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Electronic structures of metallo-carbohedrenes

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Abstract. The electronic structures of metallo-carbohedrenes M_mC_n , a new class of molecular clusters, have been investigated using the universal parameter tight-binding method. We have studied the cases of different transition metals M ($M = \text{Ti}, \text{V}, \text{Zr}$) with single-cage structure and unusual double-cage structure and triple-cage structures.

1. Introduction

In recent research on fullerenes and other carbon-related clusters, many efforts have been made to obtain novel doped fullerenes which may have some new properties, especially since the discovery of the superconductivity of alkali-doped C_{60} [1]. For example, the substitutional doped fullerenes with boron and nitrogen atoms $C_{59}B$, $C_{59}N$, $C_{58}B_2$, etc, have been studied experimentally [2] and theoretically [3].

Recently, a new class of molecular clusters, namely metallo-carbohedrenes (met-car) M_mC_n , were discovered in mass spectra. When (m, n) are magic numbers, there are corresponding peaks in the mass spectra. The cluster structure of M_8C_{12} ($M = \text{Ti}, \text{V}, \text{Zr}$) [4, 5] can be thought as the pentagonal dodecahedron structure for C_{20} with eight carbon atoms replaced by eight metal atoms. The $M-C$ bond is longer than the $C-C$ bond. Figure 1(a) shows this distorted dodecahedron structure of M_8C_{12} which displays a T_h point group symmetry. In order to account for the magic numbers corresponding to the peaks in the mass spectra, the double-cage structure of $M_{14}C_{21}$ as shown in figure 1(b) and the triple-cage structure of $M_{18}C_{29}$ as shown in figure 1(c) have been proposed [6]. Very recently, some first-principles calculations on the electronic structure of Ti_8C_{12} have been made [7–10]. However, studies of the electronic structures of the met-car with multicage cluster structures have not been made. As the unusual growth mechanism of the multicage structure is of great interest, we want to understand the general features of the electronic structures of this new class molecular clusters, for different metal atoms and from single-cage to multicage structures.

In this paper, we adopt the modified universal-parameter tight-binding method [11–14] to calculate the electronic structures of these novel clusters. The matrix elements between the s , p and d orbitals of nearest-neighbour sites depend on the relative direction between the sites. We use the Slater–Koster formula [11–14] to express them. The primary matrix elements between s , p and d orbitals come first from Harrison's universal parameters [12], then from some modified ones [13, 14]. We first calculate that of Ti_8C_{12} and compare the results with those of the first-principles local density approximation (LDA) calculations [7–10]. We then use the thus-determined parameters to calculate the cases of multicage structures, which are complicated for the first-principles calculations. We study the cases

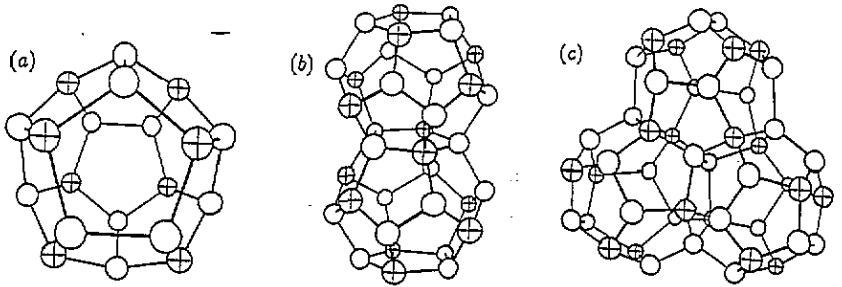


Figure 1. Proposed metallo-carbohedrenes cluster structures for (a) single-cage M_8C_{12} (b) double-cage $M_{14}C_{21}$ (c) triple-cage $M_{18}C_{29}$. The open circles indicate carbon atoms; circles with crosses indicate metal atoms.

of different metal atoms, and compare the results with each other. Our results may account for the stability of Zr_mC_n clusters observed in experiment [6].

