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VB₂ and ZrB₂: a density functional study

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Abstract

Structural, mechanical and elastic behaviour, density of states, electronic charge density and band structure of VB₂ and ZrB₂ are studied by the *ab initio* density functional method. The calculations carried out using the gradient-corrected approximation of the density functional theory are in excellent agreement with the experimental results where available. The five independent elastic constants have been calculated for the first time for VB₂ and ZrB₂. The elastic behaviour of these compounds is compared with the measured values for ZrB₂ and TiB₂. The origin of the pseudogap in the total density of states, a common feature of the compounds, is interactions between boron p states. The analyses of calculated density of states and band structure do not indicate superconductivity in the compounds.

1. Introduction

The discovery of superconductivity in MgB₂ at $T_c \sim 40$ K in the simple AlB₂-type structure [1] has aroused renewed interest in finding superconductivity in other material diborides. A recent review [2] shows that diborides of transition metals MB₂ (M = Ti, Zr, V, Cr, Mo) are not superconducting so far with the exception of NbB₂. Since then, contradictory reports about superconductivity of ZrB₂ have appeared. The study of Gasparov *et al* [3] of the temperature dependence of resistivity and ac susceptibility reveals a superconducting transition of ZrB₂ with $T_c = 5.5$ K. Pereira *et al* [4] studied experimentally the pressure behaviour of VB₂ and ZrB₂, which shows no obvious phase transition up to a pressure of 50 GPa. Naidyuk *et al* [5] investigated electron–phonon interaction (EPI) in ZrB₂ by point-contact spectroscopy. The estimated value of $\lambda \leq 0.1$ raised questions about the reported bulk superconductivity in this compound. Fermi surfaces presented by Shein and Ivanovskii [6] and those by Rosner *et al* [7] are quite different. Further DOS values at Fermi level reported by these workers [6, 7] also differ considerably. The origin of the difference is unclear; the full potential linear muffin-tin orbital method used by Shein and Ivanovskii [6] is expected to yield similar results to those in [7]. Vajeeston *et al* [8] tried to explain the bonding nature with DOS and charge density plots. Singh [9] made a theoretical study of EPI in ZrB₂ and TaB₂. The LMTO calculations were performed with the generalized gradient approximation for exchange correlation. Although

the results indicated a $T_c \sim 12$ K for TaB₂ the study did not indicate superconductivity for ZrB₂ at equilibrium volume.

In view of the contradictory reports about a possible superconducting transition in ZrB₂, the system still warrants study in all possible directions. We include VB₂ along with ZrB₂ to investigate their various properties using an *ab initio* method. Although near the end of our present investigations we became aware of an experimental study on the elastic coefficients of ZrB₂ there are no data available for VB₂. The proposed study should be helpful in view of the potential use of these diborides for high performance applications. For example, ZrB₂ is in practical use as a refractory crucible and sheath in steel making industries (see [10]). Further, it is being considered for use (i) as substrate for heteroepitaxial growth of GaN in the form of single crystals because of small lattice mismatch and (ii) in thermal protection systems of hypersonic vehicles in the form of composites reinforced with C and SiC.

The purpose of the present study is to provide, among other things, reliable theoretical information on elastic and other properties to help fill the gap in the literature. After we completed this paper we became aware of the elastic constants of a single crystal of ZrB₂ by Okamoto *et al* [10]. We also include these results in our discussions.

2. Computational method

Calculations were carried out using the CRYSTAL98 package [11], which is essentially a Hartree–Fock program. We used it with an added option, namely, the DFT functionals. The electron–electron interaction was treated within the local density approximation (LDA) with the exchange–correlation functional [12, 13]. In the case of VB₂, the basis sets used are 6-21G* and that of [14] for B and V, respectively. On the other hand, for ZrB₂ the basis sets are the valence electron basis sets Durand [15] and ECP HAYWSC [16] for B and Zr, respectively. Other details of Brillouin zone integration and accuracy are given elsewhere [17] and hence will be omitted here.

