Vol 17 No 9, September 2008
1674-1056/2008/17(09)/3336-07

Chinese Physics B

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First-principles calculations for titanium monoxide clusters Ti_nO (n=1–9)*

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(Received 20 December 2007; revised manuscript received 21 February 2008)

Based on the density-functional theory, this paper studies the geometric and magnetic properties of Ti_nO (n=1–9) clusters. The resulting geometries show that the oxygen atom remains on the surface of clusters and does not change the geometry of Ti_n significantly. The binding energy, second-order energy differences with the size of clusters show that Ti_7O cluster is endowed with special stability. The stability of Ti_nO clusters is validated by the recent time-of-flight mass spectra. The total magnetic moments for Ti_nO clusters with n=1–4, 8–9 are constant with 2 and drop to zero at n=5–7. The local magnetic moment and charge partition of each atom, and the density of states are discussed. The magnetic moment of the Ti_nO is clearly dominated by the localized 3d electrons of Ti atoms while the oxygen atom contributes a very small amount of spin in Ti_nO clusters.

Keywords: Ti_nO clusters, density functional theory, stability, magnetic moment
PACC: 3640B, 3640C, 7115M

1. Introduction

The stability of atomic cluster has been one of the most important subjects in the cluster science. In 1984, Knight *et al* [1] observed that alkali metal clusters with 8, 20, 40, ... atoms are particularly stable. The stability of these so-called magic clusters has been successfully explained by jellium model, according to which clusters containing 2, 8, 20, 40, etc., valence electrons have higher stability due to the closure of electronic shells. Due to the existence of opened d shells, the physical and chemical properties of transition-metal (TM) clusters show remarkable size-dependent variations that cannot be explained by the shell model of s valence electrons.[2] It presents a tremendous challenge to study the properties of TM clusters both experimentally and theoretically.[3] Recently, with the rapid development of experimental and computer techniques, studies on TM clusters have increased significantly.[4−17] For titanium clusters, experimental studies on clusters include collision-induced dissociation on Ti_n^+ (n=2–22),[4] size-selected anion photoelectron spectra of Ti_n^- (n=3–65).[5] Sakurai *et al* [6] measured the time-of-flight mass spectra of TM free clusters, and showed that N=7, 13, 15, 19, and 25 are the magic numbers of Ti clusters, which were also confirmed by the first-principle calculations.[7−10]

In addition to Ti clusters, Sakurai *et al* [6] have also observed oxidized titanium clusters, which show similar trend with Ti clusters in the size dependent abundance. Despite success in stability of clusters, however, the time-of-flight mass spectra experiment provides poor information on the other properties such as geometrical and electronic structures. It was shown that properties of titanium-based binary clusters such as optical, magnetic, thermal stability and dynamical behaviour are dependent on the composition, the relative proportion of the two types of atoms and structures.[11−14] Therefore, it is interesting to investigate the effects of the doped oxygen atom on the structures and electronic properties of transition metal clusters. We perform spin-density functional calculations for oxygen-doped titanium clusters to explain the enhanced stability of clusters observed by the experiment and present a detailed study of the growth behaviour and magnetic properties.

*Project supported by National Natural Science Foundation of China (Grant No 10674113), Program for New Century Excellent Talents in University of China (Grant No NCET-06-0707), Foundation for the Author of National Excellent Doctoral Dissertation of China (Grant No 200726).

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2. Calculation details

Our calculations are based on the density–functional theory[18] (DFT) with the spin-polarized generalized gradient approximation[19,20] (GGA) implemented in the Vienna *ab initio* simulation package (VASP).[21] The interactions of the valence electrons with the ionic cores are described by the projected augmented wave method.[22] The wave functions are expanded in plane waves with an energy cutoff of about 400eV. We use a simple cubic cell of 1.4 nm edge length with a periodic boundary condition, and the Γ point approximation for the Brillouin zone sampling. The geometries are considered to be converged when the force on each ion becomes 0.1 eV/nm or less. To check the validity of the method we used, we first perform the calculation of Ti_2 and TiO dimers. The results show that interatomic distances are 0.189 and 0.167 nm, which are well consistent with the experimental data of 0.194[23] and 0.162[24] nm. This indicates that our approach is reasonable for such clusters.

