Structure stability and magnetic properties of Os_nB ($n = 11\text{--}20$) clusters[†]

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Abstract. The structure and magnetic properties of Os_nB ($n = 11\text{--}20$) clusters have been systematically investigated by using density functional theory within the generalized gradient approximation (GGA). For each size, the average binding energy per atom, the second-order differences of total energies, the dissociation energies and the formation energies are calculated to analyse the stability of clusters. Os_{12}B , Os_{15}B , Os_{17}B and Os_{19}B clusters are found to be more stable than other clusters. The B atom has little influence on Os_nB cluster stability. d electrons exhibit locality compared to s and p electrons in most cases. Os_{14}B cluster has the strongest magnetism among all the clusters, and the local magnetic moment of B atom does little effect to the total magnetic moment.

Keywords. Os_nB ($n = 11\text{--}20$) clusters; structure stability; magnetic property.

1. Introduction

Recently, much attention has been paid to study the atomic clusters, especially the doped clusters in theory and experiment, because the doped clusters exhibit special properties that are different from the pure clusters. When different atoms are doped into sufficiently large pure transition metal clusters, the hybrid system will exhibit different behaviours with regard to size selectivity, charge transfer, density of states and the highest-occupied molecular orbital and lowest-unoccupied molecular orbital, while it is just only those properties that may lead to novel properties and new materials, which is very important for developing cluster-based materials and technologies.^{1–8} The bulk modulus of osmium is very close to that of diamond; however, its hardness is much lower than that of diamond, because osmium has metallic bonding. Hence, some researchers studied the metallic–metalloid bonds, and they found that the hardness of some osmium borides, carbides and nitrides are very high.^{9–12}

There have been a number of first-principles calculations on mixing C, N, B, O and other light elements into osmium in theory. Gou *et al.*¹³ used first-principles calculations to investigate the structural, stable and electronic properties of OsB_2 and OsB clusters, respectively. They found that OsB in tungsten carbide phase is more stable than that in the metastable cesium chloride phase under ambient condition. On the basis

of semiempirical theory, they found that OsB_2 is an ultra-incompressible material, but not a superhard material. Yang *et al.*¹⁴ reported first-principles calculations of ideal tensile and shear strength for the recently synthesized orthorhombic OsB_2 , which is a primary example of a new class of ultra-hard materials synthesized by combining the element that can form covalent bond and is small, light with large, electron-rich transition metals. The result showed that the shear strength on the (001) plane is highly anisotropic with a low peak stress of 9.1 GPa in the (001) [010] shear direction, but a much higher peak stress of 26.9 GPa in the (001) [100] direction. These results highlight the importance of understanding atomistic deformation modes under various conditions in designing new ultra-hard materials. Ren *et al.*¹⁵ performed first-principles calculations to study the possibility of the phase transition of OsB_2 . The analysis of enthalpy showed that orthorhombic OsB_2 can transfer to the hexagonal phase at 10.8 GPa and this phase transition pressure is little affected by the thermal effect. The phonon dispersion curves showed that OsB_2 cluster in the hexagonal $P6_3/mmc$ structure (high-pressure phase) is more stable. Zheng¹⁶ calculated Os, OsC and OsN clusters by using first-principles calculations, and their results confirmed that Os, OsC and OsN in the hexagonal structures are more stable than those under the structure of sodium chloride, they also predicted that hexagonal structure of osmium carbide had the potential to be superhard materials.

In order to find some particular properties of doping Os clusters, our research group have studied the Os_n ($n = 11\text{--}22$) clusters, $(\text{Os}_n\text{N})^{0,\pm}$ ($n = 1\text{--}6$) and $(\text{OsB})_n$ ($n = 1\text{--}6$)

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clusters by the density functional theory (DFT).^{17–19} However, there is hardly any research about Os_nB ($n = 11–20$) clusters. In this paper, based on the research of Os_n ($n = 11–22$) clusters, we performed first-principles calculations to investigate the structure, stability, electronic property and magnetic property of Os_nB ($n = 11–20$) clusters.