3. Results and discussions

3.1. Structural properties and pressure effects

First-principles calculations of the total energy E of VB₂ and ZrB₂ are the basis for the determination of the equation of state (EOS). The energy was calculated as a function of unit cell volume V . It was then minimized as a function of the c/a ratio for the selected volume. The calculated values of $\Delta E (=E - E_0, E_0 = \text{minimum energy})$ for VB₂ and ZrB₂ have been plotted as a function of volume in figures 1(a) and (b). The insets show c/a ratio versus V .

The pressure dependence of lattice parameters of the two compounds is shown in figure 2. The structural parameters are summarized in table 1, along with some recent results. The calculated equilibrium volumes of VB₂ and ZrB₂ are 1.02% and 1.23% larger than the relevant volumes measured at room temperature. The pressure dependence of the lattice parameters is smooth and does not show any structural phase transition in the pressure range up to ~ 45 GPa. The variation of the lattice parameters with pressure clearly shows the isotropy in bonding of both the compounds.

3.2. Bonding and elastic properties

3.2.1. Bulk moduli and pressure derivative. The zero-pressure bulk modulus B_0 and its pressure dependence $B'_0 (=dB_0/dP)$ are determined by fitting the $E(V)$ curve by the

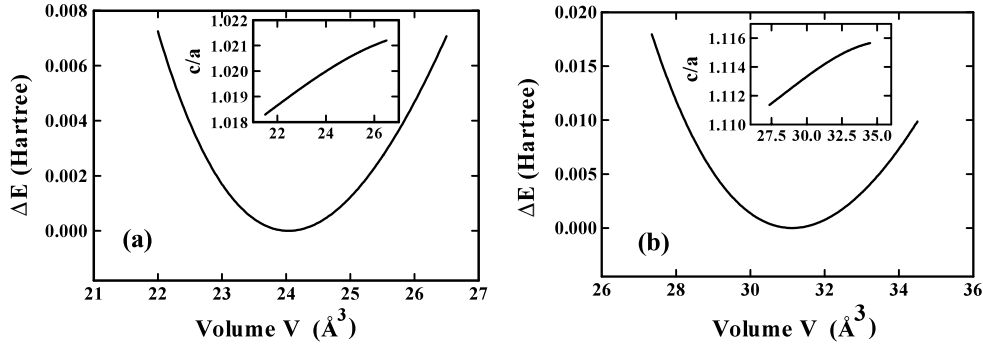


Figure 1. The energy ΔE as a function of the primitive-cell volume of (a) VB₂ and (b) ZrB₂. The solid curve is the resulting fit of the Murnaghan equation of state. Inset: c/a ratio versus V .

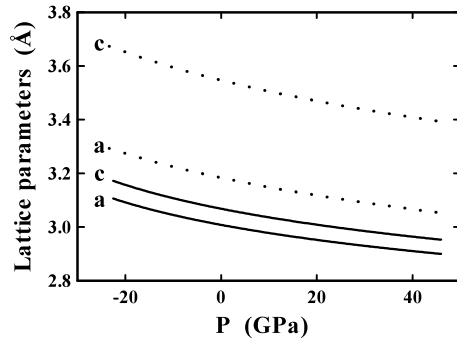


Figure 2. The pressure dependence of the lattice parameters of VB₂ (solid curves) and ZrB₂ (dotted curves).

Table 1. Structural parameters of VB₂ and ZrB₂ at equilibrium. M–X and X–X (M ≡ V, Zr; X ≡ B) refer to bond lengths.

	Method	a (Å)	c (Å)	c/a	V (Å ³)	M–X	X–X	Ref.
VB ₂	LCAO-DFT	3.0079	3.0681	1.02	24.04	2.317	1.7366	This work
	TB-LMTO	2.983	3.047	1.021	23.48	2.297	1.722	[8]
	FP-LMTO	3.0068	3.0477	1.014	23.86	—	—	[6]
	Expt	2.997	3.056	1.020	23.77	—	—	[6]
ZrB ₂	LCAO-DFT	3.1832	3.5464	1.114	31.12	2.554	1.8378	This work
	TB-LMTO	3.197	3.561	1.114	31.52	2.564	1.846	[8]
	FP-LMTO	3.1693	3.5313	1.114	30.72	—	—	[6]
	Expt	3.170	3.532	1.114	30.74	—	—	[3]
	Expt	3.165	3.547	1.120	30.77	—	—	[18]

