

# Superconducting properties of Zinc Diboride Nanoclusters

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Cite this article: J. Sci. Res. Adv. Vol. 2, No. 1, 2015, 48-50.

ISSN 2395-0226



Structural, vibrational and superconducting properties of Zinc diboride clusters  $[(ZnB_2)_x]$  for  $x = 1, 2,$  and  $3,$  are calculated to investigate the changes by Density functional theory with the B3LYP exchange-correlation functional using LANL2DZ as the basis set. In the first step, geometrical optimization of the nanoclusters has been carried out then remaining calculations have been done. For comparison, boron clusters  $[B_x]$  for  $x = 2, 4,$  and  $6]$  were also considered. The  $ZnB_2$  and  $(ZnB_2)_2$  showed equilibrium structures with the boron atoms in arrangements similar to what was obtained for pure boron atoms, whereas, for  $(ZnB_2)_3,$  a different arrangement of boron was obtained. From the NBO analysis, it is shown that larger electronic density in a specific plane increases the superconductivity behavior of this material, then it can be expected that these clusters should exhibit a similar super conducting behavior.

## Introduction

Materials composed of diborides have attracted the attention of researchers in recent years because of its superconductivity properties [1, 2]. In particular, it has been found that  $MgB_2$  behaves as a superconductor at relatively high critical temperature,  $T_c = 40$  K. Although  $T_c$  for this material is not as high as other oxides with super conducting properties, its preparation is less expensive and it has a lower anisotropy, making smoother grain boundaries and hence increasing current flow [3]. Non-oxide ceramics, such as carbides, nitrides and borides represent one of the fastest growing classes of new advanced materials to be considered and pursued by today's industries. The economic and technological significance of using these ceramics to improve present material structures and designs is now well documented. Transition metals ceramic diborides, such as titanium, hafnium and zirconium diborides, are members of a family of materials with extremely high melting temperatures, high thermal and electrical conductivity, excellent thermal shock resistance, high hardness and chemical inertness. These compounds, also referred to as Ultra High Temperature Ceramics (UHTCs), constitute a class of promising materials for use in high performance applications, where high temperatures, high thermal fluxes, severe surface stresses are involved. These conditions are met in the design of sharp edges on re-entry vehicles, thermal insulations in combustion chambers, special inserts in advanced brakes, cutting tools and plasma arc electrodes [4]. The lowest energy equilibrium structure was obtained and corroborated with a harmonic vibrational analysis. Natural orbital analysis was performed in order to characterize the electron density of the system. Boron clusters were also considered for comparison purposes with the results obtained being in agreement with recent studies [5].

## Computational Methods

The theoretical methods used in this study were based on ab-initio methods within the density functional theory [6]

approximation using the three-parameter hybrid functional B3LYP/LANL2DZ [7, 8] as the basis set. The standard LanL2DZ basis as effective core potential with no symmetry constraint is employed here. This basis set provides an effective way to solve two-electron integrals even in case of heavy elements. The previous calculations [9-12] revealed that LanL2DZ basis sets of the effective core potential theory were proven to be reliable for the geometries, stabilities, and electronic properties of  $SnTM$  ( $TM =$  transition metals) clusters. For all systems, a full geometry optimization was performed and various initial geometries were used to guarantee the determination of the lowest energy equilibrium structure. Harmonic vibrational analysis was performed for each system not only to obtain the vibrational frequencies, but also to characterize the nature of the structure obtained in the potential energy surface (PES). All calculations were performed using the Gaussian 09 software package [13]. In order to analyze the charge distribution in the system, natural bond orbital (NBO) analysis was performed on the optimized wave function using the NBO program of the Gaussian 09 package. This analysis provides an improvement to the Mulliken population analysis usually used in the description of the charge distribution.

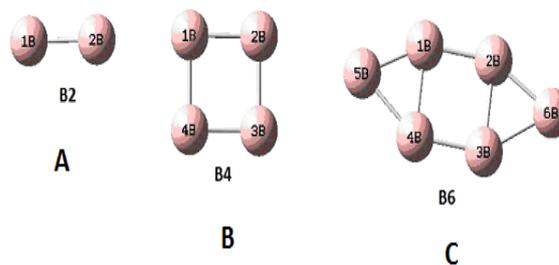


Fig. 1. Optimized structure of boron clusters.

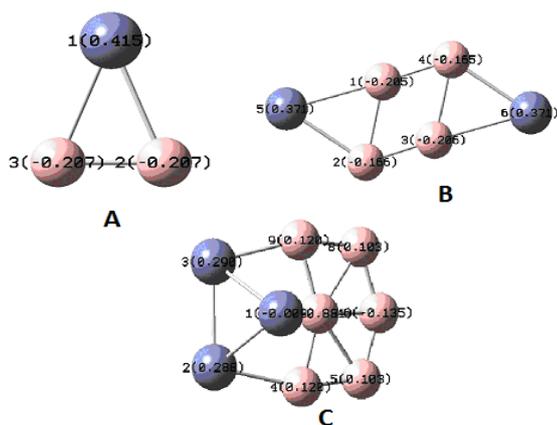


Fig. 2. Optimized structure of zinc diboride clusters.

