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# First-principles calculation of the electronic structure of $\text{Ti}_8\text{C}_{12}$ and $\text{Zr}_8\text{C}_{12}$

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**Abstract.** The electronic structure of  $\text{Ti}_8\text{C}_{12}$  and  $\text{Zr}_8\text{C}_{12}$ , in both  $D_{2d}$  and  $T_h$  symmetry, are investigated by the first-principles DV- $X\alpha$  SCC method. The calculated binding energies of the  $D_{2d}$  structure are stronger than those of the  $T_h$  structure. It reveals that the  $D_{2d}$  cluster is more stable than the  $T_h$  cluster. Strong interactions between C–C and Ti–C, Zr–C covalent bonding are observed. When the transition-state procedure is used, ionization potentials of 7.04 eV and 6.58 eV are obtained for  $D_{2d}$   $\text{Ti}_8\text{C}_{12}$  and  $\text{Zr}_8\text{C}_{12}$  molecules, respectively.

## 1. Introduction

Since the discovery and practical synthesis of  $\text{C}_{60}$  [1, 2], much effort has been dedicated to the study of fullerenes, fullerites and other cage-like systems. Recently, Guo and co-workers [3] observed exceptional and abundant molecular clusters  $\text{Ti}_8\text{C}_{12}$ ,  $\text{Zr}_8\text{C}_{12}$ ,  $\text{V}_8\text{C}_{12}$  and  $\text{Hf}_8\text{C}_{12}$  using laser vaporization techniques. Interestingly, these systems may exhibit a rich variety of electronic and magnetic properties due to the presence of transition-metal elements. A cage-like dodecahedral structure of  $T_h$  point group symmetry is proposed by Guo and co-workers to account for the unusual stability of these molecular clusters. Ceulemans and Fowler have made a qualitative discussion based on the Hückel model and symmetry aspects of Jahn–Teller instabilities for the  $\text{Ti}_8\text{C}_{12}$  cluster [4]. They think that full pairing of electron spins occurs not for the tetrahedral ( $T_h$ ) cage but for a trigonal ( $D_{3d}$ ) alternative. Total-energy density-functional calculations carried out by Methfessel and co-workers [5] and Li and co-workers [6] for the cluster  $\text{Ti}_8\text{C}_{12}$  conclude that the structure of  $\text{Ti}_8\text{C}_{12}$  is only slightly distorted from the perfect dodecahedron due to the difference between C–C and Ti–C interatomic distances, and the  $T_h$  symmetry remains stable and strongly bound. Subsequently, Chen and co-workers [7] have investigated the stability, bonding and geometric structure of these systems by the use of a density-functional calculation. They make the proposal of a new, stable and more strongly bound structure with  $D_{2d}$  symmetry. However as yet, to the best of our knowledge, because of lack of experimental evidence none of the proposed structures have been confirmed. In order to give more information, in this work we used the DV- $X\alpha$  SCC method to calculate self-consistently the electronic structure of  $\text{Ti}_8\text{C}_{12}$  and  $\text{Zr}_8\text{C}_{12}$  molecules. By presenting the binding energy, charge density distribution and density of states, we studied the energetics and the chemical bonding in detail.

## 2. Theoretical approach

The calculation is carried out using the first-principles DV- $X\alpha$  SCC method. This method has been successfully used in the physics and chemistry of condensed matter [8, 9]. A recent calculation on  $C_{60}$  got excellent results compared with experiment [10].

In non-relativistic local density theory, the self-consistent HFS one-electron Hamiltonian is

$$H = T + V_{\text{Coul}}(r) + V_{\text{xc}}(r) = -\frac{1}{2}\nabla^2 - \sum_{\nu} \frac{Z_{\nu}}{|r - R_{\nu}|} + \int \frac{\rho(r') dr'}{|r - r'|} - 3\alpha \left( \frac{3\rho_{\sigma}(r)}{8\pi} \right)^{1/3} \quad (1)$$

where  $T$ ,  $V_{\text{Coul}}(r)$  and  $V_{\text{xc}}$  are the kinetic energy and Coulomb and exchange correlation potentials respectively. The simplest Kohn-Sham [11] formula with  $\alpha = 0.7$  is used for the local density exchange correlation throughout this work. The wavefunctions of clusters are expanded in terms of symmetry orbitals, which are linear combinations, corresponding to the group symmetry of atomic orbitals located on the atomic site of the cluster