3. Results and discussion

3.1. Atomic structure

The lowest energy geometries of Ti_nO (n=2–9) clusters are shown in Fig.1, together with the optimized Ti_n (n=2–9) clusters structures. The results of pure Ti clusters agree well with the previous calculations.[8,9] It can be seen that the oxygen atom hardly changes the main frame structure of the Ti_n

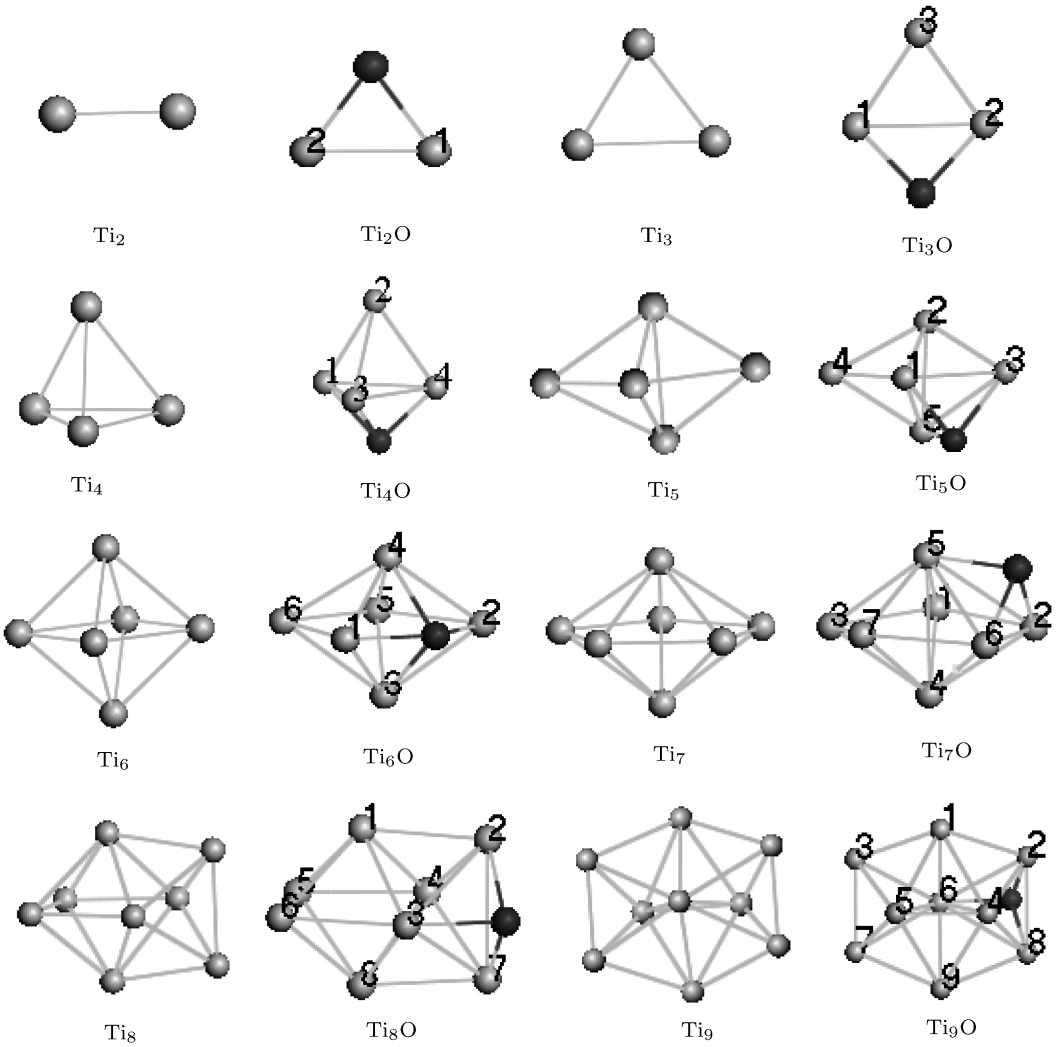


Fig.1. Schematic showing of structures for the Ti_n (n=2–9) clusters and Ti_nO (n=2–9) clusters. The grey spheres for Ti atoms, and black spheres for oxygen atom.

