluster and beyond, where the  $3d$  states are broadened and evolved into the band of the bulk. Recently, Sakurai *et al.*<sup>10</sup> measured the time-of-flight mass spectra of TM free clusters, and assigned that  $N=7, 13, 15, 19$ , and  $25$  are the magic numbers of titanium clusters. Theoretically Anderson<sup>11</sup> attempted to characterize the atomic structures of titanium clusters by utilizing molecular orbital method. His preliminary calculations concluded that titanium clusters containing two to six atoms have tightly packed structures, i.e., equilateral triangle for  $\text{Ti}_3$ , rhombic for  $\text{Ti}_4$ , trigonal bipyramid for  $\text{Ti}_5$ , and octahedron for  $\text{Ti}_6$ . More recently, Bauschlicher *et al.*<sup>6</sup> studied the low-lying states of  $\text{Ti}_2$  by using a multireference configuration-interaction (MRCI) approach, and pointed out the difficulties of making a definitive assignment of the ground state due to many low-lying states and the large effect of inner-shell ( $3s$  and  $3p$ ) correlation.

In this paper, we present a theoretical study on the atomic structure and properties of titanium clusters by the density-functional theory (DFT) with a local spin density approximation (LSDA).<sup>12</sup> We find that the inner-shell effect is a crucial factor in the binding of small Ti clusters. The electronic properties and ionization potentials for the small titanium clusters on the calculated ground structure are also discussed.

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## II. COMPUTATIONAL METHODS

The discrete variational approach, known as DVM,<sup>13,14</sup> is used through this work in the framework of the density functional theory with a local spin density approximation. The Kohn–Sham equations<sup>15</sup> (in Hartree atomic units)

$$(-\frac{1}{2}\nabla^2 + V_c + V_{xc})\phi_{i\sigma} = \epsilon_{i\sigma}\phi_{i\sigma}, \quad (1)$$

are solved self-consistently by iterating the charge density

$$\rho_\sigma(\mathbf{r}) = \sum_i n_{i\sigma} |\phi_{i\sigma}(\mathbf{r})|^2, \quad (2)$$

and the spin density

$$\rho_s = \rho_+ - \rho_-, \quad (3)$$

where  $\sigma = \pm$  denotes the spin up and spin down, and  $\phi_{i\sigma}$  is the single particle wave function for the molecule with occupation  $n_{i\sigma}$ .  $V_c$  is the Coulomb potential of nuclei and electrons. The von Barth–Hedin exchange-correlation potential  $V_{xc}$ <sup>14–18</sup> is adapted. The single particle wave function are expanded as a linear combination of numerical atomic orbitals  $3s3p3d4s4p$  of the titanium atom. All other deep-lying atomic orbitals are treated in the frozen-core approximation. The variational method leads to the secular equations, which are solved self-consistently in a three-dimensional numerical grid.<sup>18,19</sup> A Mulliken-type population analysis is performed to obtain atomic orbital populations, atomic charges and spin moments.<sup>20</sup> With the Lorentzian broadening scheme,<sup>21</sup> the partial density of states (PDOS) is defined as

$$D_{nl\sigma}^q = \sum_i P_{nl\sigma}^q \frac{\delta/\pi}{(\epsilon - \epsilon_{i\sigma})^2 + \delta^2}, \quad (4)$$

where  $P_{nl\sigma}^q$  is the Mulliken population of atomic orbital  $\chi_{nl}$  of atom  $q$  in the single particle spin orbital  $\phi_{i\sigma}$ . The density of states of the atom  $q$  with spin  $\sigma$  is obtained by summing over  $n$ ,  $l$ , and  $i$ , and the total DOS of spin  $\sigma$  of the cluster is given by summing over all atoms.

The total energy of the cluster can be obtained from the electronic density

$$E_{\text{tot}} = \sum_{k,\sigma} n_{k,\sigma} \epsilon_{k,\sigma} - \sum_{\sigma} \left[ \frac{1}{2} \int \int \frac{\rho_{\sigma}(\mathbf{r})\rho_{\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}(\rho_{\sigma}) - \int \rho_{\sigma}(\mathbf{r})V_{xc,\sigma}(\mathbf{r})d\mathbf{r} \right] + \sum_{p < q} \frac{Z_p Z_q}{\tau_{pq}}, \quad (5)$$

where  $\epsilon_{k,\sigma}$  are the Kohn–Sham eigenvalues of Eq. (1), and  $Z_p$  is the nuclear charge. The exchange-correlation potential,  $V_{xc,\sigma}$ , is defined as

$$V_{xc,\sigma}(\mathbf{r}) = \frac{\delta E_{xc}(\rho_{\sigma})}{\delta \rho_{\sigma}(\mathbf{r})}, \quad (6)$$

where  $E_{xc}(\rho_{\sigma})$  is the exchange-correlation energy.<sup>22</sup> The binding energy of the cluster is calculated from  $E_b = E_{\text{ref}} - E_{\text{tot}}$ , where  $E_{\text{tot}}$  is the total energy of the cluster and  $E_{\text{ref}}$  is the sum of the energy of the free atoms in the cluster. No zero-point energy is included in the binding energy calculation.