2. Theoretical methods

The structure and magnetic properties of Os_nB ($n = 11–20$) clusters were computed using DFT semicore pseudopotentials in the DMOL3 package. In the electronic structure

calculations, a relativistic semicore pseudopotential (DSPP) and double numerical basis set that includes d-polarization functions (DND) were chosen. The exchange–correlation interaction was treated within the generalized approximation (GGA) using PW91 functional. Self-consistent field (SCF) calculation was done with a convergence criterion of 10^{-5} Hartree. The direct inversion in an iterative subspace (DIIS) approach was used to speed up the SCF convergence. In the structure optimization we consider the smearing, and the smearing of molecular orbital occupation is 0.002 Hartree. In the geometry optimization, converge thresholds were set to 0.0004 Hartree $\text{\AA}^{-1}$ for the forces, 0.005 $\text{\AA}$ for the displacement and 10^{-5} Hartree for the energy change. We designed

Figure 1. The lowest energy structures of Os_nB ($n = 11–20$) clusters.

different initial configuration, started with the lowest spin multiplicity for Os_nB ($n = 11-20$) cluster, by adding B atom in the Os_n cluster or replacing one Os atom from Os_{n+1} cluster, and then spin-unrestricted calculations were performed to find the stable structure with the positive frequency, and then we calculated some relative properties of ground-state structure.

To verify the effectiveness of the proposed method, we calculated the dimer Os_2 and got the bond length to be 2.215 Å, which is very close to the experimental value (2.28 Å).²⁰

3. Results and discussion

3.1 Structures and stabilities

Using the computational scheme described in Section 2, we have explored a number of low lying isomers to make sure to find the lowest energy structures of Os_nB clusters ($n = 11-20$). The obtained lowest energy structures (na) and the isomers (nb) with a slightly higher energy are shown in figure 1. The spin multiplicities, symmetry and the energy of the lowest energy structures are also labelled below the structural plot of figure 1.

For the purpose of comparison, we investigated the Os_n clusters¹⁷ from $n = 11$ to 22 by using the spin-unrestricted DFT as described in Section 2. The lowest energy structures of Os_n ($n = 11-22$) clusters are shown in figure 2 in the study by Zhang *et al.*¹⁷

As shown in figure 1, the lowest energy structures of $Os_{11}B$ and $Os_{12}B$ clusters are based on the trigonal prism, which is the lowest energy structure of Os_{12} cluster. Compared with the lowest energy structure of Os_{12} cluster, the

B atom in $Os_{11}B$ cluster replaces one Os atom in the edge of Os_{12} cluster and the symmetry decreased because the acting force of Os-B and Os-Os is different. The average Os-B bond length of $Os_{11}B$ cluster is 2.31 Å. The lowest energy structure of $Os_{12}B$ cluster is much different from that of Os_{13} cluster, because the lowest energy structure of Os_{13} cluster is based on regular hexagonal prism. The $Os_{12}B$ and $Os_{11}B$ clusters have the same symmetry (C_s). Similar to the structure of $Os_{11}B$ cluster, the lowest energy structure of $Os_{13}B$ is based on the lowest energy structure of Os_{14} cluster (one Os atom in the corner is replaced by B atom). Based on the Os_{15} cluster, we replaced the Os atom outside of the regular hexagonal prism with B atom and found that it is the lowest energy structure of $Os_{14}B$ cluster, and found that the Os-B bond length is shorter than Os-Os (the average Os-B length is 2.09 Å), because the Os-B is polar bond and the interaction force between the two atoms is stronger. Compared with the structure of Os_{16} cluster, the $Os_{15}B$ is a little different, B atom is much more close to the major functional group than the previous Os atom, but they have the same symmetry C_s . By adding one atom on the opposite of the ground-state structure of Os_{16} cluster, we can get the lowest energy structure of $Os_{16}B$ cluster, just the same as Os_{17} cluster. It has the smallest average Os-B bond length (2.049 Å). Based on the structure of Os_{18} cluster, we replaced the Os atom in the corner of the pure cluster with B atom, which turns out to be the lowest energy structure of $Os_{17}B$ cluster. Because of the existence of polar bond, the symmetry of $Os_{17}B$ cluster is just C_s . The average Os-B bond length of Os_nB is just around 2.10 Å when $n = 12-17$. From $Os_{18}B$ to $Os_{20}B$ clusters, the lowest energy structures are just the copy of Os_{19} , Os_{20} , Os_{21} clusters, except some change in the bond length. All had same