$$\psi_i = \sum_j C_{ij} \phi_j. \quad (2)$$

The expansion coefficients  $C_{ij}$  are obtained by solving the matrix secular equation

$$\|H_{ij} - \epsilon_i S_{ij}\| C_{ij} = 0. \quad (3)$$

The discrete variational method is used to evaluate the Hamiltonian matrix elements  $H_{ij}$  and overlap matrix elements  $S_{ij}$ , and is described elsewhere [12]. The cluster charge density is constructed by summing over all orbitals of the cluster

$$\rho_{\text{model}}(r) = \sum_i f_i |\psi_i(r)|^2 \quad (4)$$

where  $f_i$  is the occupation number of the  $i$ th cluster orbital. The charge density is decomposed approximately by Mulliken populations [13] as

$$\rho_{\text{model}}(r) \approx \rho_{\text{SCC}}(r) = \sum_{\nu nl} f_{nl}^{\nu} |R_{nl}(r_{\nu})|^2 \quad (5)$$

where  $f_{nl}^{\nu}$  is the population of the  $nl$  atomic orbital of atom  $\nu$  and  $R_{nl}(r_{\nu})$  is the corresponding radial function. The self-consistent charge density (SCC) procedure starts with this new charge density  $\rho_{\text{SCC}}$  to obtain the new potential and one-electron equation.

The density of states (DOS) is defined as

$$D(E) = \sum_{\nu nl} D_{nl}^{\nu}(E) \quad (6)$$

with

$$D_{nl}^{\nu}(E) = \sum_{\text{unl}} D_{nl}^{\nu} = \sum_p A_{nl,p}^{\nu} \frac{\sigma/\pi}{(E - \epsilon_p)^2 + \sigma^2} \quad (7)$$

where  $\nu$  is the index for the atom,  $p$  denotes each eigenfunction,  $\epsilon_p$  is its eigenvalue,  $\sigma$  is a broadening factor (0.001 eV in this study), and  $A_{nl,p}^{\nu}$  is the contribution of the  $nl$  atomic orbital of the  $\nu$  atom to the  $p$  molecular orbital, based on the Mulliken population [13].

According to the local density approximation [11], the total energy is evaluated by

$$E_t = \sum_i f_{i\sigma} \varepsilon_{i\sigma} - \frac{1}{2} \int \int \frac{\rho(r')\rho(r)}{|r-r'|} d^3r d^3r' + \int \rho(r)[E_{xc}(r) - V_{xc}] d^3r + \frac{1}{2} \sum_{\mu,\nu} \frac{z_\mu z_\nu}{R_{\mu\nu}} \quad (8)$$

where  $\varepsilon_{i\sigma}$ ,  $f_{i\sigma}$  are the energy eigenvalue and occupation number of the  $i$ th state of spin  $\sigma$ ,  $\rho$  is the electron number density ( $\rho_\sigma$  is the spin density,  $\sigma = +, -$  and  $\rho = \rho_+ + \rho_-$ ),  $E_{xc}$  and  $V_{xc}$  are the exchange and correlation energy and potential, respectively, and  $R_{\mu\nu}$  is the distance between the  $z_\mu$  and  $z_\nu$  atoms. The binding energy is determined by taking the difference between the total energy of the cluster and that of a reference system:  $E_b = E_t - E_{ref}$ .

### 3. Results

The proposed  $T_h$  dodecahedral structure and  $D_{2d}$  structure are plotted in figure 1 (left) and figure 1 (right), respectively. The  $T_h$  structure can be viewed as a  $C_{20}$  cluster with eight carbon atoms replaced by transition-metal atoms. In this configuration, transition-metal atoms form a perfect cube and six pairs of  $C_2$  orient toward the middle of metal-atom bonds; all metal atoms are equivalent to each other, as are C atoms. Unlike in the  $T_h$  dodecahedron structure, there are two types of metal atom (Ti or Zr) in the  $D_{2d}$  structure, as marked in figure 1 (right). There are four metal atoms (Ti(1) or Zr(1)) each with five carbon nearest neighbours and four other metal atoms (Ti(2) or Zr(2)) each with four carbon nearest neighbours. Eight metal atoms form a cage of a distorted cube. Carbon atoms are also divided into two groups here. Two pairs of C(1) atoms are at the top and the bottom of figure 1 (right). Four pairs of C(2) atoms are absorbed onto the centre of four parallelograms formed by the eight metal atoms, with the C-C bond bridging along the longest diagonal.