TABLE I. The equilibrium bond length  $r_0$  (in a.u.) and the corresponding binding energy  $E_b$  (in eV) with different basis functions for  $\text{Ti}_2$ .

	$3d4s4p$	$3p3d4s4p$	$3s3p3d4s4p$	Exp. <sup>a</sup>	Theory <sup>b</sup>
$r_0$	0.94	3.680	3.660	3.677	3.72
$E_b$	663.76	4.082	3.833	1.54	0.32

<sup>a</sup>Reference 5.

<sup>b</sup>Reference 24.

tion. The equilibrium atomic structures of the clusters are obtained by maximizing the binding energy  $E_b$  with respect to the interatomic distances.

## III. RESULTS AND DISCUSSIONS

### A. The inner-shell effect

It is well known that, for the most TM clusters,  $3s$  and  $3p$  orbitals can be considered as core states and the minimal basis functions can give a quite reasonable description of the electronic structure and the binding property. While for the earlier transition metals like titanium,  $3s$  and  $3p$  are close to valence states, which will probably play an important role in the formation of the cluster.

We study the dependence of the bond length and the binding energy of  $\text{Ti}_2$  on the inner-shell effect. We find that the  $3s$  and  $3p$  inner-shells contribute significantly to the electronic structure and the binding energy of  $\text{Ti}_2$ . Table I shows the calculated equilibrium bond length and the corresponding binding energy with different basis functions for  $\text{Ti}_2$ . By using only the minimal basis function  $3d4s4p$ , the obtained equilibrium bond length  $r_0$  and the huge binding energy are obviously unphysical. While including the inner-shell orbital  $3s3p$  in the basis function, either the bond length or the binding energy is very much improved, the obtained bond length is in very good agreement with the experimental result of 3.66 a.u.<sup>5</sup> The binding energy,  $E_b = 3.833$  eV, however, becomes close to the experimental value, but it is still overestimated as usual. This overestimation can be attributed to the LSDA method used in the present calculation. Thus from the above calculations, we can conclude that the inner-shell orbitals of titanium atom do contribute significantly to the binding in small titanium clusters, and including the  $3s3p$  orbitals in the basis function is necessary. The present results also suggest that one must be very careful to use the valence electron based methods, such as the pseudo-potential method, for Ti clusters.

### B. Atomic structure

The equilibrium atomic structures of  $\text{Ti}_N$  ( $N=2-10$ ) clusters are obtained by maximizing the binding energy  $E_b$  with respect to the interatomic distances. For the small clusters ( $N < 7$ ), the initial possible structures are assumed either by making reference to other TM clusters or by constructing symmetric structures. As the size of the cluster increases up to seven or even larger, the number of possible structures increases significantly. To make sure we do not miss the important structures, we used the TB-LMTO-MD method<sup>23</sup> and the conventional molecular dynamics with Sutton–Chen

TABLE II. The binding energy per atom  $E_b$  (eV), the average coordination number  $n_0$  and the average bond lengths  $r_0$  (a.u.) for small  $\text{Ti}_N$  ( $N=2-10$ ) clusters. Only those geometries with larger binding energies among isomers are presented.