Figure 2. The lowest energy structures of Os_n ($n = 11-22$) clusters.

symmetry C_s . The average Os-B bond length of these clusters was above 2.20 Å. From the total energy, we found that the total energy of Os_nB cluster is just a little lower than Os_n cluster, but it is much lower than that of Os_{n+1} cluster.

Based on the lowest energy structures, the size-dependent physical properties of these clusters are discussed to analyse the stability in the following. The binding energy per atom (E_b per atom), the second-order energy differences ($\Delta_2 E(n)$), the dissociation energies (E_d) and the formation energies (E_f) are plotted in figures 3–6, respectively.

The average binding energies per atom, the second-order differences and the dissociation energies can be obtained using the following formulas:

$$E_b(Os_n) = [nE(Os) - E(Os_n)]/n$$

$$E_b(Os_nB) = [nE(Os) + E(B) - E(Os_nB)]/(n+1)$$

Figure 3. Average binding energies (E_b /atom) of Os_n and Os_nB clusters as a function of cluster size.

Figure 4. The second-order differences $\Delta_2 E(n)$ of Os_nB cluster energies as a function of the cluster size n .

$$\Delta_2 E(Os_nB) = E(Os_{n+1}B) + E(Os_{n-1}B) - 2E(Os_nB)$$

$$E_d = E(Os_{n-1}B) + E(Os) - E(Os_nB),$$

where $E(Os)$ and $E(B)$ represent the energy of isolated Os and B atoms, $E(Os_n)$, $E(Os_nB)$, $E(Os_{n+1}B)$ and $E(Os_{n-1}B)$ represent the total energies of the most stable structure of Os_n , Os_nB , $Os_{n+1}B$ and $Os_{n-1}B$ clusters, respectively.

From figure 3, it can be seen that there is obvious odd-even oscillation in the curve of the average binding energies of Os_n clusters. For $n = 12, 14, 16$ and 18 , the clusters possess higher stabilities than their adjacent clusters. However, there was no odd-even oscillation in the average binding energy curve of Os_nB clusters. The values generally increase with cluster size n increasing (except $n = 18$), and there are two slight lifts corresponding to $n = 12, 15$ as well as two prominent peaks corresponding to $n = 17, 19$, indicating that these clusters are more stable than their neighbouring clusters. From figure 3, we can find that $n = 19$ is the

Figure 5. The dissociation energies (E_d) of Os_nB clusters as a function of cluster size.

Figure 6. Size dependence of the formation energies (E_f) for the lowest energy structures of Os_nB clusters.

Figure 7. The partial density of states (PDOS) of s, p and d orbital and total density of states (TDOS) of Os_nB clusters with size of $n = 11$ –14. The vertical line indicates the Fermi level.

Figure 8. The partial density of states (PDOS) of s, p and d orbital and total density of states (TDOS) of Os_nB clusters with size of $n = 15\text{--}18$. The vertical line indicates the Fermi level.

turning point of binding energy variation trend of Os_n clusters, while for Os_nB clusters the value turned to be $n = 18$. When $n = 11$ – 17 , most of the Os_nB clusters are close-packed hexagonal structures (especially when $n = 13$ – 17). However, for Os_{18}B , Os_{19}B and Os_{20}B clusters, the cage-like geometries are more stable than others. This conclusion is consistent with the Os_n cluster variation trend in the study by Zhang *et al.*¹⁷ From figure 3, we can easily find that the average binding energies of B-doped osmium clusters are larger than those of the pure osmium clusters with the same size. This indicates that the doping of B atom would increase the stability of osmium clusters.

