First principles calculations of thermodynamic properties of ZrB2

TANVEER AHMAD WANI[*]
BASANT KUMAR DAS

Department of Physics, Noida International University, Greater Noida
India -201310

Abstract   The thermodynamic properties, which are the important bulk properties for solids, have been investigated for ZrB_2 under pressure through the quasi harmonic Debye model. The dependences of thermal expansion, Gruneisen parameter, Debye temperature and specific heat on pressure P are successfully obtained. The obtained results are in a good agreement with the available experimental and other theoretical data.

Keywords: TMB_2; Thermal expansion; Gruneisen parameter; Debye temperature; Specific heat

1   Introduction

Transition metal diborides are of interest for fundamental reasons as well as for practical applications. The diborides are members of a broad class of materials known as the boron-rich solids [1], which consist of extended networks of covalently bonded boron (B) atoms stabilized through donation of electrons from the metal atoms. Although the structures of the diborides are unique, their physical properties are somewhat similar to those of nitrides and carbides; they are extremely hard and have very high melting points [2]. The diborides are good electrical conductors with resistivities that are often lower than those of the parent metal. They are attractive

---

[*]Corresponding Author. Email: tanveerur_rahman@yahoo.com

for the same types of applications as other hard, refractory materials, such as in composites and in hard coatings. Traditional applications of such materials are based on their interesting combination of mechanical and transport properties. Thus, in order to extend our present understanding regarding the behaviour of these materials to external influences as well as for the future technological developments, the thermodynamic properties of ZrB_2 compound has been investigated under pressure through the quasi-harmonic Debye model.

2   Quasi-harmonic Debye model

The non-equilibrium Gibbs function is given by [3,4]

$$G^*(V; P, T) = E(V) + PV + A_{Vib}(\Theta(V); T) \; , \tag{1}$$

where $E(V)$ is the total energy per unit cell, P is the pressure, V is the cell volume, PV corresponds to the constant hydrostatic pressure condition, T is the absolute temperature, and $\Theta(V)$ is the Debye temperature.

The vibrational term, $A_{Vib}(\Theta(V); T)$, is given by

$$A_{Vib}(\Theta(V); T) = nKT \times \left[\frac{9}{8} \frac{\Theta}{T} + 3 \ln \left(1 - e^{-\frac{\Theta}{T}} \right) - D \left(\frac{\Theta}{T} \right) \right] \; , \tag{2}$$

where n is the number of atoms in the molecule, and K is the Boltzmann constant. The Debye integral is expressed as [3]

$$D(y) = \frac{3}{y^3} \int_0^y \frac{x^3}{e^x - 1} dx \; . \tag{3}$$

For an isotropic solid, Θ is given by

$$\Theta = \frac{\hbar}{K} \left[6\pi^2 V^{1/2} n \right]^{1/3} f(\sigma) \sqrt{\frac{B_s}{m}} \; , \tag{4}$$

where $\hbar$ is the Planck constant (divided by 2π) M and B_s represents the molecular mass per formula unit and the adiabatic bulk modulus respectively. The adiabatic bulk modulus is approximated as [3]

$$B_s \sim B(V) = V \left(\frac{d^2 E(V)}{dV^2} \right) \; . \tag{5}$$

The Poisson ratio and $f(\sigma)$ are given by [4]

$$\sigma = \frac{3B - 2G}{6B + 2G} \ , \tag{6}$$

$$\left[f(\sigma)\right]^3 = 3 \left[2 \left(\frac{2}{3}\frac{1 + \sigma}{1 - 2\sigma}\right)^{3/2} + \left(\frac{11 + \sigma}{31 - \sigma}\right)^{3/2}\right]^{-1} \ , \tag{7}$$

where B and G are the bulk modulus and shear modulus, respectively. The non-equilibrium Gibbs function is minimized with respect to volume:

$$\left[\frac{\partial G^*(V; P, T)}{\partial V}\right]_{P,T} = 0 \ . \tag{8}$$

Thus, the expressions for isothermal bulk modulus, heat capacity and the thermal expansion coefficient [3] are given by

$$B_T(P, T) = V\left[\frac{\partial^2 G^*(V; P, T)}{\partial V^2}\right]_{P,T} = 0 \ , \tag{9}$$

$$C_V = 3nk\left[4D\left(\frac{\Theta}{T}\right) - \frac{3\frac{\Theta}{T}}{e^{\frac{\Theta}{T}} - 1}\right] \ , \tag{10}$$

$$\alpha = \frac{\gamma C_V}{B_T V} \ , \tag{11}$$

where k is the Boltzmann's constant. The Grüneisen parameter is given by

$$\gamma = -\frac{d\ln\Theta(V)}{d\ln V} \ . \tag{12}$$

3 Results and discussion

The density functional theory (DFT) Hamiltonian has been used where the electronic correlation and the exchange potential are chosen according to the Perdew-Zunger-Ceperly functional [5,6]. A first principles calculation with a relativistic analytic pseudopotential of Hartwigsen, Goedecker and Hutter (HGH) [7] scheme in the frame of density functional theory within LDA has been applied. The HGH type pseudopotential requires about 10 parameters. In our calculations, the kinetic energy cut-off criterion of 10 hartree is adopted to get the convergence of 10^{-7} Hartree in energy. The total energy and the ground state wave functions are calculated on a