$n$	Symmetry	$E_b$	$n_0$	$r_0$
2	Linear	1.9165	1.00	3.66
3	$D_{3h}$	2.3723	2.00	4.45
	$C_{2v}$	2.3277	2.00	4.53
4	Linear	2.2137	1.33	3.93
	$C_{3v}$	2.9463	3.00	4.76
	$D_{2d}$	2.8170	3.00	4.81
	$D_{2h}$	2.8080	2.50	4.51
	$T_d$	2.8040	3.00	4.81
	$D_{4h}$	2.4980	3.00	5.02
	$D_{3h}$	2.1603	3.00	5.11
5	$C_{2v}$	3.4026	3.60	4.74
	$D_{3h}$	3.2502	3.60	4.68
	$C_{2v}$	3.0408	2.80	4.44
	$C_{1h}$	3.0300	3.20	4.95
	$C_{4v}$	3.0158	3.20	4.72
	$C_{2v}$	3.7285	4.00	4.81
6	$D_{4h}$	3.5763	5.00	4.87
	$D_{3d}$	3.5647	5.00	5.28
	$D_{2h}$	3.5330	4.67	5.06
	$O_h$	3.4652	5.00	5.33
	$D_{5h}$	3.9830	4.57	4.97
	$C_{1h}$	3.7653	5.14	5.17
7	$C_{3v}$	3.7029	5.14	5.17
	$D_{3d}$	3.4941	3.43	4.42
	$D_{3d}$	3.4476	3.43	4.68
	$C_{2h}$	3.9983	4.50	5.11
	$C_{1h}$	3.9739	4.96	4.75
	$D_{2d}$	3.8293	5.00	5.00
8	$D_{6h}$	3.8233	4.75	5.00
	$C_{2v}$	3.8004	4.50	4.89
	$C_{1h}$	4.2110	5.11	4.89
	$C_{1h}$	4.1138	4.89	4.84
	$C_{2v}$	4.0794	5.11	4.93
	$C_{2v}$	4.0158	4.67	5.00
9	$C_2$	4.0113	4.89	4.90
	$C_{1h}$	4.0110	4.89	4.86
	$C_{3v}$	4.1820	5.00	4.99
	$C_{2v}$	3.9516	5.00	5.04
	$D_{2h}$	3.9206	5.00	4.99
	$D_{4d}$	3.9200	4.80	5.05
10	$D_{4h}$	3.7432	6.40	5.64

potential<sup>24</sup> to generate the possible structures by simulated annealing. Taking those possible structures as the initial structures, we have maximized the binding energy via the interatomic distance. Only a few obtained structures with larger binding energies are listed in Table II. The symmetries, the binding energy per atom, the average coordination number and the average bond length are presented in this table.

Figure 1 shows the most stable structures for  $\text{Ti}_N$  ( $N=2-10$ ) clusters. For  $\text{Ti}_3$ , the possible structures are the equilateral triangle ( $D_{3h}$ ), the isosceles triangle ( $C_{2v}$ ) and the linear structure. Our calculation shows that the most stable structure of  $\text{Ti}_3$  is an equilateral triangle. The binding energy of the equilateral triangle structure is about 0.13 eV higher than that of the isosceles structure, and about 0.48 eV higher than that of the linear structure. The energy differences between these three structures are small so as to indi-

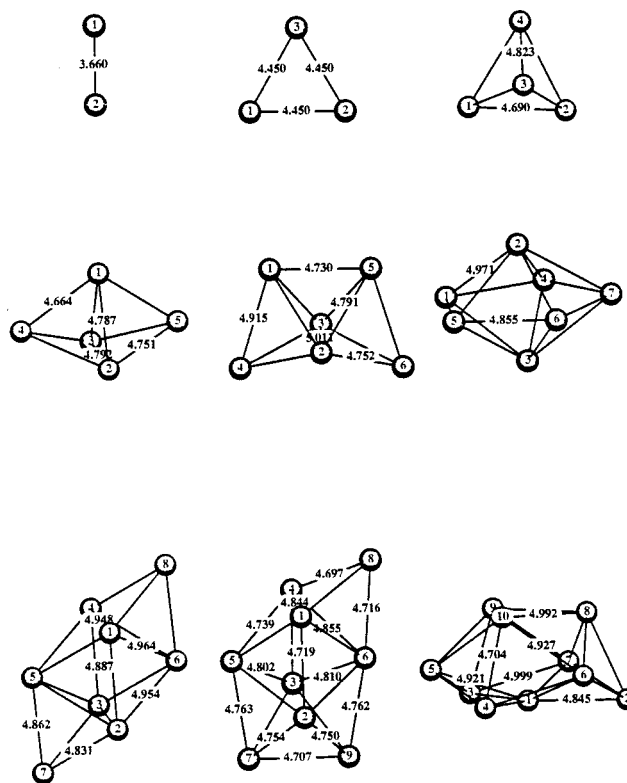


FIG. 1. Equilibrium structures of  $\text{Ti}_N$  ( $N=2-10$ ). The bond lengths (in a.u.) are labeled along the bond.