In order to further study the stability of Os_nB clusters, we calculated the second-order difference of cluster energies and the dissociation energies, because they are sensitive quantities to reflect the relative stability of clusters, and potted them in figures 4 and 5, respectively. In figure 4, maxima are found at $n = 12, 15, 17$ and 19 , indicating that these clusters possess stronger stabilities relative to their neighbours. This is consistent with the previous analysis of binding energies. The curve of dissociation energies (E_d) of Os_nB clusters is potted in figure 5, and we found that the variation trend is

almost the same with the second-order difference. Four major prominent peaks are found at $n = 12, 15, 17$ and 19 . The conclusion that Os_{12}B , Os_{15}B , Os_{17}B and Os_{19}B possess better stabilities than their neighbours has been confirmed once again. However, from the study by Zhang *et al.*¹⁷ we know that when $n = 12, 14, 16$ and 18 , the Os_n clusters have relatively high stabilities. This means when B atom replaces one Os atom in pure Os clusters, the stabilities variation trend will be changed more or less.

In the last part of the stability analysis, we calculated the formation energies (E_f) to testify the correctness of the conclusion expound before. The formation energies (E_f) are defined as $E_f(n) = E_b(\text{Os}_{n+1}\text{B}) - E_b(\text{Os}_n\text{B})$, where $E_b(\text{Os}_n\text{B})$ is the binding energy of Os_nB clusters system ($E_b(\text{Os}_n\text{B}) = nE(\text{Os}) + E(\text{B}) - E(\text{Os}_n\text{B})$). The quantity is depicted in figure 6. From the equation of $E_f(n)$, one can easily find that the high formation energies of cluster with size n correspond to the high stability of clusters with size $n + 1$.²¹ Four major prominent peaks are found at $n = 11, 14, 16$ and 18 , this shows that these clusters have relative high formation energies with the corresponding sizes. In other words, the Os_{12}B , Os_{15}B , Os_{17}B and Os_{19}B clusters have

Figure 9. The partial density of states (PDOS) of s, p and d orbital and total density of states (TDOS) of Os_nB clusters with size of $n = 19$ – 20 . The vertical line indicates the Fermi level.

relatively higher stabilities than other clusters, this also confirms that the previous conclusion is correct.

3.2 Electronic and magnetic properties

In order to study the electronic properties of Os_nB clusters, we analysed the partial density of states (PDOS) and total density of states (TDOS) for the lowest energy structures, and the curves are displayed in figures 7–9.

Spin alpha (up) and spin beta (down) densities are given in each figure (figures 7–9), and the vertical line at zero indicates the Fermi level. In all the clusters, all of the d curves of d electrons are narrow and sharp, this indicates that d electrons are relatively localized. From the figures we can first find that the TDOS is dominant from the contributions of d electrons in the range of -7 to 2 eV, but in the range of -7 to 10 eV the effect of s and p states cannot be neglected, and in this range there exists a one-to-one correspondence in the peaks of all orbitals. Hence they may have s–p–d hybridization. When $n = 12$ – 14 , 18 – 19 , the DOS curves are asymmetrical. This illustrates that there are unpaired electrons around the atom. According to spin multiplicities given in figure 1, we find the spin multiplicities of all lowest energy structures are not 1 and higher than others, this also proved that there exists unpaired electrons around the atom. The others have very high symmetry and their multiplicities are all 2, this means they have less unpaired electrons around the atom. For all clusters, the density of states of electrons at the Fermi level is not zero, this implies that Os_nB clusters possess metal characteristics. As we all know, if the density of states between the two peaks on each side of Fermi level is nonzero, then we can reckon that there is pseudogap in the system. The pseudogap is a direct reflection of the strength of the covalent of the corresponding system. The wider the pseudogap is, the stronger covalent the two atoms bonding

will be. Maybe there is mixed metallic-covalent bonding in the clusters because of the doping of B atom. From figures 7–9, we can find that the pseudogap of Os_{12}B , Os_{15}B and Os_{17}B clusters are wider than the others, indicating that these clusters have stronger covalent bonds and stability, which is consistent with the previous analysis.