2. Theoretical model

The tight-binding Hamiltonian can be written as

$$H = \sum_{i\alpha} \epsilon_{i\alpha}^0 |i\alpha\rangle \langle i\alpha| + \sum_{i\alpha j\beta} V_{i\alpha j\beta} (|i\alpha\rangle \langle j\beta| + |j\beta\rangle \langle i\alpha|) \quad (1)$$

where $\epsilon_{i\alpha}^0$ is the energy of orbital $|i\alpha\rangle$ at site i which we take from Herman and Skillman [15], $V_{i\alpha j\beta}$ is the matrix element between the atomic orbital $|i\alpha\rangle$ at site i and $|j\beta\rangle$ at site j which has the form of the relative direction between site i and j derived by Slater and Koster [11,12]. Here we omit the spin index. We include the 3d4s orbitals for Ti, V, the 4d5s orbitals for Zr atoms and the 2s2p orbitals for carbon atoms in the linear combination of atomic orbitals (LCAO) for the one-electron states of the cluster:

$$|n\rangle = \sum_{i\alpha} C_{ni\alpha} |i\alpha\rangle. \quad (2)$$

In the tight-binding approximation, we only consider the contributions of matrix elements between nearest-neighbour sites. The primary matrix elements between s, p orbitals are

$$V_{\alpha\beta\gamma} = \eta_{\alpha\beta\gamma} \frac{\hbar^2}{md^2} \quad (3)$$

where m is electron mass, d is the bond length and $\eta_{\alpha\beta\gamma}$ are the four universal parameters $\eta_{ss\sigma}$, $\eta_{sp\sigma}$, $\eta_{pp\sigma}$ and $\eta_{pp\pi}$, which were first proposed by Harrison [12], and which modified values have recently been successfully used to study carbon clusters [13,14]. We used the modified values, $\eta_{ss\sigma} = -1.14$, $\eta_{sp\sigma} = 1.32$, $\eta_{pp\sigma} = 1.69$ and $\eta_{pp\pi} = -0.70$, to calculate the electronic structure of C_{60} and found that they can give a result which agrees well with that of LDA. In this paper, we take these values to study the met-car. The primary matrix elements between s, p and d orbitals are [12]

$$V_{\alpha\beta\gamma} = \eta_{\alpha\beta\gamma} \frac{\hbar^2 r_d^{3/2}}{md^{7/2}}. \quad (4)$$

Here $\eta_{sd\sigma} = -3.16$, $\eta_{pd\sigma} = -2.95$, $\eta_{pdx} = 1.36$, $r_d = 1.08, 0.98, 1.41$ for Ti, V, and Zr respectively [12].

From the variation principle, the secular equation can be derived directly:

$$\det |H_{ij} - E\delta_{ij}| = 0. \quad (5)$$

Solving this equation, we get the eigenenergies and the corresponding eigenvectors $C_{ni\alpha}$.

The total density of states (TDOS) is defined as

$$D(E) = \sum_{i\alpha} D_{i\alpha}(E) \quad (6)$$

where

$$D(E)_{i\alpha} = \sum_n A_{i\alpha,n} \frac{\sigma/\pi}{(E - E_n)^2 + \sigma^2} \quad (7)$$

is the partial density of states (PDOS). Here σ is a broadening factor which we take to be 0.2 eV throughout this paper. This value is a little smaller than usual [7] since we want to see the change in electronic structures with increasing cluster size, which will result in a general broadening of the peaks in TDOS. $A_{i\alpha,n}$ is the Mulliken population, which is $C_{ni\alpha}^2$ (normalized).

3. Results

We first calculate the electronic structures of Ti_8C_{12} and compare the results with those of LDA calculations [7–10], and find they agree well with each other. The C—C bond length is taken to be 1.51 Å, the Ti—C bond length 1.96 Å, and the V—C bond length 1.85 Å [7]. It is seen that the bond length is approximately the addition of the covalent radius. We therefore set the Zr—C bond length to be 2.09 Å in order to calculate the electronic structures of Zr_mC_n which are found in experiment [6]. Figures 2–4 show the electronic structures of Ti_8C_{12} , Zr_8C_{12} and V_8C_{12} respectively. The broken lines indicate the highest occupied molecular orbitals (HOMO) which are threefold degenerate in figures 2–4 and doubly occupied in figures 2 and 3, and occupied by four electrons in figure 4. These met-car clusters are metallic.