$10{\times}10{\times}10$ k-point mesh. All the total energy electronic structure calculations are implemented through the Cambridge Serial Total Energy Package (CASTEP), a shared-source academic and commercial software package – Fortran based program [8,9].

First principles calculations of the total energy, E, of AlB$_2$ are the basis for the determination of the equation of state. The energy is calculated as a function of unit cell volume, V. It is then minimized as a function of the c/a ratio (a and c lattice parameters) for the selected volume. Since the experimental lattice parameters ratio is 1.0827 [10], we thus calculate a series of different c/a ratios from 1.080 to 1.085. It is found that the most stable structure of hexagonal close packed (HCP) AlB $_2$ (i.e., the normalized volume V_n=$V/V_0 = 1.0$, where V_0 is the equilibrium volume at zero pressure) corresponds to the ratio c/a of about 1.084.

Table 1: Energy values given together with the primitive cell volumes for HCP AlB$_2$.

V	169	170	171	172	173	174	175	176
E	-7.70216	-7.7023	-7.70237	-7.7024	-7.70241	-7.7024	-7.70234	-7.7022

In Tab. 1, the energy values have been given together with the primitive cell volumes, corresponding to the c/a value of 1.084. The crystal structure of ZrB$_2$ is designated as AlB$_2$-type transition metal diboride with the space group symmetry P6/mmm. It is simply a hexagonal lattice in which close packed TM (transition metal) layers are present alternative with graphite-like B layers. Choosing appropriate primitive lattice vectors, the atoms are positioned at TM (0,0,0), B (13,16,12), in the unit cell. The equilibrium lattice parameters are given in Tab. 2. The obtained results are consistent with the available theoretical results [11–13] and the experimental data [14–17].

To calculate the elastic constants under hydrostatic pressure P, we use the strains to be non-volume conserving, which are appropriate for the calculation of the elastic wave velocities. The elastic constants C_{ijkl} with respect to the finite strain variables are defined as [18–20]

$$C_{ij} = [\partial\sigma_{ij}(X)/\partial e_{kl}]_x \ ,$$

where σ_{ij} and e_{kl} are the applied stress and Eulerian strain tensors and X and x are the coordinates before and after the deformation. For the

Table 2: Structural parameters of ZrB$_2$.

	a(Å)	c(Å)	c/a
Present	3.1732	3.5349	1.114
Ref. [13]	3.1768	3.559	1.120
Ref. [12]	3.1832	3.5464	1.114
Ref. [11]	3.1970	3.5610	1.114
Ref. [14]	3.1693	3.5313	1.114
Ref. [16]	3.1700	3.5320	1.114
Ref. [15]	3.1650	3.5407	1.120
Ref. [17]	3.1680	3.5230	1.112

isotropic stress, we have [19–21]

$$C_{ijkl} = c_{ijkl} + \frac{P}{2}\Big(2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{ik}\delta_{ji}\Big) \,,$$

$$C_{ijkl} = \Big(\frac{1}{V(X)}\frac{\partial^2 E(X)}{\partial e_{ij}\partial e_{ki}}\Big)_x \,,$$

where c_{ijkl} denotes the second-order derivatives with respect to the infinitesimal strain (Eulerian). The fourth-rank tensor C has generally 21 independent components. However, this number is greatly reduced when taking into account the symmetry of the crystal.

The five-independent elastic constants for hexagonal crystal ZrB$_2$ have been calculated using the stress–strain relation upto pressures of 100 GPa and are given in Tab. 3. We found that the five-independent elastic constants increase linearly with pressure. If structure is mechanically stable, the five independent elastic constants should satisfy the well-known Born stability criteria [22], i.e.

$$C_{12} > 0, \quad C_{33} > 0, \quad C_{44} > 0 \,,$$

$$C_{66} = (C_{11} - C_{12})/2 > 0 \,,$$

$$(C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0 \,.$$

Further, the elastic constants also satisfy the Born stability criteria [22]. Thus, ZrB$_2$ is stable mechanically and there is no phase transition up to 100 GPa of pressure.