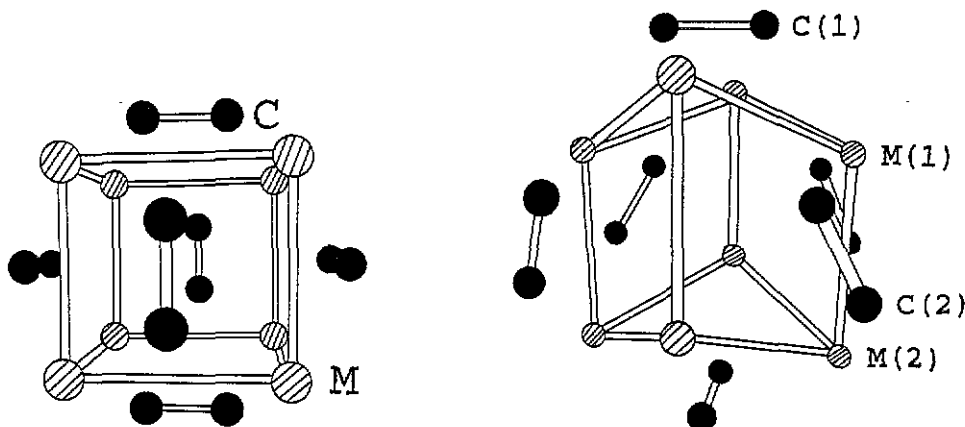


Figure 1. (Left) Geometric structure of the  $T_h$  clusters. (Right) Geometric structure of the  $D_{2d}$  clusters. Hatched circles: metal atoms; full circles: carbon atoms.

Since it is difficult to make the structure optimization by the DV- $X\alpha$  method, our calculations are based on the optimized structure parameters given by Chen and co-workers [7]. The bond lengths are listed in table 1.

**Table 1.** Bond lengths (Å) (from table I in [7]). M stands for the transition metal; A stands for carbon.

	Ti <sub>8</sub> C <sub>12</sub>		Zr <sub>8</sub> C <sub>12</sub>	
	D <sub>2d</sub>	T <sub>h</sub>	D <sub>2d</sub>	T <sub>h</sub>
M(1)–M(2)	2.77	3.04	3.00	3.25
M(1)–M(2)	2.81	3.04	3.03	3.25
A(1)–A(1)	1.36	1.41	1.37	1.43
A(2)–A(2)	1.37	1.41	1.38	1.43
A(1)–M(1)	2.04	1.97	2.18	2.09
A(1)–M(2)	2.09	1.97	2.21	2.09
A(2)–M(1)	2.08	1.97	2.21	2.09
A(2)–M(2)	1.95	1.97	2.09	2.09

In all electronic structure and total-energy calculations using variational methods to solve the Schrödinger equation, the flexibility of the basis functions is an important factor in determining the accuracy of the calculated results. By increasing the number of the basis functions of a chosen form, for example adding further *unlm* radial and angular functions, we can improve the basis flexibility. The 3d, 4s and 4p orbitals of the Ti atom, the 4d, 5s and 5p orbitals of the Zr atom and the 2s, 2p and 3s orbitals of the C atom are adopted as valence orbitals. In all calculations, the 1s, 2s, 2p, 3s and 3p orbitals on Ti, the 1s, 2s, 2p, 3s, 3p, 3d, 4s and 4p orbitals on Zr and the 1s orbital on C are frozen and the variational valence orbitals are constrained to be orthogonal to the cores.

Our results for the binding energies, charges, LUMO–HOMO gaps and ionization potentials of the Ti<sub>8</sub>C<sub>12</sub> and Zr<sub>8</sub>C<sub>12</sub> clusters are summarized in table 2, along with the corresponding results of [7] for the purpose of comparison. The binding energies, which are in good agreement with [7], show that D<sub>2d</sub> isomers are more bounded than T<sub>h</sub> isomers by nearly 0.75 eV per atom.

**Table 2.** The calculated properties. M stands for the transition metal; A stands for carbon. The numbers in parentheses are results in [7].