cate that these three isomers could alternately exist at not very high temperature. The most stable structure for  $\text{Ti}_4$  can be considered as an atom capped on an equilateral triangle with a  $C_{3v}$  symmetry, but not a regular tetrahedron ( $T_d$ ) which is the most compact structure. The energy difference between these two structures are about 0.5 eV. The most stable structure for  $\text{Ti}_5$  is not the compact triangle bipyramid structure ( $D_{3h}$ ) as obtained by Andersen,<sup>11</sup> but a distorted triangle pyramid structure ( $C_{2v}$ ). The binding energy difference between these two structures are 0.80 eV, other lower symmetric structures have much lower binding energies. The structure of  $\text{Ti}_6$  with the largest binding energy has a  $C_{2v}$  symmetry other than the octahedral structure with a higher symmetry  $O_h$ . While for the most other  $\text{TM}_6$  clusters, such as the  $\text{Fe}_6$  and  $\text{Ni}_6$  cluster,<sup>25,26</sup> for example, the octahedral structure has been proven to be with the largest binding energy. The pentagonal bipyramid of  $\text{Ti}_7$  cluster with a  $D_{5h}$  symmetry is the largest binding energy structure, and the capped octahedron structure ( $C_{1h}$ ) is an isomer with a binding energy difference as large as 1.5 eV. By symmetrically adding two titanium atoms to the octahedron structure, we get the most stable structure of  $\text{Ti}_8$  cluster with a  $C_{2h}$  symmetry, while adding a titanium atom to the most stable  $\text{Ti}_7$  cluster yields the metastable structure for  $\text{Ti}_8$ , which has a lower binding energy (about 0.2 eV). The structure of  $\text{Ti}_9$  can be obtained by adding a titanium atom to the most stable structure of  $\text{Ti}_8$ . The most stable structure for  $\text{Ti}_{10}$  has a  $C_{3v}$  symmetry as shown in Fig. 1.

It is interesting to find out the general growth trend of the structure for the small titanium clusters. As can be seen

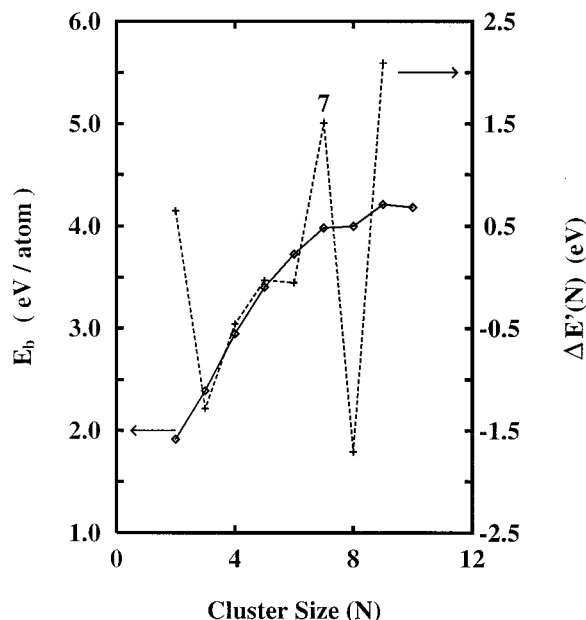


FIG. 2. The binding energy per atom  $E_b$  (solid line) and the second energy difference  $\Delta E'(N) = E(N+1) + E(N-1) - 2E(N)$  (dotted line) for the most stable structure. The local maximum shows the high stability of the cluster.

in Fig. 1, generally the most stable structure of  $Ti_N$  cluster can be obtained by adding one atom to the most stable structure of  $Ti_{N-1}$ . We may briefly refer to this growth mode as “+1” rule, for the most stable structure of  $Ti_N$  comes from  $Ti_{N-1} + Ti$  without significantly modifying the structure of the preceding cluster. However, this growth route is interrupted from  $Ti_7$  to  $Ti_8$  as well as from  $Ti_9$  to  $Ti_{10}$ . The most stable structure of  $Ti_8$  with  $C_{2h}$  symmetry is not from the most stable structure of  $Ti_7$  with a  $D_{5h}$  symmetry but from symmetrically adding two titanium atoms to the octahedron structure of  $Ti_6$ . When adding one titanium atom to the most stable structure of  $Ti_7$  with  $D_{5h}$  symmetry, only the metastable structure of  $Ti_8$  is obtained, although the energy difference between the most stable structure and the metastable structure for  $Ti_8$  is very small (0.2 eV). Also the most stable structure for  $Ti_{10}$  with a  $C_{3v}$  symmetry can not be obtained by adding one atom to the most stable of  $Ti_9$ . This interruption of the growth route at  $Ti_7$  to  $Ti_8$  as well as at  $Ti_9$  to  $Ti_{10}$ , as we will show below, are related to the stability of the cluster.