In order to describe the magnetic properties of the Os_nB clusters, we analysed both total and average magnetic moments of Os_nB (shown in figure 10). Local magnetic moment of B atom and the electron spin density of Os_nB clusters are provided in figures 11 and 12, respectively.

Based on the optimized geometries, we calculated the magnetic moment (including total and average). In figure 10, Os_{14}B cluster has the highest total ($5.00 \mu_B$) and average ($0.33 \mu_B$) magnetic moment among all the clusters. When $n = 11, 15, 16, 17$ and 20 , the Os_nB clusters have relatively low total magnetic moment, indicating that they have smaller magnetism; however their average magnetic moment approaches to zero, that is, the value is just around $0.05 \mu_B$. This means their ability for the electron magnetic moment to combine with the orbital magnetic moment is very weak. Os_{16}B cluster has very high symmetry and very low magnetism, this may be caused by the electron transfer differences, adds or replaces of an atom in the different place of different structure, and large difference in electron transfer.

In order to further study the contribution of B atom to the magnetic moment, we also calculated the local magnetic moment of B atom. When local magnetic moment is positive, it will promote the total magnetic moment. On the other hand, it will reduce the total magnetic moment. We can find that when $n = 12$ the promoting effect is the best. However, compared to the total magnetic moment we can find that the value is very small, which can even be neglected. So we can say that the local magnetic moments of B atom have a little effect on the total magnetic moment.

To describe the local magnetic moment of each atom and their contribution to the total magnetic moment intuitively, we depicted the electron spin density map of Os_nB clusters.

Figure 10. Size dependence of average and total magnetic moments of Os_nB clusters for the lowest energy structure.

Figure 11. The local magnetic moment of B atom in Os_nB clusters for the lowest energy structure.

Figure 12. Electron spin density map of Os_nB ($n = 11-20$) clusters at the ground state.

In the map, the blue one represents the contribution from spin-up electron states, and the yellow one stands for the contribution from spin-down electron states. As we know, the bigger the electron spin density of clusters they have, the more unpaired electrons around the atom and the bigger magnetic moment there will be. Otherwise, their contribution to the total magnetic moment will be smaller. From the map we can find that the Os_nB clusters have bigger electron spin density when $n = 12-14$. This means they have relatively big magnetic moment that is very consistent with the conclusion mentioned in the analysis of magnetic moment before. Also, there is hardly any electron spin density around the B atom, just a little in the $Os_{12}B$ cluster. This phenomenon indicates that the contribution to total magnetic moment from B atom can be ignored. From $Os_{11}B$ to $Os_{20}B$ clusters, most of the electron is spin up and focus around the Os atom, which is connected with the B atom. This also means there are many unpaired electrons around the Os atom which is connected with the B atom.

4. Conclusion

By using first-principles DFT-GGA calculations, the geometries, stabilities, electronic and magnetic properties of Os_nB ($n = 11-20$) clusters have been systematically studied. The results are summarized as follows:

- (1) For each cluster size, an extensive search of the lowest energy structure has been conducted by considering a number of structure isomers. In the lowest energy structures of Os_nB clusters, $Os_{12}B$, $Os_{15}B$, $Os_{17}B$ and

$Os_{19}B$ clusters are found to have relatively higher stabilities and the doping of B atom would increase the stability of osmium clusters.

- (2) The density of states, magnetic moment and electron spin density of the lowest energy structures of Os_nB clusters are discussed. The DOS is dominant from the contributions of d electrons, and $Os_{12}B$, $Os_{15}B$ and $Os_{17}B$ clusters have wider pseudogap than the others, $Os_{14}B$ cluster has the strongest magnetism among all the clusters, and the local magnetic moment of B atom does little effect on the total magnetic moment.

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