Murnaghan equation of state [19]:

$$E(V) = E_0 + B_0 V_0 \left[\frac{V_n}{B'_0} + \frac{1}{1 - B'_0} + \frac{V_n^{1-B'_0}}{B'_0(B'_0 - 1)} \right]. \quad (1)$$

This equation (with the equilibrium energy E_0) provides the static equilibrium volume V_0 as well as the bulk modulus B_0 and its pressure derivative B'_0 at zero pressure.

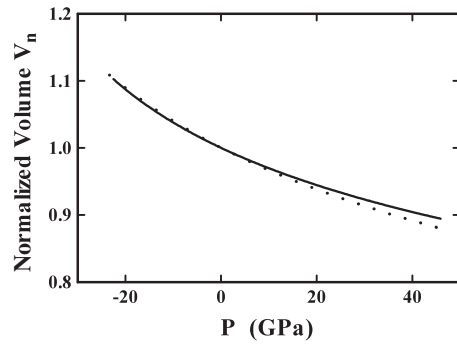


Figure 3. Normalized volume versus pressure of VB₂ (solid curve) and ZrB₂ (dotted curve).

Table 2. Bulk modulus, pressure derivative of bulk modulus and their in- and out-of-plane linear values for VB₂ and ZrB₂.

Comp.	Method	B_0 (GPa)	B'_0	B_{a0} (GPa)	B'_{a0}	B_{c0} (GPa)	B'_{c0}	Ref.
VB ₂	LCAO-DFT	298	5.49	907	16.8	870.5	15.85	This work
		297	4.0 ^a	—	—	—	—	This work
	TB-LMTO	175	1.67	—	—	—	—	[8]
	Expt	322 ± 7	4.0 ^a	1344 ± 20	4.0 ^a	813 ± 10	4.0 ^a	[4]
ZrB ₂	LCAO-DFT	275.5	3.93	841	12.1	800	11.16	This work
		275.1	4.0 ^a	—	—	—	—	This work
	TB-LMTO	195	1.94	—	—	—	—	[8]
	Expt	317 ± 7	4.0 ^a	1143 ± 18	4.0 ^a	955 ± 17	4.0 ^a	[4]

^a Kept fixed during fitting.

The pressure versus volume curves of VB₂ and ZrB₂ are obtained via the thermodynamic relationship

$$P = -\frac{dE}{dV} = \frac{B_0}{B'_0} \left[V_n^{-B'_0} - 1 \right] \quad (2)$$

and are shown in figure 3. The details of these can be seen in [20]. The linear bulk modulus at $P = 0$ along the crystallographic axes a and c (B_{a0} and B_{c0}) and their pressure derivatives are then obtained from figure 2 and equation (2). Table 2 shows different moduli along with other results. Pereira *et al* [4] kept B'_0 fixed during fitting because the scatter of the experimental data prevented the use of B'_0 as a free fitting parameter. Comparison with the experimental values due to Pereira *et al* [4] shows that our obtained values are reasonably good.

3.2.2. Independent elastic constants. We shall consider only small lattice distortions in order to remain within the elastic limit of the crystal. The internal energy of a crystal under strain δ can be expanded in powers of the strain tensor with respect to the initial internal energy of the unstrained crystal. There are five independent components of the elasticity tensor for MB₂ ($M = V, Zr$), instead of three as in the cubic case. The energy of a strained system [21] can be expressed in terms of the elastic constants C_{ij} as

$$E(V, \delta) = E(V_0, 0) + V_0 \left[\sum_i \tau_i \xi_i \delta_i + \frac{1}{2} \sum_{ij} C_{ij} \delta_i \xi_i \delta_j \xi_j \right] \quad (3)$$

where $E(V_0, 0)$ is the energy of the unstrained system with volume V_0 . τ_i is an element in the stress tensor; ξ_i is a factor to take care of the Voigt index.