### C. The stability and the magic number

The binding energy per atom of  $Ti_N$  clusters, shown in Fig. 2, increases monotonically as the size of clusters increases, but it is still far from the theoretical value (6.122 eV) of the bulk cohesive energy,<sup>27</sup> which indicates that the convergence of the binding energy to the bulk value is still far away. In order to study the relative stability of clusters, we calculated the second order difference of the binding energy

$$\Delta E'(N) = E(N+1) + E(N-1) - 2E(N), \quad (7)$$

where  $E(N)$  is the binding energy of the cluster with  $N$  atoms. The calculated  $\Delta E'(N)$  is shown in Fig. 2. The local maximum at  $N=7$  indicates that  $Ti_7$  is more stable than its neighboring clusters, i.e., the number of  $N=7$  can be a magic number for  $Ti_N$  clusters. This is in good agreement with the experimental results of Sakurai *et al.*,<sup>10</sup> in which the numbers of  $N=7, 13, 15, 19, 25$  were assigned as the magic numbers for  $Ti_N$  clusters.

The increment in energy of adding one atom to the preceding cluster

$$\Delta E(N) = -[E(N) - E(N-1)], \quad (8)$$

can provide the information on the stability of clusters, and we also calculate the difference of the binding energy between the ground-state structure and its first isomer

$$\Delta E_{\text{isomer}}(N) = -[E(N) - E'_{\text{isomer}}(N)], \quad (9)$$

where  $E'_{\text{isomer}}(N)$  is the binding energy of the metastable structure.  $\Delta E_{\text{isomer}}$  can provide the information on the stability of a cluster relative to its isomer. The large  $\Delta E_{\text{isomer}}$  prohibits the transformation from the ground state structure to its isomer and the small  $\Delta E_{\text{isomer}}$  could make the cluster fluctuating from one structure to another. In the limit of very large cluster,  $\Delta E$  would approach to the cohesive energy of the corresponding bulk solid, and  $\Delta E_{\text{isomer}}$  would approach to the energy difference between different phases.  $\Delta E$  and  $\Delta E_{\text{isomer}}$  as a function of cluster size are plotted in Fig. 3. Both  $\Delta E$  and  $\Delta E_{\text{isomer}}$  monotonically increase from  $N=2$  to  $N=7$ . The local maximum is again found at  $N=7$ . A conclusion can thus be made from these results that  $Ti_7$  with a  $D_{5h}$  symmetry is the most stable among the isomers calculated in this work. There is a local maximum at  $N=9$  in  $\Delta E(N)$ , which is an indication of high stability of  $Ti_9$  cluster.

Figure 4 shows the average coordination number ( $n_0$ ) and average bond length ( $r_0$ ) of the small titanium clusters (see also Table II). We can see that  $n_0$  increases nonmonotonically as the size of clusters growing and two local maxima appear at  $N=7$  and  $N=9$ . This indicates that  $Ti_7$  and  $Ti_9$  have more compact structures, which is another indication that  $Ti_7$  and  $Ti_9$  clusters are very stable. In the plot of the average bond lengths, a local maximum at  $N=8$  with a value of 5.11 a.u., which is slightly smaller than the nearest neighbor distance of 5.47 a.u. in the bulk phase, suggests that  $Ti_8$  has a large bond lengths comparing with other Ti clusters. And we also notice that the most stable structure of  $Ti_8$  has the bulklike hcp structure (Fig. 1), this might be one of the reasons that the electronic state evolves into bulk behavior at  $N \geq 8$ .<sup>9</sup>

### D. Electronic structure

The calculated electronic density of states (DOS) of the small titanium clusters from  $N=2-10$  are shown in Fig. 5. For comparison, DOS of the bulk titanium (hcp) obtained by WIEN97 code<sup>28</sup> is also included. As can be seen from Fig. 5, the band width of Ti clusters increases gradually from  $Ti_2$  (2.5 eV) to  $Ti_8$  (4.3 eV), however those for  $Ti_8$ ,  $Ti_9$ , and  $Ti_{10}$  are very close to each other. The band width of 4.3 eV is also very close to the theoretical band width of the titanium bulk.