Table 3: Elastic constants for ZrB_2.

Pressure	Constants				
GPa	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
0	562	56	120	432	244
10	600	68	165	485	272
20	641	82	198	526	298
30	678	96	238	582	336
40	730	112	285	626	368
50	795	131	315	678	398
60	850	148	338	712	428
70	910	168	372	758	451
80	960	178	389	786	469
90	1005	189	398	812	476
100	1050	200	410	855	498

The Grüneisen parameter γ is based on the lattice's change in volume as the temperature changes. The dependence of Grüneisen parameter on pressure and temperature of ZrB_2 have been determined and given in Tabs. 4 and 5.

Table 4: Grüneisen parameter of ZrB_2.

Pressure	Grüneisen parameter γ			
GPa	300 K	600 K	900 K	1100 K
0	1.96	1.94	1.93	1.89
20	1.76	1.75	1.74	1.73
40	1.64	1.63	1.62	1.61
60	1.54	1.53	1.52	1.51
80	1.45	1.44	1.43	1.42
100	1.38	1.37	1.36	1.35

The above results are due to the fact that the effect of temperature on Grüneisen parameter is not as significant as that of pressure.
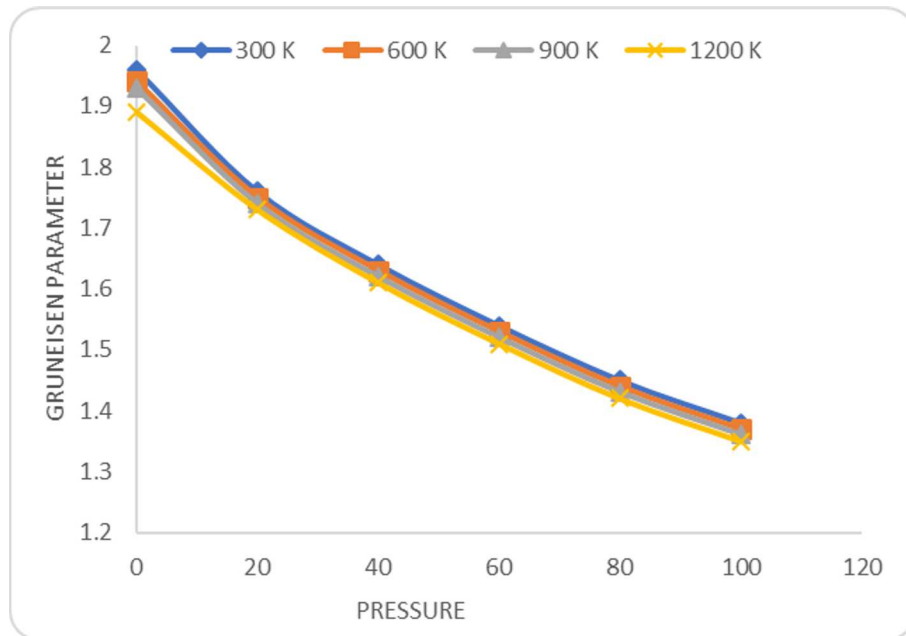
Figure 1: The dependences of Grüneisen parameter γ with pressure P.

Table 5: Values of Grüneisen parameter γ with temperature.

Temperature	Grüneisen parameter γ			
K	0 GPa	5 GPa	10 GPa	15 GPa
0	1.88	1.83	1.79	1.75
500	1.90	1.85	1.80	1.76
1000	1.94	1.88	1.84	1.79
1500	1.99	1.93	1.87	1.82
2000	2.04	1.97	1.90	1.86

From the graphical representations in Figs. 1 and 2, it is evident that at a given pressure, with the temperature, Grüneisen parameter γ increases with temperature. At fixed temperature γ decreases with pressure. As the temperature goes high, Grüneisen parameter decreases more with the increase of pressure. This shows that the effect of pressure is significant on the Grüneisen parameter.
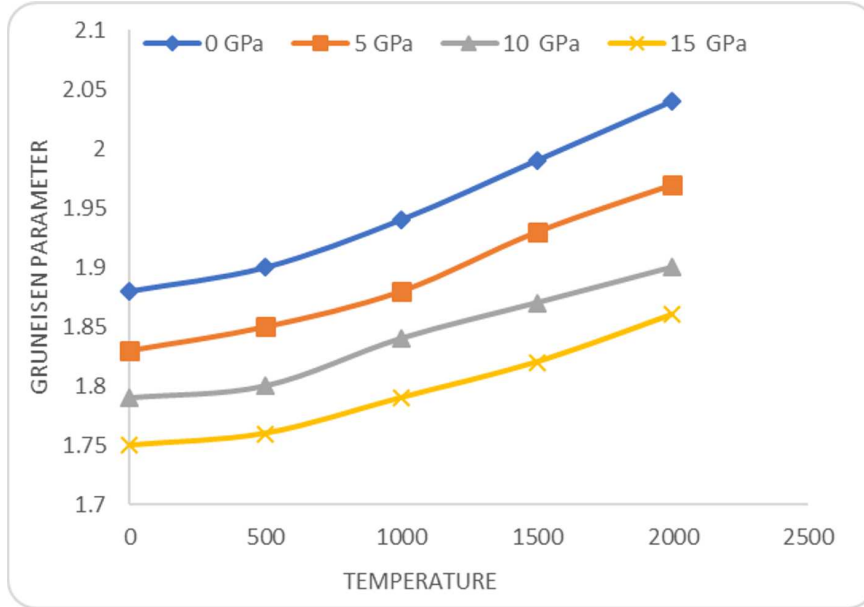
Figure 2: The dependences of Grüneisen parameter with temperature.