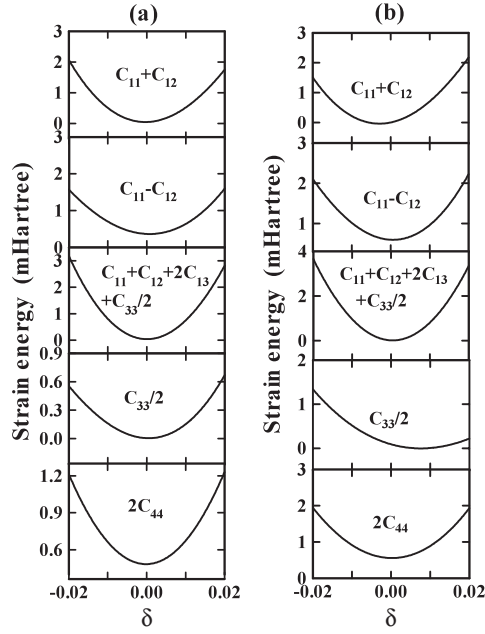


Figure 4. The dependence of the strain energy on the lattice deformation parameter δ of (a) VB₂ and (b) ZrB₂. Inset in each panel: specific combination of C_{ij} in the second-order term of the $E(\delta)$ expansion, from which the elastic constants are obtained (see the text).

With the five distinct lattice deformations, applicable for VB₂ and ZrB₂, we calculated the energy using the appropriate expressions [22]. The dependence of calculated strain energy, $[E(V, \delta) - E(V_0, \delta)]$ on δ is shown in figure 4. The coordinates of M and B atoms were not optimized each time the lattice was deformed. This should not affect the results for $C_{11} + C_{12}$ and C_{13} , as the site symmetries and the Bravais lattice remain unchanged in these cases. The maximum deformation was kept under $\pm 1\%$ of the equilibrium lattice parameters in order to reduce the influence of the higher order terms in the expansion of the strain energy. Third order polynomials were fitted to the data in figure 4, from which the five elastic constants of MB₂ (M = V, Zr) were calculated. It is to be noted here that the third order component of the fit affects the total energy by an amount which is less than an order of magnitude compared with the second order term. The results of the calculations are given in table 3. Experimental values of elastic constants are not yet available for comparison, except that of single-crystal ZrB₂ [10]. The room temperature experimental values of a similar type of material, TiB₂, due to Spoor *et al* [23] and theoretical calculations due to Milman and Warren [24] are also shown in table 3. It is observed that for ZrB₂ our calculated values are in good agreement with the measured values at room temperature. One should further note that the temperature dependence of the measured C_{ij} is weak.

The isotropic bulk modulus B_{iso} can be obtained under the assumption that the c/a ratio remains unchanged when the lattice is subjected to an isotropic stress, from [21]

$$B_{\text{iso}} = \frac{2}{9}(C_{11} + C_{12} + 2C_{13} + \frac{1}{2}C_{33}). \quad (4)$$

The set of calculated elastic constants gives $B_{\text{iso}} = 298$ and 272 GPa for VB₂ and ZrB₂, respectively. These may be compared with the bulk moduli obtained through the analysis of the data of energy versus primitive cell volume of MB₂. The fit yielded $B = 298$ and 276 GPa

Table 3. Elastic constants C_{ij} and bulk moduli B_{iso} of VB_2 and ZrB_2 compared to those of TiB_2 (in GPa).