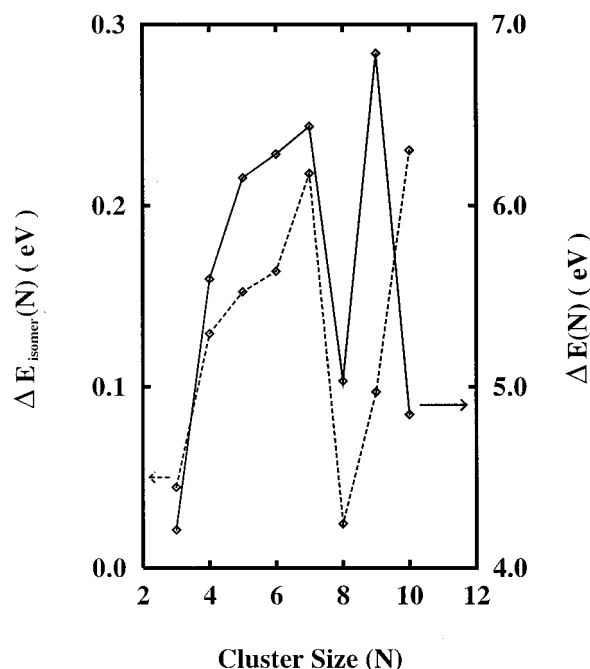


FIG. 3. The increment in energy  $\Delta E(N)$  by adding an atom to the preceding cluster (solid line) and the energy difference  $\Delta E_{\text{isomer}}(N)$  between the most stable and metastable structure. Both of them monotonically increase from  $N=2-7$ , and the turning point is at  $N=7$  which indicates that the pentagonal bipyramid structure for  $\text{Ti}_7$  is very stable.

From the band width and the shape of DOS, we can see that some features of the bulk phase have been developed in  $\text{Ti}_8$ , which is in very good agreement with the size-selected anion photoelectron spectroscopy results.<sup>9</sup> While for other transi-

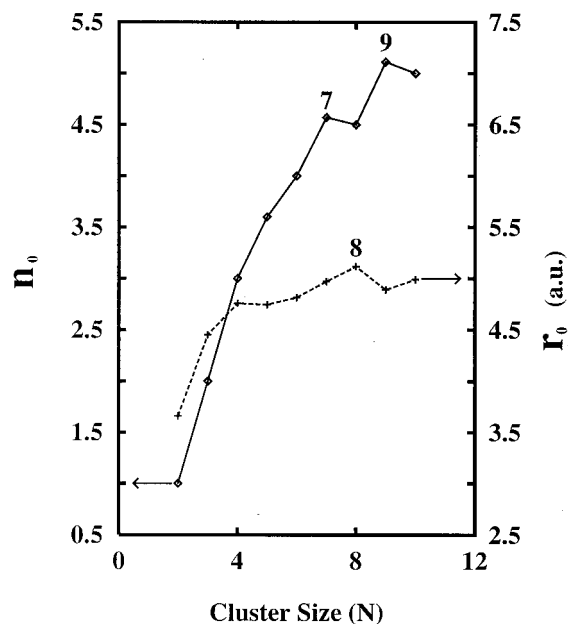


FIG. 4. The average coordination number  $n_0$  (solid line) and the average bond length ( $r_0$ ) of the titanium clusters (dotted line). The local maxima of  $n_0$  at  $N=7$  and  $N=9$  as well as the local maximum of the  $r_0$  is at  $N=8$  suggest that the titanium clusters tend to form the compact structure at  $N=7$  and  $N=9$ .

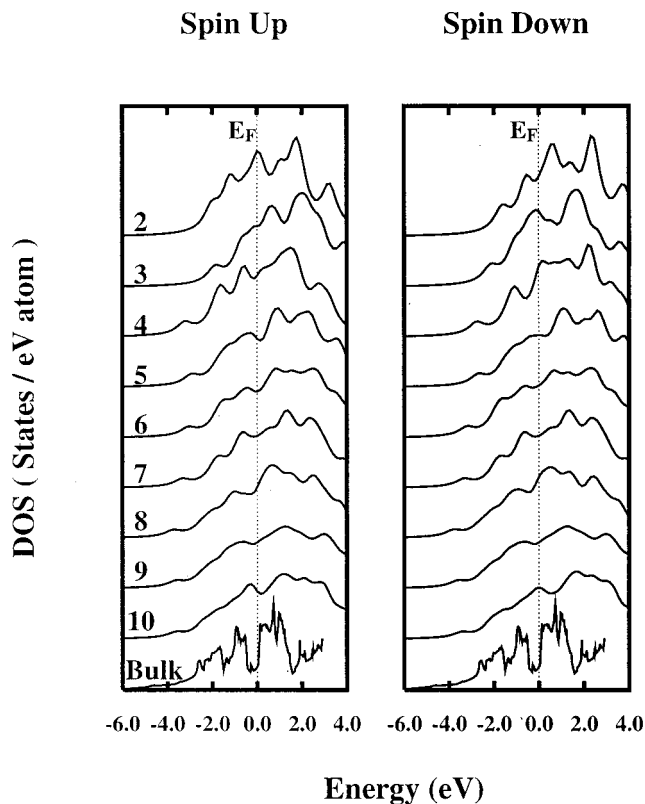


FIG. 5. The DOS of titanium clusters ( $N=2-8$ ) as well as DOS of hcp bulk. The Fermi energy is shift to zero.