	Ti <sub>8</sub> C <sub>12</sub>		Zr <sub>8</sub> C <sub>12</sub>	
	D <sub>2d</sub>	T <sub>h</sub>	D <sub>2d</sub>	T <sub>h</sub>
Binding energy (eV)	7.38 (7.47)	6.65 (6.79)	7.28 (7.37)	6.48 (6.60)
Mulliken charges				
M(1)	1.16 (0.39)	0.94 (0.48)	1.01 (0.42)	0.96 (0.50)
M(2)	0.87 (0.33)	0.94 (0.48)	0.95 (0.43)	0.96 (0.50)
A(1)	–0.64 (–0.22)	–0.65 (–0.32)	–0.55 (–0.30)	–0.63 (–0.33)
A(2)	–0.69 (–0.25)	–0.65 (–0.32)	–0.71 (–0.27)	–0.63 (–0.33)
LUMO–HOMO gaps (eV)	0.06	0.08	0.10	0.07
Ionization potentials (eV)	7.05		6.58	

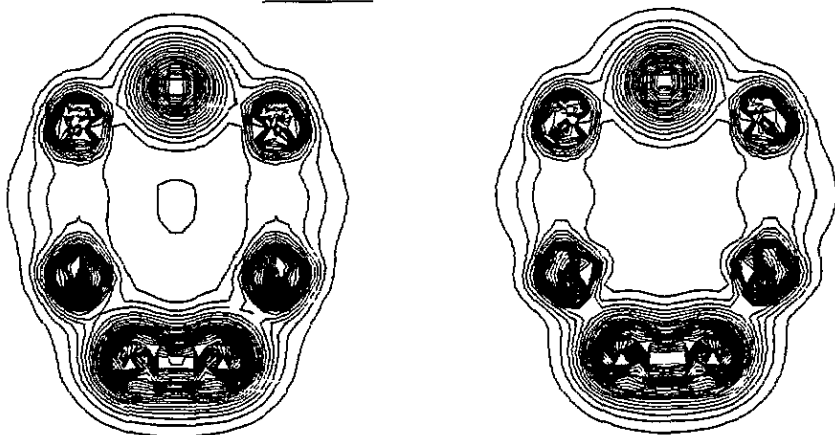
It has been reported that the dodecahedral C<sub>20</sub> cluster is not a stable fullerene because it contains only 12 five-membered rings without six-membered rings [14]. The calculated ground state is degenerate and thus subject to the first-order Jahn–Teller distortion. The

electronic origin for this is the unfavourable severe strain of the C–C  $\pi$ -bonding which is reduced by decoration with 20 hydrogen atoms [15].

When Guo and co-workers proposed a dodecahedral structure for  $Ti_8C_{12}$ , they made the reasonable suggestion that the bonding mechanism is similar to that of graphite and  $C_{60}$ . First, they postulated a network of Ti–C and C–C  $\sigma$  bonds, involving d–sp hybrids on the Ti atoms. Second, ' $\pi$ -bonding' states made from metal  $d_\pi$  and carbon  $p_\pi$  orbitals were assumed to hold the remaining electrons. The transition metal is assigned a relevant role in stabilizing the molecule by reducing the strain, due to the strong curvature, which would make a hypothetical  $C_{20}$  molecule unstable. The previous report [6] predicted that the ideal  $T_h$  cluster  $Ti_8C_{12}$  would have two unpaired electrons in a triply degenerate HOMO, whereas the distorted  $T_h$  dodecahedral structure would have a completely electron-occupied HOMO. A similar conclusion can be found in [5].

In contrast to the conclusion obtained in [5, 6], our results show that  $Ti_8C_{12}$  and  $Zr_8C_{12}$  in the  $T_h$  symmetry are unstable. In the  $T_h$  molecular symmetry, the HOMO is found to be a triply degenerate orbital ( $T_u$  for  $Ti_8C_{12}$  and  $T_g$  for  $Zr_8C_{12}$ ); yet there are only two electrons occupying these orbitals. Further geometric distortion to a subject of  $T_h$  would be needed to resolve the Jahn–Teller instability. In the  $D_{2d}$  cluster, the highest level ( $B_2$  in  $Ti_8C_{12}$  and  $E$  in  $Zr_8C_{12}$ ) is fully filled by electrons. It appears that the  $D_{2d}$  structure for  $Ti_8C_{12}$  and  $Zr_8C_{12}$  is consistent with its enhanced stability. In addition, atoms in the  $D_{2d}$  structure have higher coordination numbers, which enhance the interatomic interactions. We thus conclude that the neutral  $Ti_8C_{12}$  and  $Zr_8C_{12}$  cluster should be a  $D_{2d}$  structure, in agreement with [7].