clusters. The most stable structure of Ti_nO cluster can be obtained by adding one oxygen atom to that of Ti_n. The most stable structures obtained for Ti_2O is an isosceles triangle in which Ti–Ti distance is slightly longer than the Ti dimer bond-length. Additionally, two linear chains (not shown in the figure) are found to be metastable because they have higher energy than the trigonal structure. For the chain-like structures, the total energy with oxygen atom occupying a central position is about 0.967 eV lower than that with a terminal position for oxygen. The ground state structure obtained for Ti_3O is a planar quadrangle, which can be constructed by capping one oxygen atom on one of edges of the lowest energy structure of Ti_3. A tetrahedron with oxygen being face-capped is 0.61 eV higher in energy. Other planar structures are found to be unfavourable. The lowest energy configuration obtained for Ti_4O is a distorted triangle bipyramid structure. The observation of three-dimensional configurations starting from Ti_4O indicates that the tightly bounded close-packed structures may be favourable in the Ti_nO clusters. An additional oxygen atom capped on trigonal bipyramid of Ti_5 yields the lowest energy structure for Ti_5O. In the case of Ti_6O, the ground-state structure is not a regular octahedron in which the oxygen atom gets trapped in the Ti cage, but a distorted pentagonal bipyramid with an impurity atom becoming a part of the pentagonal ring. A capped pentagonal bipyramid is obtained for Ti_7O as the most stable structure. The geometry optimization of Ti_8O, starting from the structure which the addition of one oxygen atom capped the ground-state structure of Ti_8, results in a three-capped octahedron. The structure of Ti_9O can be obtained by adding an oxygen atom to the most stable structure of Ti_9 as shown in Fig.1.

3.2. The stability

The binding energy per atom for Ti_nO clusters is shown in Fig.2. The average binding energy of Ti_n clusters is also plotted for comparison. It can be seen that the corresponding binding energy per atom of Ti_nO clusters is larger than that of Ti_n clusters. Thus, the doping of oxygen atom improves the stability of pure Ti_n clusters. This is due to the higher bond strength of the Ti–O than that of Ti–Ti, 4.25 and 2.13 eV, respectively. For Ti_n and Ti_nO clusters, the binding energy shows an increase up to n=7, followed by a dip at n=8. The features clearly indicate the higher stabilities of Ti_7 and Ti_7O clusters in the series of Ti_n and Ti_nO clusters, respectively.

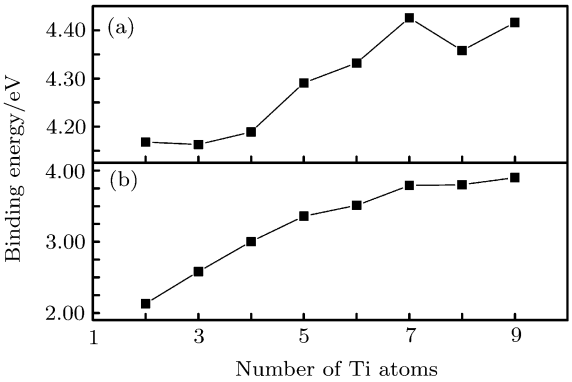


Fig.2. (a) The average binding energy (eV) of Ti_nO; (b) The average binding energy of Ti_n for the most stable structure shown as a function of the number of Ti atoms.

In cluster physics, the second-order energy difference ($\Delta_2E(n)$) of the cluster total energy is a sensitive quantity which reflects the relative stability of clusters and can be directly compared to the experimental relative abundance. In Fig.3, we present the calculated $\Delta_2E(n)$ which is defined by $\Delta_2E(n) = E(n+1) + E(n-1) - 2E(n)$, where $E(n)$ is the total energy of the cluster with n atoms. Differing from that of pure Ti_n clusters, we observe a clear odd–even staggering in $\Delta_2E(n)$ of Ti_nO clusters. The odd–even pattern in $\Delta_2E(n)$ may be due to the doping of oxygen atom. However, a noticeable peak at n=7 found for Ti_n cluster is also observed in the case of Ti_nO. The large values of $\Delta_2E(n)$ for Ti_7 and Ti_7O further establish their magical stability in these series of clusters. Our calculations about the stability of Ti_n clusters are consistent with previous results,[6–9] and the stability of Ti_nO clusters is validated by Sakurai's experimental results.[6]

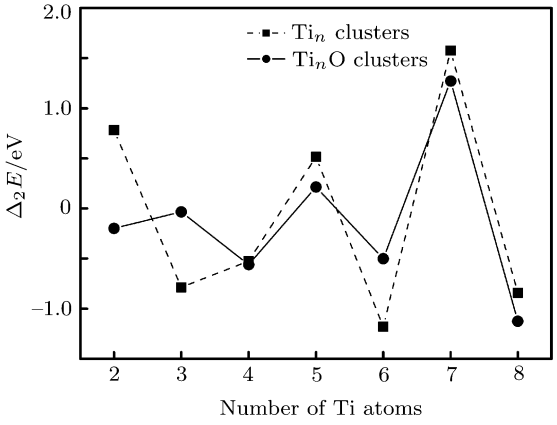


Fig.3. The second-order energy differences (Δ_2E) for Ti_n (solid squares) and Ti_nO (solid circles) clusters.