Comp.	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	B_{iso}	A	B_{a0}	B_{c0}	Ref.
VB_2	699	146	109	552	167	298	1.27	999	706	This work
ZrB_2	596	48	169	482	240	272	1.24	809	828	This work
ZrB_2	568	57	121	436	248	—	1.30	—	—	[10] ^a
TiB_2	660	48	93	432	260	244	1.53	851	553	[23] ^a
TiB_2	656	66	98	461	259	250	1.42	—	—	[24]

^a Experimental data. B_{a0} and B_{c0} under TiB_2 are the derived values.

for the two compounds. Thus the values are in very good agreement with those obtained from our calculated elastic constants. We also estimated the zero-pressure bulk modulus B for a single crystal with hexagonal symmetry, when there is no constraint on the c/a dependence on lattice strain. The expression for this is [21, 25]

$$B = \frac{C_{33}(C_{11} + C_{12}) - 2C_{13}^2}{C_{11} + C_{12} - 4C_{13} + 2C_{33}}. \quad (5)$$

Using this equation our calculated data in table 3 yield $B = 292.6$ and 271.8 GPa for VB_2 and ZrB_2 , respectively. The isotropic bulk modulus B_{iso} for VB_2 is 1.7% (0.07% for ZrB_2) above the value obtained when there is relaxation of the c/a ratio (equation (5)). The corresponding value is $\sim 2.3\%$ for TiB_2 [23], indicating a somewhat larger anisotropy for this compound. The layered cuprates show much larger (a factor ~ 2) compression anisotropy [26].

One can also define the bulk modulus for a hexagonal crystal along the a - and c -axes

$$B_{a0} = \frac{2(C_{11} + C_{12}) + 4C_{13}\tau + C_{33}\tau^2}{2 + \tau}; \quad B_{c0} = \frac{B_{a0}}{\tau} \quad (6)$$

where

$$\tau = \frac{C_{11} + C_{12} - 2C_{13}}{C_{33} - C_{13}}.$$

Our calculated single-crystal elastic constants and equation (6) yield the values of B_{a0} and B_{c0} , which are shown in table 3. These values may be compared with the values shown in table 2 obtained using different methods. We note that for MB_2 ($M = \text{V}, \text{Zr}$) the basal plane in which the covalent B–B bonds lie has nearly equal compressibility with the out-of-plane compressibility. This can be compared with the value of MgB_2 . The interlayer linear compressibility $d \ln c / dP$ of MgB_2 is ~ 1.4 times larger than the in-plane value. It is to be noted that the structurally related alkali-metal intercalated graphite is strongly anisotropic with interlayer compressibility ~ 10 times larger than the corresponding value in MgB_2 [27].

We notice that the anisotropy factor A ($=C_{11}/C_{33}$) is 1.27 for VB_2 . The corresponding value for ZrB_2 is 1.24, which is in very good agreement with the observed value of 1.3 [10]. Although this anisotropy factor is by no means sufficient to confirm the anisotropy of the system, our results do indicate a smaller anisotropy than even TiB_2 (1.53).

The comparison between the isotropic and fully relaxed bulk moduli also suggests that MB_2 ($M = \text{V}, \text{Zr}$) is less anisotropic than one would think on the basis of its ‘planar’ crystal structure. The same observation was made earlier for TiB_2 [28], which was further corroborated by a study of the directional dependence of Young and bulk moduli. It is, therefore, likely that in MB_2 the interactions between B planes are also not negligible and should be taken into account for a better understanding of the origin of the mechanical behaviour.

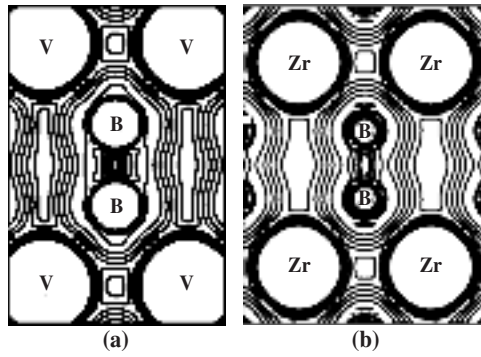


Figure 5. Total electron charge density map on the (110) plane through (a) V and B and (b) Zr and B atoms at equilibrium i.e. $P = 0$. Isodensity curves are separated by $0.01 e \text{ \AA}^{-3}$.

Table 4. Total density of states, $N(E_F)$, of VB₂ and ZrB₂ at equilibrium (in states/Hartree).