We also calculate the partial density of states and find that the two peaks at lower energy come mainly from the C 2s orbital contributions, and the states near the Fermi energy mainly come from the contributions of the hybridization of d orbitals of metal atoms and C 2p orbitals. Figure 2 is similar to figure 3, and they are both different from figure 4 whose Fermi surface mainly comes from the contribution of 3d orbitals of the vanadium atom.

We then calculate the electronic structures of $M_{14}C_{21}$, which have double-cage cluster structures as shown in figure 1(b). The results are plotted in figure 5(a) for $Ti_{14}C_{21}$, 5(b) for $Zr_{14}C_{21}$ and 5(c) for $V_{14}C_{21}$. Figure 6(a), (b) and (c) show the results for $Ti_{18}C_{29}$, $Zr_{18}C_{29}$ and $V_{18}C_{29}$ respectively, which have triple-cage cluster structures as shown in figure 1(c). In figures 5 and 6, the broken lines indicate the position of the Fermi energy. In experiment, only Zr_mC_n clusters have been found. In order to find the features by comparison, we have calculated all the electronic structures for Ti_mC_n , Zr_mC_n and V_mC_n . We can now compare the results for different metal atoms with single-cage, double-cage and triple-cage met-car

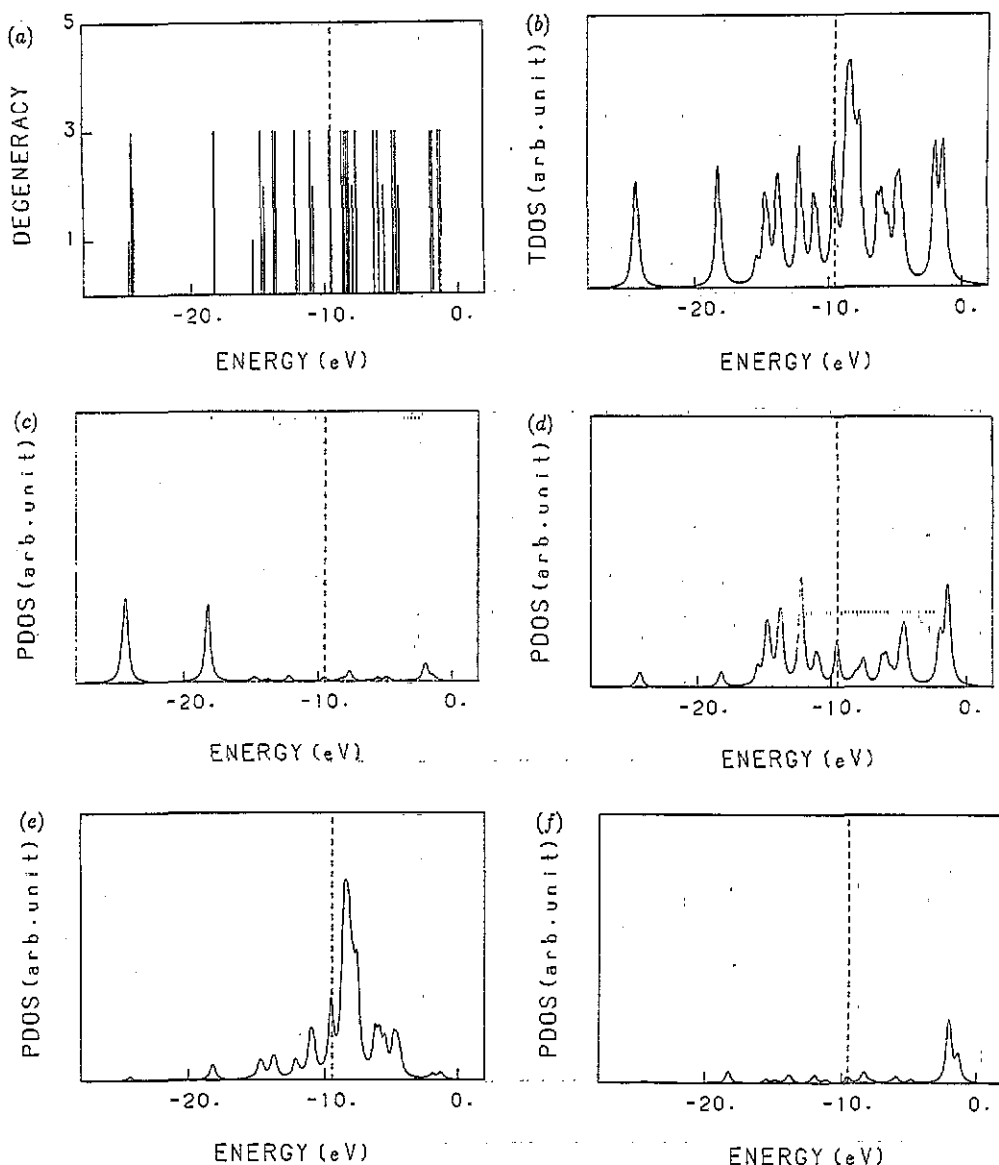


Figure 2. Electronic structures for Ti_3C_{12} . (b) shows the total density of states (TDOS) corresponding (a) to an 0.2 eV broadening factor. Parts (c)–(f) show the partial density of states (PDOS) for C:2s; C:2p; Ti:3d; and Ti:4s respectively.

structures, and find the similarities and changes in figures 2–6. We find that in each figure the DOS at the Fermi energy shows a peak; these met-car with multicage cluster structures are metallic too. We can also see that when the cluster size (m, n) increases, the peaks in the DOS generally become broadened, the DOS at the Fermi energy becomes relatively smaller for Ti_mC_n , and especially for Zr_mC_n , but becomes bigger for V_mC_n . Let us make it clear that with increasing cluster size (m, n), compared with Ti_mC_n and V_mC_n , the DOS of Zr_mC_n at the Fermi energy decreases; as a result, it seems that there appears to be an effective pseudo-gap at the Fermi level. This is the reason why the multicage Zr_mC_n cluster