tion metal clusters, such as Fe and Cu clusters, the convergence of the electronic structure to that of the bulk phase seems much slower and there always involves much larger clusters including hundreds and thousands of atoms.<sup>29,30</sup>

The broadening of  $3d$  states is the main contribution to the increment of the band width of the cluster. We have calculated the partial DOS for the  $3d$  and  $4s$  orbitals, which are shown in Fig. 6. From  $\text{Ti}_7$  to  $\text{Ti}_8$ , the broadening of  $3d$  states can be clearly observed,  $\text{Ti}_9$  has the similar behavior of  $\text{Ti}_8$ . The effect of broadening extends the band width of the cluster to the band width of the bulk. While there is no significant changes in the partial density of state (PDOS) of  $4s$  orbitals. These results are in good agreement with experimental data, in which Wu *et al.*<sup>9</sup> have attributed the rapid convergence of Ti clusters toward that of the bulk to the strong delocalization of the  $3d$  orbital.

We have calculated the ionization potential (IP) and the electron affinity (EA) versus the cluster size from  $N=2-10$ , as shown in Fig. 7. The IP(EA) are obtained by calculating the binding energy difference between the neutral and positively(negatively) charged clusters at the equilibrium structure. EA of the small titanium clusters exhibits roughly monotonic increasing and evolving into the bulk value (4.33 eV),<sup>31,32</sup> which is in reasonable agreement with the experimental result.<sup>9</sup> The magic cluster  $\text{Ti}_7$  has a very small EA compared to its nearest-neighbor clusters. IP of the small titanium clusters decreases as the function of the cluster size. The dip at  $N=4$  could be probably from the uncompact structure.

Figure 8 shows the average number of electrons of  $3d$ ,

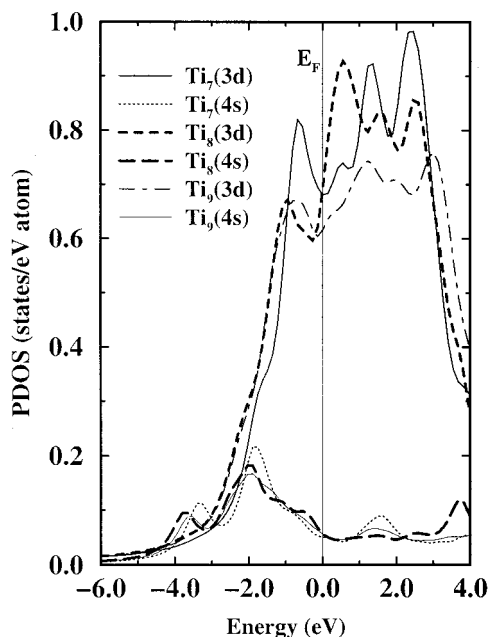


FIG. 6. The partial density of state (PDOS) for titanium clusters ( $N=7-9$ ). The Fermi energy is shift to zero. What makes DOS broaden is mainly from the 3dPDOS.

4s, and 4p orbitals for the titanium clusters obtained by the Mulliken population analysis. For the Ti atom, there are two electrons in 3d and 4s orbital, respectively. However, in the Ti clusters, we find that there are 0.8 electrons transferred from the 4s orbital to the 3d orbital, and only a small fraction of electrons is found in the 4p orbital. The significant charge transfer suggests the strong hybridization between 3d and 4s orbitals.

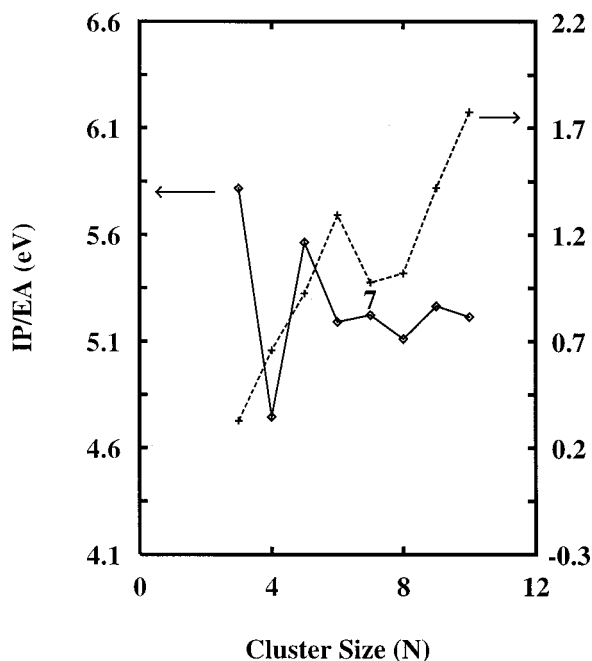


FIG. 7. The ionization potential (solid line) and the electron affinity (dotted line) vs the cluster size for the titanium clusters.