Moreover, we have calculated the oxygen atom adsorption energy [ΔE (oxygen on Ti_n)=

$E(Ti_nO)-E(Ti_n) - E(O)]$ with Ti_n clusters, which is shown in Fig.4. The dashed horizontal line represents the single oxygen atom adsorption energy in Ti (0001) surface. For n=3–9, the oxygen atom adsorption energy on Ti_n clusters is close to that of the single oxygen atom adsorbed at Ti (0001) surface face-centred cubic sites.[25] For Ti_6O cluster, oxygen binds with four Ti atoms to form a distorted pentagonal bipyramid structure and enhances the bonds strength of oxygen-Ti_6 bonds which may be responsible for the higher adsorption energy of oxygen atom on the Ti_6 cluster. This similarity in adsorption energy between oxygen-doped titanium clusters and surface indicates that the oxygen atom tends to be on the surface of clusters.

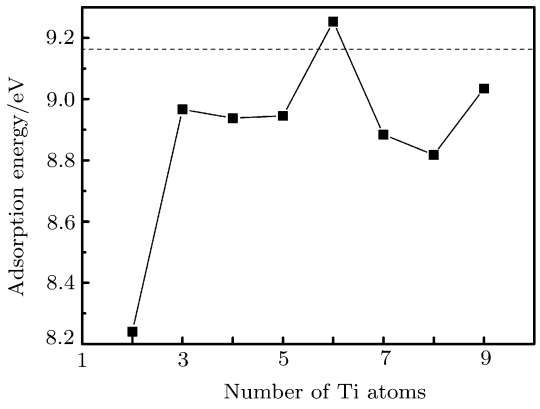


Fig.4. The oxygen atom adsorption energy (eV) with the Ti_n clusters. The dashed horizontal line represents the single oxygen atom adsorption energy on Ti (0001) surface.

The stability of typical transition metal clusters as a function of the cluster size is often discussed in terms of shells of atoms, relating the number of atoms needed to form a compact symmetric structure to an enhanced stability. One could believe that the geometric effect may be the key ingredient for the stability of the oxygen-doped titanium clusters. As discussed above, the introduction of oxygen atom does not significantly change the geometry of Ti_n clusters. One suspects that the frame of Ti atoms in Ti_nO clusters may be one of the main reasons for the stability of Ti_nO clusters. The stability of Ti_n cluster is interpreted by atomic motif. Thus, the high stability of Ti_7O may be attributed to the pentagonal bipyramid of Ti_7.

3.3. Magnetic properties

Although Ti bulk is nonmagnetic, we find that the small Ti clusters have significant magnetic moments[7,9] and the magnetic moments of transition metal clusters are sensitive to their structures. For Ti_nO clusters, the structures of Ti_n clusters undergo little change induced by the introduction of oxygen atom. It is of interest to investigate the effects of the doped oxygen atom on the magnetism of titanium clusters. Based on the optimized geometries, we have calculated the magnetic moments of Ti_nO clusters and presented the results in Fig.5. In our calculations, we consider different spin states for multiplicity of the state. For proper comparison we have also calculated the magnetic moments of Ti_n clusters in Fig.5, which are in good agreement with the results obtained by Castro *et al.*.[9] The total magnetic moments for Ti_nO clusters with n=1–4, 8–9 are constant with 2 and drop to zero when n=5–7. It can be seen from Fig.5 that the doping of the oxygen atom significantly reduces the magnetic moments of the Ti_n clusters with n=3–6, the magnetic moments for Ti_3-Ti_6 from 6, 4, 2, and $2\mu_B$ decrease to 2, 2, 0, and $0\mu_B$, respectively. However, it hardly affects the original spin state of pure Ti_n with n=1–2 and 7–9.