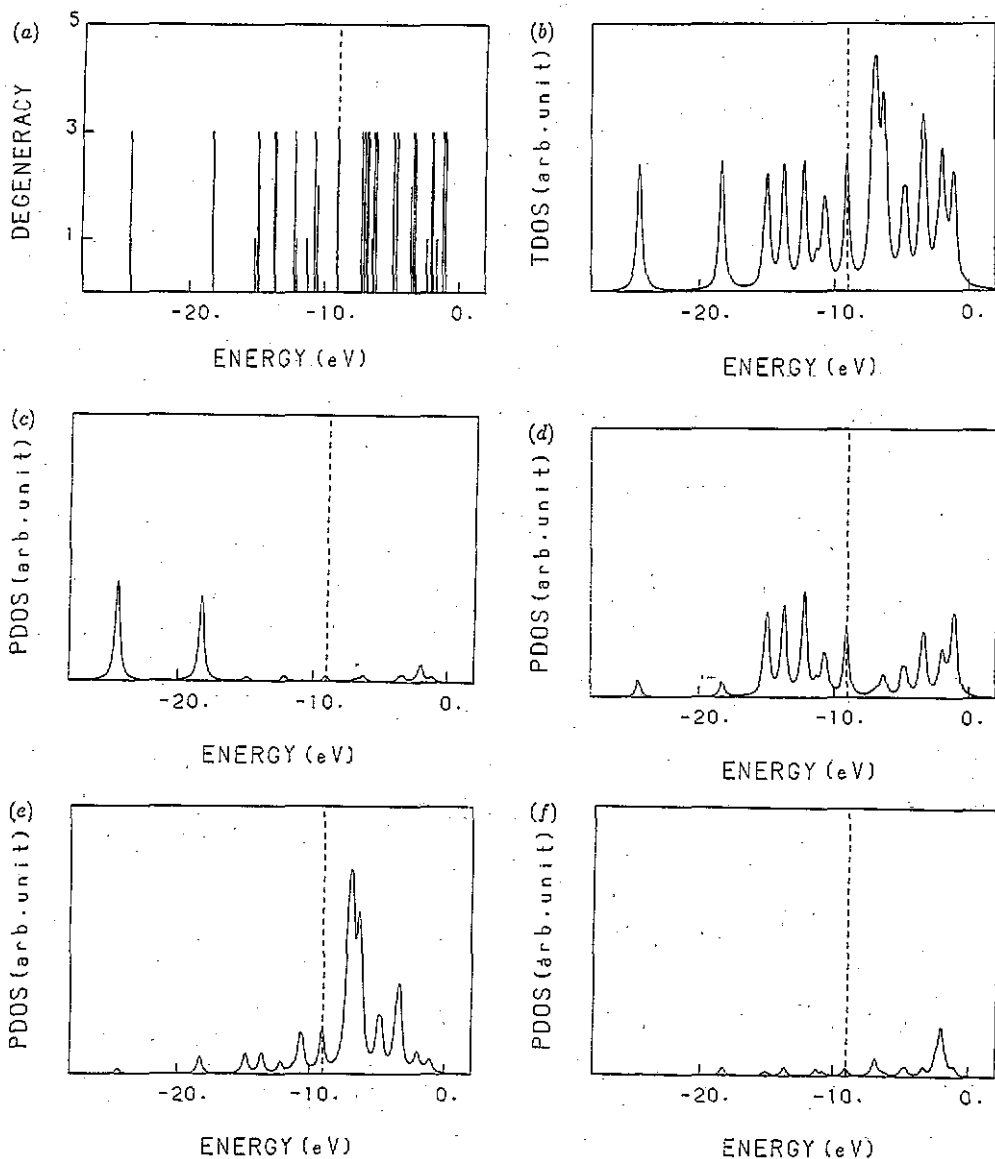


Figure 3. Electronic structures for Zr_3C_{12} . (b) is the total density of states (TDOS) corresponding (a) to an 0.2 eV broadening factor. Parts (c)–(f) show the partial density of states (PDOS) for C:2s; C:2p; Zr:4d; and Zr:5s respectively.

is observed in experiment [6], and is thus relatively more stable than the multicage Ti_mC_n and V_mC_n clusters which have not yet been found in experiment. We can also conclude that the Ti_mC_n cluster is more stable and thus may be more easily synthesized than the V_mC_n cluster.

4. Summary

We have calculated the electronic structures of met-car clusters M_mC_n for the cases of