It should be noted that, unlike the pure carbon cage cluster, LUMO–HOMO gaps in  $Ti_8C_{12}$  and  $Zr_8C_{12}$  are very small. This may imply that solid  $Ti_8C_{12}$  and  $Zr_8C_{12}$  could exhibit metallic character.



**Figure 2.** (Left) The contour map of the charge density distribution (spin-up) of the  $D_{2d}$   $Ti_8C_{12}$  cluster on the plane which contains two Ti(1), two Ti(2) and two C(1) atoms. First contour and contour spacing are 0 and 5 in units of  $10^{-3} \text{ bohr}^{-3}$ . (Right) The contour map of the charge density distribution (spin-down) of the  $D_{2d}$   $Ti_8C_{12}$  cluster on the plane which contains two Ti(1), two Ti(2) and two C(1) atoms. First contour and contour spacing are 0 and 5 in units of  $10^{-3} \text{ bohr}^{-3}$ .

Strong bonding between C–C and Ti–C, Zr–C covalent bonding are observed in the  $D_{2d}$  cluster in our calculation. This is reflected in the valence charge contour maps shown in figures 2 and 3. We can see from these figures that there is much more charge along the

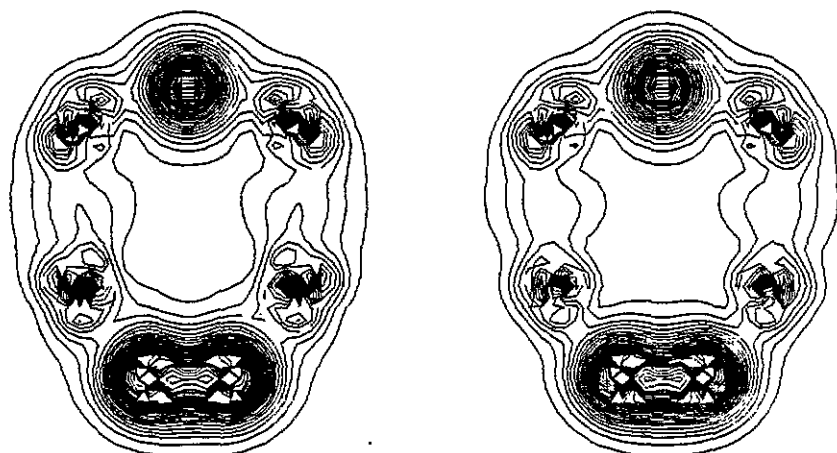


Figure 3. (Left) The contour map of the charge density distribution (spin-up) of the  $D_{2d}$   $Zr_8C_{12}$  cluster on the plane which contains two Zr(1), two Zr(2) and two C(1) atoms. First contour and contour spacing are 0 and 5 in units of  $10^{-3}$  bohr $^{-3}$ . (Right) The contour map of the charge density distribution (spin-down) of the  $D_{2d}$   $Zr_8C_{12}$  cluster on the plane which contains two Zr(1), two Zr(2) and two C(1) atoms. First contour and contour spacing are 0 and 5 in units of  $10^{-3}$  bohr $^{-3}$ .