## 5 Results and Discussion

The equilibrium bond lengths of all the optimized structures are presented in Table 1 and the structures are shown in Figures 1 and 2. Table 2 shows the harmonic vibrational spectrum of ZnB2 and B2 and it can be observed that all frequencies obtained have a positive sign, which means that the global minimum was obtained.

In the case of ZnB2, the frequency that corresponds to the diboride stretching vibration, frequency, is higher than in the B2 molecule because the bond shortening. Figures 1(B) and 2(B) show the lowest energy for equilibrium structure of B4 and (ZnB2)2, respectively. Both structures show a planar arrangement of atoms, with the boron atoms in a two-dimensional unsymmetrical rhombic arrangement for (ZnB2)2 and a perfect square for B4. Specifically, two of the boron-boron bonds in (ZnB2)2, the molecular species do not change and the other two were stretched by 0.04 Å.

Table 1. Optimized bond lengths in angstrom.

ZnB2	(ZnB2) <sub>2</sub>	(ZnB2) <sub>3</sub>	B <sub>2</sub>	B <sub>4</sub>	B <sub>6</sub>
R(1,2)=2.18	R(1,2)=1.81	R(1,2)= 2.32	R (1-2)=1.68	R (1-2)= 1.56	R (1-2)=1.60
R(1,3)= 2.18	R(1,4)= 1.60	R(1,3)= 2.32		R (1-4)= 1.56	R (1-5)=1.60
R(2,3)= 1.59	R(1,5)= 2.23	R(1,7)= 2.49		R (2-3)= 1.56	R (2-6)=1.60
	R(2,3)= 1.60	R(2,3)= 2.15		R (3-4)= 1.56	R (4-6)=1.60
	R(2,5)= 2.12	R(2,4)= 1.98			R (3-4)=1.60
	R(3,4)= 1.81	R(2,7)= 2.59			R (3-5)=1.60
	R(3,6)= 2.23	R(3,7)= 2.58			
	R(4,6)= 2.12	R(3,9)= 1.98			
		R(4,5)= 1.50			
		R(4,7)= 1.55			
		R(5,6)= 1.42			
		R(5,7)= 1.73			
		R(6,7)= 1.52			
		R(6,8)= 1.42			
		R(7,8)= 1.73			
		R(7,9)= 1.55			
		R(8,9)= 1.50			

The zinc atoms were accommodated at a relatively long distance when compared to the separation of the boron atoms. The vibrational frequency analysis shown in Table 2 demonstrates that the structure is a minimum in the PES. A direct comparison between the modes in the molecular species and the pure boron clusters was not possible. Figure 2(B) shows the NBO density analysis for the dimer and it can be observed that all the boron atoms forming the 2D rhombic arrangement have a negative charge. The boron atoms, which are closer to the Zn atoms, showed larger value of electron density than the other atoms, which has the zinc at a larger distance. Hence, the electron density is being concentrated on the boron atoms in a nonsymmetrical fashion and is being donated by the Zn atoms. Figures 1(C) and 2(C) show the lowest energy equilibrium structure of B6 and (ZnB2)3. Boron atoms form a nonsymmetrical nonplanar arrangement. Although the B6 do not show a planar structure, the arrangement of atoms is different to the one obtained in the molecular species. The vibrational analysis shows all positive frequencies and similar to the previous system, it is not possible to correlate the frequencies between the

B6 and the molecular system. The NBO analysis for the molecular systems shows a similar electronic distribution to the one observed for the dimer, namely, the electronic distribution is located on the boron atoms. Two of the boron atoms show a larger electronic distribution (-0.881) because of their closeness to the Zn atoms.

## Conclusion

In all cases considered, the lowest energy equilibrium structure for ZnB<sub>2</sub> clusters showed an arrangement of boron atoms that are two-dimensional or quasi-two dimensional. The electron densities concentrated on the boron atoms and hence the zinc atoms are acting as electronic donating species. The larger electronic density in a specific plane increases the superconductivity behavior of this material, then it can be expected that these clusters should exhibit a similar super conducting behavior.

## Acknowledgement

The corresponding author (Abhishek Kumar Bajpai) is thankful

to University Grants Commissions, New Delhi for its financial assistance.

**Table 2.** Vibrational frequencies of stable structures

ZnB <sub>2</sub>	(ZnB <sub>2</sub> ) <sub>2</sub>	(ZnB <sub>2</sub> ) <sub>3</sub>	B <sub>2</sub>	B <sub>4</sub>	B <sub>6</sub>
354	58	30	913	234	123
375	87	62		320	134
1076	105	94		1015	336
	238	126		1162	431
	304	152		1182	475
	320	183		1212	489
	352	245			663
	452	259			802
	467	283			1009
	838	320			1019
	1042	329			1304
	1093	486			1353
		496			
		544			
		572			
		883			
		899			
		1194			
		1233			
		1257			
		1465			

## 5 Notes and References

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