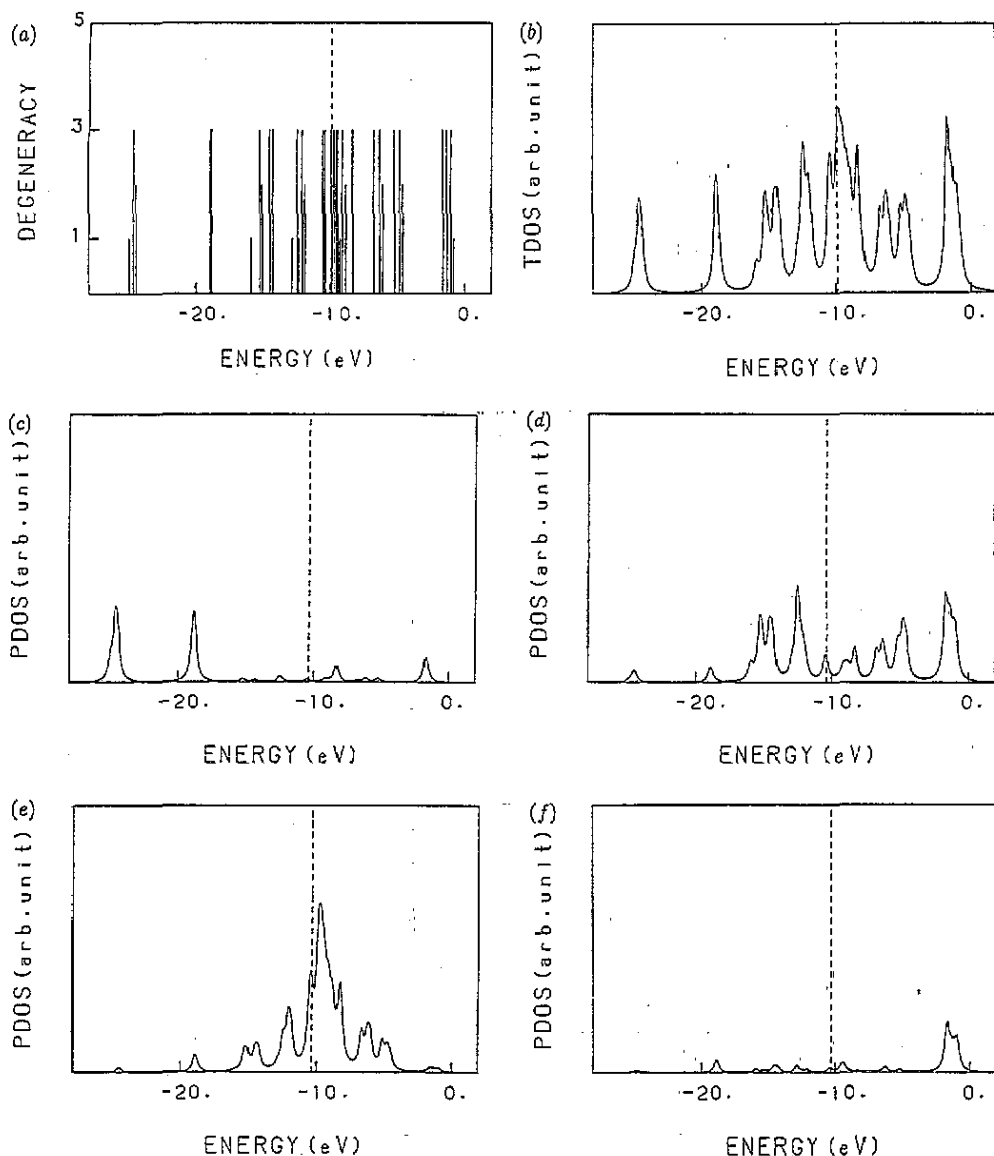


Figure 4. Electronic structures for V_8C_{12} . (b) is the total density of states (TDOS) corresponding (a) to an 0.2 eV broadening factor. Parts (c)–(f) show the partial density of states (PDOS) for C:2s; C:2p; V:3d; and V:4s respectively.

different metal atoms M ($M = \text{Ti}, \text{Zr}, \text{V}$) and different cluster size with (m, n) equal to (8, 12), (14, 21), (18, 29) for the proposed unusual multicage cluster structures [4–6]. The method we used was the Slater–Koster tight-binding model (TBA) for all s, p, d valence electrons [11–14], and the primary matrix elements between these s, p, d orbitals we take are the modified Harrison universal parameters [11–14]. This method is simple and effective, especially for the cases of unusual multicage cluster structures which are too complicated for first-principles calculations. Based on these results, we discussed the relative stability of the Zr_mC_n , Ti_mC_n and V_mC_n clusters with multicage structures.