C–C and Ti–C (Zr–C) bonds, and there is only very weak bonding between Ti–Ti (Zr–Zr) atoms. It should be noted that there are various shapes between spin-up and spin-down charge density, due to the d orbital of transition-metal atoms. In fact, C–C distances of the  $D_{2d}$  structures are very close to the bond length (1.32 Å) of a free  $C_2$  dimer. It is important to realize that the  $C_2$  dimer forms a very strong unit in the cluster. In table 2, according to the Mulliken population analysis, we find that there is considerable charge transfer from Ti (or Zr) to the C atom. Transferred electrons tend to occupy the antibonding  $\pi_g$  orbitals of  $C_2$  dimers. More charge transfer corresponds to higher coordination numbers on the Ti (or Zr) atoms. About one electron (note that this value may differ from different calculation methods or basis sets due to the approximate partition of the Mulliken population, and the charge is not a well defined value in a molecular method) from each transition-metal atom in  $Ti_8C_{12}$  and  $Zr_8C_{12}$  clusters is transferred to the C atoms. This means that the Ti or Zr and C atoms in the cluster are positive and negative ions, respectively, in agreement with the experimental and theoretical investigations on bulk TiC [16, 17]. Such a large transfer implies that the ionic interaction between the Ti–C or Zr–C atoms may play an important role in the electronic structure of the cluster. This is in contrast to the situation in the  $C_{20}$  cluster. For  $Ti_8C_{12}$  and  $Zr_8C_{12}$  clusters, of the total valence charge on the Ti (Zr) atoms, 6% (3%) and 20% (12%) is associated with the s and p orbitals, respectively. Therefore, it is mainly the Ti (or Zr) d orbitals which participate in the bonding with carbon. On the metal-atom surface, strong carbon p atomic states and metal-atom d hybridization lowers the antibonding  $\pi_g$  orbitals of  $C_2$ . Transferred electrons will occupy these states to strengthen the Ti–C (Zr–C) bonding.

That there is strong covalent bonding between Ti or Zr d and C p states can also be understood from the plot of the density of states shown in figures 4 and 5. Since the shape of  $Ti_8C_{12}$  and  $Zr_8C_{12}$  are very similar, as expected, the discussion below is devoted to the DOS of the  $D_{2d}$   $Zr_8C_{12}$  cluster.

The low-energy peaks, between  $-15$  eV  $\sim$   $-12$  eV and between  $-8$  eV  $\sim$   $-6$  eV below the Fermi level, are mainly of C s character with a small amount of p character along the C–C bond mixed in. The main carbon p state peaks locate in the range  $-6$  eV to  $\sim$   $-2$  eV.

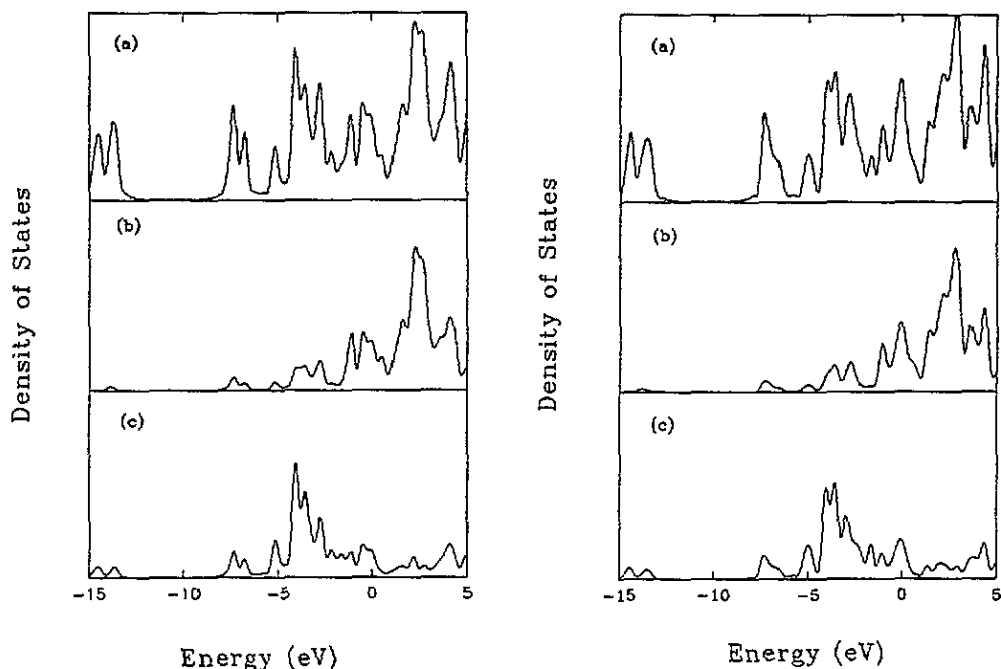


Figure 4. (Left) The density of states (spin-up) of the  $D_{2d}$   $\text{Ti}_8\text{C}_{12}$  cluster. The Fermi level is shifted to  $E = 0$ . (Right) The density of states (spin-down) of the  $D_{2d}$   $\text{Ti}_8\text{C}_{12}$  cluster. The Fermi level is shifted to  $E = 0$ . (a) Total density of states; (b) partial density of states of Ti 3d; (c) partial density of states of C 2p.