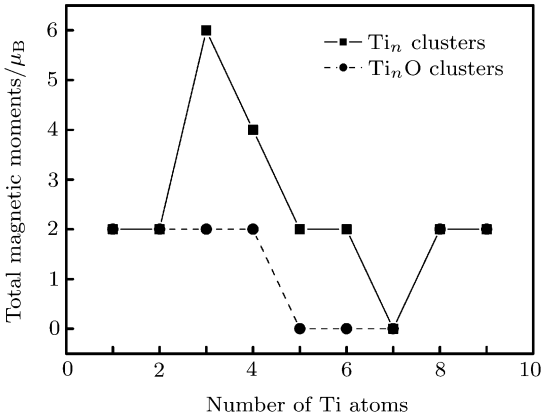


Fig.5. The total magnetic moments (in μ_B) for Ti_n (solid squares) and Ti_nO (solid circles) clusters.

We perform a detailed analysis of the atomic charge and the local magnetic moment. The charge and spin for each Ti atom and oxygen atom in Ti_nO clusters are given in Table 1. Two features can be observed from Table 1. First, there is a charge transfer between Ti atoms and the oxygen atom. Generally, the atom being farthest away from the oxygen atom in each Ti_nO has the smallest amount of charge. Second, there is a structure-dependence for the cluster magnetism and site-dependence for the local magnetic moment of Ti atom. For all the magnetic clusters, the Ti atom directly binding to the oxygen atom has a relatively large amount of magnetic moment. For

small magnetic Ti_nO with n=2–4, the Ti atom with the smallest amount charge, i.e. largest Ti–O distance, has the largest magnetic moment. However, for large clusters, Ti_8O and Ti_9O, the trend is largely different. The Ti atom being farthest away from the oxygen atom is still magnetic, but the magnetic moment is so small that it can almost be neglected. In both clusters, the Ti atoms with the second largest Ti–O distance have the largest amount of magnetic moments. Moreover, it can be seen from Table 1 that the magnetic moment of Ti atoms is mainly due to its 3d electrons while the oxygen atom contributes a very small amount of spin in Ti_nO clusters.

Table 1. The charge (in e) and total magnetic moment (TM, in μ_B), local magnetic moments of 3d (Ti-3d, in μ_B) for each atom in Ti_nO, and distances between Ti atoms and O atom (d_{Ti-O} in nm). Numbers (N) represent the atoms labelled in Fig.1 and O is the oxygen atom.

system	N	charge	TM/Ti-3d	d_{Ti-O}	system	N	charge	TM/Ti-3d	d_{Ti-O}
	1	3.580	0.948/0.917	0.1870		1	3.481	0.0/0.0	0.3502
Ti_2O	2	3.580	0.948/0.917	0.1870		2	3.597	0.0/0.0	0.1941
	O	4.996	–0.039/0.000			3	3.457	0.0/0.0	0.4311
	1	3.701	0.482/0.424	0.1840		4	3.671	0.0/0.0	0.3318
Ti_3O	2	3.701	0.482/0.424	0.1840	Ti_7O	5	3.731	0.0/0.0	0.1983
	3	3.554	0.909/0.850	0.3110		6	3.597	0.0/0.0	0.1941
	O	5.020	–0.034/0.000			7	3.480	0.0/0.0	0.3502
	1	3.691	0.274/0.241	0.1889		O	5.055	0.0/0.0	
	2	3.376	1.082/1.039	0.3261		1	3.646	–0.031/–0.047	0.3599
Ti_4O	3	3.507	0.403/0.393	0.2175		2	3.572	0.372/0.332	0.1908
	4	3.691	0.274/0.241	0.1889		3	3.533	0.022/0.010	0.2049
	O	5.030	–0.016/0.000			4	3.572	0.015/0.006	0.3373
	1	3.721	0.0/0.0	0.1907	Ti_8O	5	3.429	0.131/0.132	0.5091
	2	3.631	0.0/0.0	0.3236		6	3.393	0.620/0.605	0.4568
Ti_5O	3	3.474	0.0/0.0	0.2076		7	3.572	0.372/0.332	0.1908
	4	3.377	0.0/0.0	0.3401		8	3.646	–0.031/–0.047	0.3599
	5	3.721	0.0/0.0	0.1907		O	5.057	0.002/0.000	
	O	5.044	0.0/0.0			1	3.448	0.521/0.466	0.3606
	1	3.582	0.0/0.0	0.1945		2	3.601	0.119/0.075	0.1922
	2	3.582	0.0/0.0	0.1945		3	3.415	0.028/–0.003	0.4585
	3	3.686	0.0/0.0	0.2071		4	3.659	–0.033/–0.032	0.3304
	4	3.686	0.0/0.0	0.2071		5	3.699	–0.036/–0.048	0.4490
Ti_6O	5	3.460	0.0/0.0	0.3374	Ti_9O	6	3.769	0.065/–0.004	0.2072
	6	3.460	0.0/0.0	0.3374		7	3.415	0.028/–0.003	0.4585
	O	5.066	0.0/0.0			8	3.601	0.119/0.075	0.1922
						9	3.448	0.521/0.466	0.3606
						O	5.049	0.002/0.000	