Method	VB ₂	ZrB ₂	Ref.
LCAO-DFT	37.20	7.50	This work
FP-LMTO	37.52	4.43	[6]
TB-LMTO	31.72	7.68	[8]
FP-LMTO	36.98	7.44	[9]
FLAPW	—	7.08	[7]
FP-LAPW	—	8.18	[29]

3.3. Electronic charge density

A non-uniformity in the charge density and hence bonding property is expected in both VB₂ and ZrB₂ because of their crystal structure. The charge-density profiles of these compounds are reported in figure 5. Including also MgB₂ results [17], the M–M covalent bond character is found to increase in the sequence $\text{Mg} \rightarrow \text{V} \rightarrow \text{Zr}$. In contrast, in the boron planes the B–B bonding is strong and covalent, as is evidenced by the maxima in the charge density at the bond middle point. M–M bonding in both VB₂ and ZrB₂ is not dominantly of covalent nature. A finite uniformly distributed charge between M atoms indicates a metallic bonding between them. Compared to the MgB₂ case, the covalent strength of the M–B bond in each of the two compounds under study is stronger.

3.4. Band structure and DOS

The band structures for VB₂ and ZrB₂ are presented in figures 6(a) and (b). These may be compared with other previous results of VB₂ [6] and ZrB₂ [6, 7, 30–32], based on a variety of computational methods. Overall these have common features, typical of d metals. The superconducting MgB₂ has some distinctive characteristics of its band structure [17]. These are the location of $\sigma(p_{x,y})$ bands relative to the Fermi level and also their dispersion in the Γ –A direction, $\Delta E_{(\Gamma-A)}^\sigma$. Boron $\sigma(p_{x,y})$ bands for both VB₂ and ZrB₂ are located below the Fermi level and hence hole states are absent, unlike the case in MgB₂. The dispersions, $\Delta E_{(\Gamma-A)}^\sigma$, are 1.88 and 1.62 eV for the two compounds, respectively. Unlike MgB₂, the σ bands here are of 3D type for both the compounds.

The calculated DOSs for the two compounds are displayed in figures 7(a) and (b). Our values of DOS for VB₂ and ZrB₂ (table 4) are consistent with those from other works [6–9, 29],

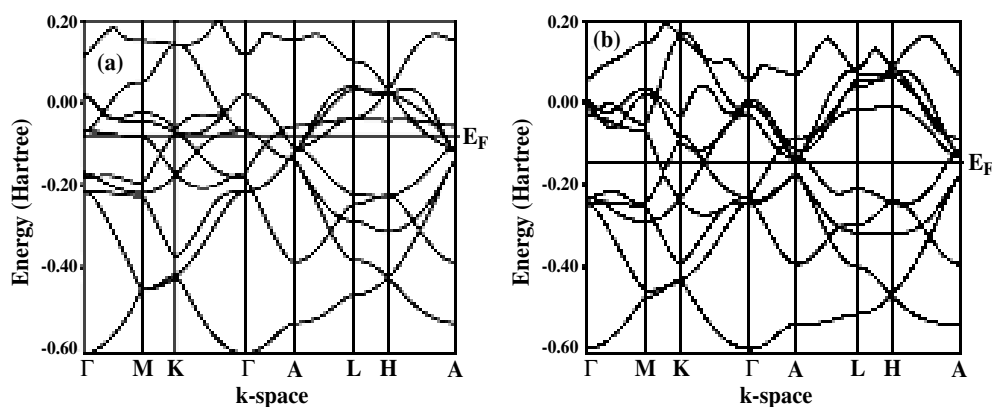


Figure 6. Band structure of (a) VB_2 and (b) ZrB_2 along some symmetry directions at equilibrium.