These states are mainly carbon  $\pi_u$  bonding orbitals which, together with  $\sigma_g$  bonds of C 2s, are responsible for the interatomic C–C bonding. We can see from figure 4 that at higher energies carbon p states are delocalized and an appreciable amount of C p states are spread in a wide range of energies around  $E_F$ . The majority of Zr d states are above the Fermi level. The occupied states near  $E_F$  have a substantial amount of Zr d components and show a strong C–p–Zr–d resonance. The strong C–Zr bonding is primarily due to these states. It is interesting to note from figure 4 that there are obvious differences between spin-up and spin-down DOS. This means that this cluster may display a small magnetic moment.

The ionization potentials (IP) of the  $D_{2d}$  cluster given in table 2 are obtained by the transition state method. The IP of the  $D_{2d}$   $\text{Ti}_8\text{C}_{12}$  cluster is about 1 eV higher than that of the  $T_h$   $\text{Ti}_8\text{C}_{12}$  cluster [6]. Though there is much evidence to suggest that the SCC method may have difficulty in predicting accurate values for ionization potentials, we hope that it could provide information for comparison with experiment in the future.

#### 4. Conclusion

We have calculated the electronic structure of  $\text{Ti}_8\text{C}_{12}$  and  $\text{Zr}_8\text{C}_{12}$  clusters by using the first-principles DV- $X\alpha$  SCC method. In favour of suggestions made in [7], we find that the  $D_{2d}$  structure is more stable than the  $T_h$  dodecahedral structure. The electronic origin is mainly due to strong C–C dimer interactions and covalent bonding between metal-atom d and  $\text{C}_2$   $\pi_g$  orbitals. We will extend our work to a calculation of the vibrational spectra in the near future.



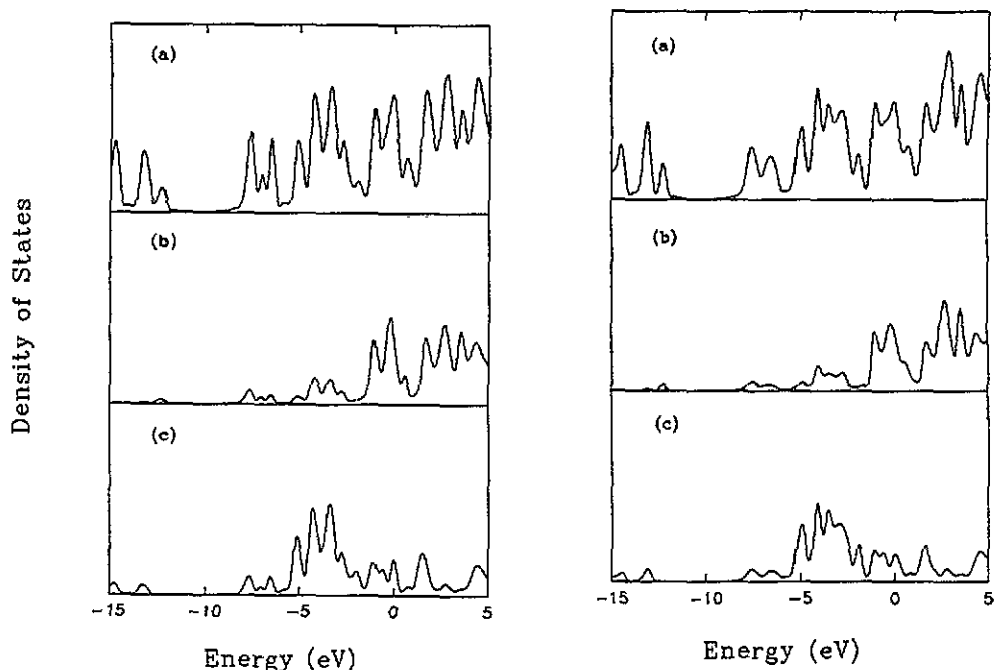


Figure 5. (Left) The density of states (spin-up) of the  $D_{2d}$   $Zr_8C_{12}$  cluster. The Fermi level is shifted to  $E = 0$ . (Right) The density of states (spin-down) of the  $D_{2d}$   $Zr_8C_{12}$  cluster. The Fermi level is shifted to  $E = 0$ . (a) Total density of states; (b) partial density of states of Zr 4d; (c) partial density of states of C 2p.

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