To further investigate the origin of peculiar magnetic properties, we show the total density of states (DOS) of Ti atoms in Ti_nO clusters and partial density of states (PDOS) of Ti atoms which mainly contribute to the magnetism for several represented Ti_nO clusters in Fig.6. It can be seen that the DOS of Ti_5O (Fig.6(b)) and Ti_7O (Fig.6(c)) for spin-up and spin-down is symmetrical, which results in zero magnetic moment. For the total DOS of Ti atoms of magnetic Ti_4O (Fig.6(a)) and Ti_8O (Fig.6(d)) clusters there is an exchange splitting in the range of –3.3 to 0.0 eV, though it almost distributes symmetrically on inner energy levels. One can also find that the local DOS of the Ti atom with the largest magnetic moment mainly distributes on outer levels of Ti_nO and hardly locates at inner. It suggests that the magnetism of Ti_nO cluster may be due to the exchange splitting in outer energy levels. Moreover, the DOS of Ti_4O and Ti_5O

are apparently molecular-like and show some discrete peaks. Continuous bands start to emerge in the DOS of Ti_6O and Ti_8O. One could suspect that as the cluster size further increases, these molecular levels tend to overlap and form a continuous band with pure-titanium-like characteristics.

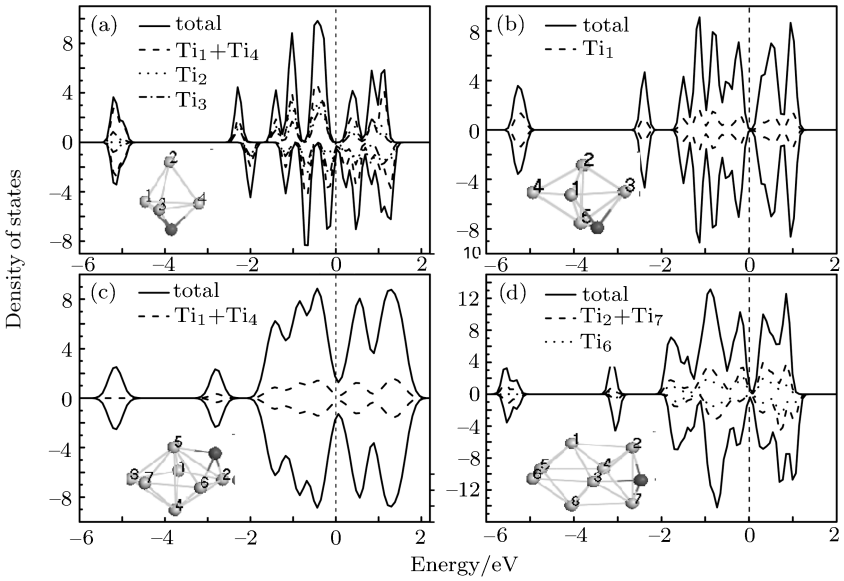


Fig.6. The total density of states of Ti atoms in Ti_nO clusters and PDOS of Ti atoms which mainly contribute to the magnetism of (a) Ti_4O; (b) Ti_5O; (c) Ti_7O;(d) Ti_8O; spin-up (positive) and spin-down (negative) densities are given in each case. The dash lines locate at the HOMO.

4. Conclusions

In this work, we have investigated the structural, energetic, electronic and magnetic properties of Ti_nO (n=1–9) clusters by using DFT-GGA calculations. In the ground-state structures of Ti_nO clusters, the oxygen atom occupies a peripheral position and hardly changes the main frame structure of the Ti_n cluster. The binding energy, second-order energy differences with the size of clusters indicate that the Ti_7O is the most stable cluster among those studied. The stability of Ti_nO cluster may be interpreted with the help of atomic shell model. Generally, the total magnetic moment of small Ti_nO clusters is lower than the corresponding Ti_n cluster due to the doping oxygen atom. Detailed analysis revealed that the magnetic moments for Ti_nO cluster are dominated by the 3d electrons of Ti atoms. It will be very interesting to perform further magnetic deflection experiments to confirm the magnetic behaviour of these systems.

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