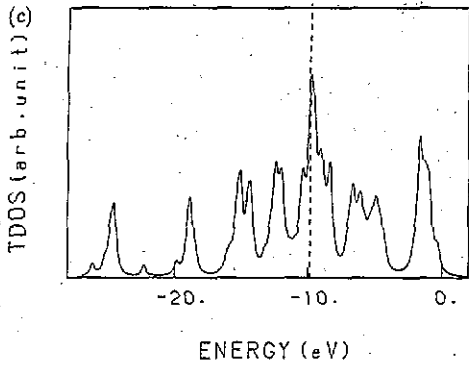
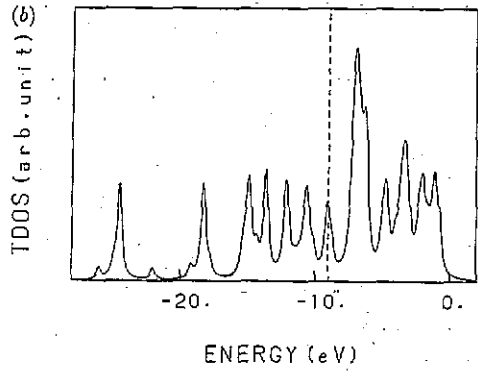
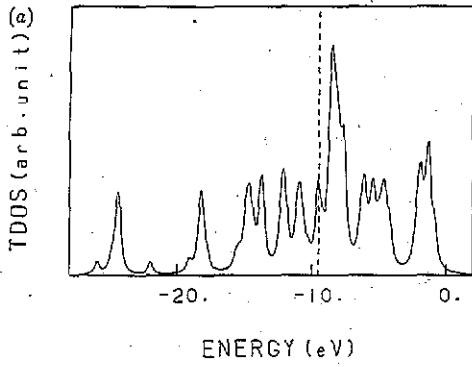


Figure 5. Total density of states (TDOS) for (a) $\text{Ti}_{14}\text{C}_{21}$, (b) $\text{Zr}_{14}\text{C}_{21}$ and (c) $\text{V}_{14}\text{C}_{21}$, which have the double-cage cluster structure as shown in figure 1(b).

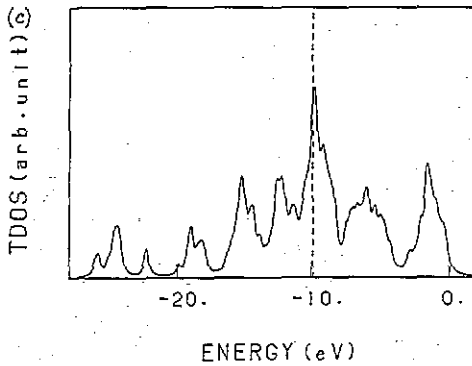
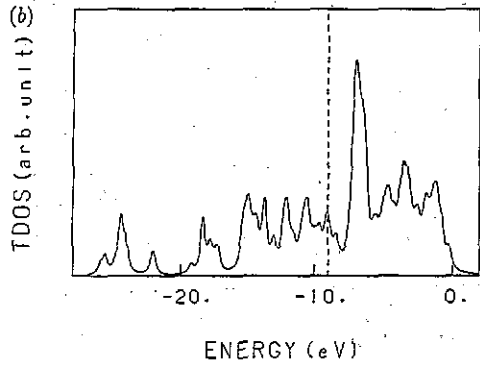
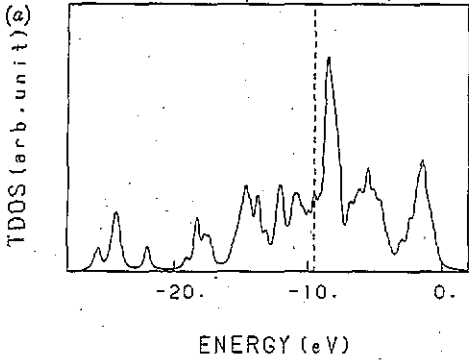


Figure 6. Total density of states (TDOS) for (a) $\text{Ti}_{18}\text{C}_{29}$, (b) $\text{Zr}_{18}\text{C}_{29}$ and (c) $\text{V}_{18}\text{C}_{29}$, which have the triple-cage cluster structure as shown in figure 1(c).

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