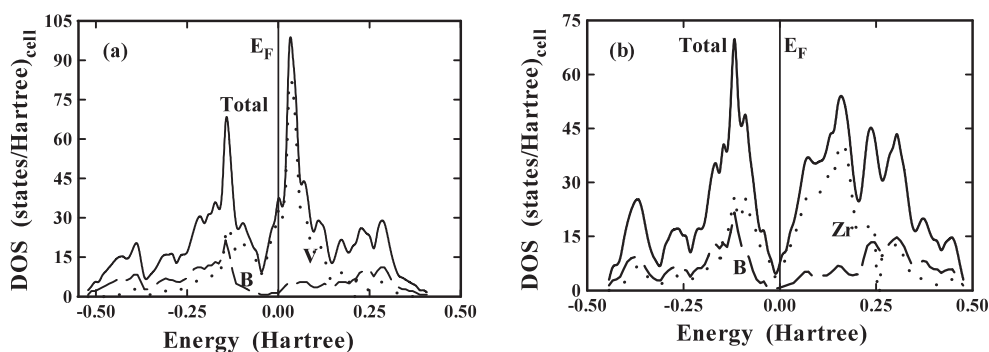


Figure 7. Total and partial electronic density of states (DOS) of (a) VB_2 and (b) ZrB_2 at equilibrium.

except that the DOS for ZrB_2 determined by Shein and Ivanovskii [6] is quite small compared to our calculation. The general shape of the DOS of ZrB_2 and the value of the DOS at E_F are consistent with x-ray photoemission spectra measurements [30]. The relatively low DOS at the Fermi energy E_F for ZrB_2 leads to a weak electron–phonon coupling in this system. However, at E_F there is a sufficient number of d electrons that may indicate a more active role of Zr and V in showing the lattice dynamical and possible superconducting properties of the two diborides.

A sharp valley around the Fermi energy is a typical feature of the total DOS of VB_2 and ZrB_2 . This ‘pseudogap’ was observed earlier by Rosner *et al* [7]. The pseudogap in binary alloys is believed to be of ionic origin or from the covalent hybridization [8]. Ionicity does not contribute much to bonding here. The most popular belief is that the pseudogap arises due to the p–d σ bonding between B and M atoms. According to Vajeeston *et al* [8], it originates from strong covalent bonding between boron atoms, i.e. from the B(p)–B(p) covalent contribution. Rosner *et al* [7] points out that the pseudogap is due to relatively large velocities in the region of E_F rather than any semimetallic overlapping of bands. The weaker M–M hybridization is evident from our charge-density plots (figure 7). The relatively stronger B–B hybridization in our calculation does support the conclusion of Vajeeston *et al* [8].

The major electronic factors responsible for the formation of superconducting properties for a BCS type superconductor are the higher density of states at E_F and a strong coupling. The

electron–phonon couplings estimated are 0.14 [9] and 0.28 [33] for ZrB₂ and VB₂, respectively. The Debye temperature of ZrB₂ is about half of that of VB₂. Thus it is apparent that, if the two compounds should show low-temperature superconductivity, larger T_c is expected for VB₂, which is not the case as yet. The low value of DOS obtained in this study and the weak coupling [9] do suggest a vanishing T_c for ZrB₂ and exclude the possibility of superconductivity with noticeable T_c .

4. Conclusions

In this work we have performed a density functional study of structural, mechanical, elastic properties, density of states, electronic charge density and band structure of VB₂ and ZrB₂ compounds. The important conclusions arrived at from our calculations are the following.

- (i) The calculated equilibrium volume is found to be in good agreement with experiment. The pressure dependence of the lattice parameters is smooth and does not show any structure up to 45 GPa.
- (ii) We note that the basal plane, in which the covalent B–B bonds lie, has nearly equal compressibility with the out-of-plane compressibility. We find a small anisotropy in the mechanical properties from our calculated elastic constants.
- (iii) The single-crystal elastic constants calculated for the first time yield isotropic bulk moduli. These, when compared with the bulk moduli obtained through the analysis of the data of energy versus primitive cell volume, are in very good agreement with those obtained from our calculated elastic constants.
- (iv) The bonding behaviour in the compounds under study is of a combination of covalent, ionic and metallic natures. Ground state behaviours of the compounds originate from the band filling effect, i.e., the falling of E_F at the pseudogap.
- (v) The calculations in conjunction with other results suggest that, if the two compounds should show low-temperature superconductivity, larger T_c (<1 K) is expected for VB₂. The low value of DOS obtained in this study and the weak coupling [9] do not suggest the occurrence of superconductivity in ZrB₂.

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