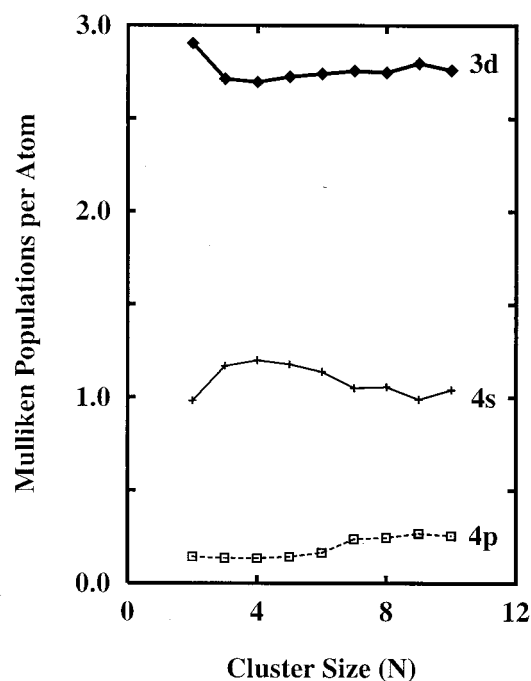


FIG. 8. The Mulliken population per atom as a function of the cluster size from  $N=2-N=10$ .

Although titanium bulk is nonmagnetic, we find the small Ti clusters have significant magnetic moments. The average magnetic moments versus the cluster size are shown in Fig. 9. In the very small clusters, the magnetic moment can be as large as  $1 \mu_B$ . As the size of the cluster increases, the magnetic moment decreases, which is in agreement with

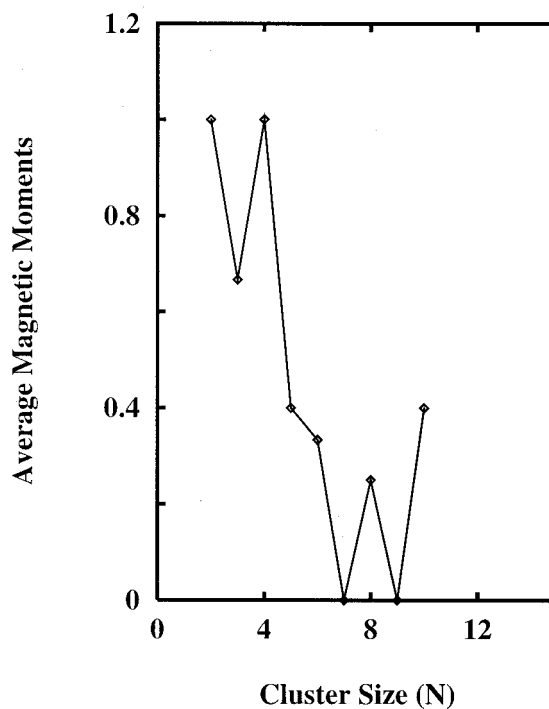


FIG. 9. The average magnetic moments (in  $\mu_B$ ) as a function of the cluster size from  $N=2$  to  $N=10$ .

the fact that the bulk phase is nonmagnetic. Particularly for the  $Ti_7$  and  $Ti_9$  clusters, all the magnetic moments are zero. This could be probably because these two clusters have very compact structure.

#### IV. SUMMARY

In summary, for the first time, we have studied the structures and electronic properties of the small  $Ti_N$  ( $N=2-10$ ) clusters by using the density-functional theory with a local spin density approximation. The most stable geometrical structures of  $Ti_N$  ( $N=2-10$ ) are obtained by maximizing the binding energy respect to the interatomic distance. We find that the  $Ti_7$  cluster is a magic cluster, which is in agreement with the experimental results. In contrast to many other TM clusters such as Fe, Ni, and Cu, the inner-shell orbitals  $3s3p$  are found being the key factor to get the reasonable bond length and the binding energy of the titanium dimmer as well as small clusters, the electronic structures of the titanium clusters develop some bulklike features at rather small size. A general “+1” growth mode is found in the structure of the small titanium clusters: adding a titanium atom to the most stable structure of  $Ti_{N-1}$  yields the most stable structure of  $Ti_N$ , however  $Ti_7$  and  $Ti_9$  have very compact structures and do not follow this “+1” rule. Starting from the eight-atom cluster, DOS broadens and evolves into that of the bulk phase, and what makes DOS broaden is confirmed to be the delocalization  $3d$  orbital, which is consistent with the experimental results.

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