Table 6: Values of thermodynamic parameters with pressure.

Pressure	Θ		C_V	
GPa	1800 K	300 K	1800 K	300 K
0	0	0	0	0
20	0.20	0.15	0	-0.05
40	0.35	0.25	0	-0.09
60	0.46	0.35	0	-0.13
80	0.56	0.45	0	-0.16
100	0.65	0.52	0	-0.20

The values of heat capacity C_V and the Debye temperature Θ as a function of pressure, P, are given in Tab. 6 and their ratios are shown in Fig. 3. The ordinate is showing the ratio of the heat capacity and Debye temperature.

The Debye temperature increases non-linearly at constant temperature with increasing pressures. This indicates the change of the vibration fre-

quency of particles. However, with the applied pressures, the heat capacity decreases. The values of Debye temperature for ZrB_2 with temperature at different pressures are written in Tab. 7.
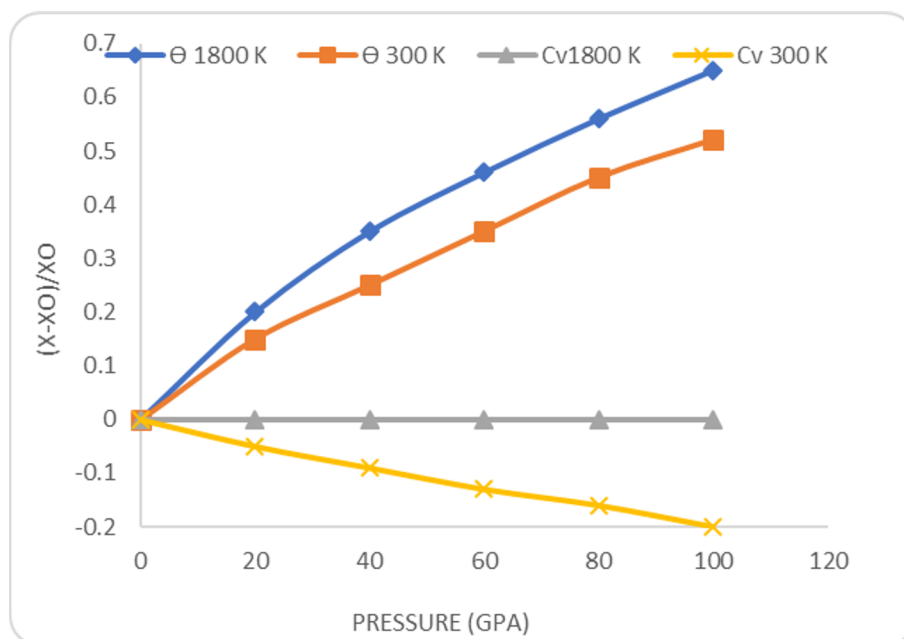

Figure 3: The dependences of thermodynamic parameters with pressure.

At temperature range of 0 to 500 K, the Debye temperature decreases at low pressure. The lowered magnitude of Debye temperature becomes small as pressure is increased. The variation of Debye temperature is very minute at a pressure of 10 GPa. Therefore, the importance of pressure on Debye temperature is much greater than that of temperature.

4 Conclusions

The description of lattice parameters of ZrB_2 compound has been given. The five-independent elastic constants have been calculated using the stress-strain relation. It is found that ZrB_2 is stable mechanically and there is no phase transition up to 100 GPa of pressure. It is also found that the Debye temperature increases monotonically. Furthermore, the high temperature leads to a smaller Debye temperature. But the high pressure gives birth

Table 7: Values of Debye temperature, Θ, with temperature at different pressures.

Temperature	Debye temperature		
K	0 GPa	5 GPa	10 GPa
0	545	567	587
50	545	567	587
100	544.8	566	586
150	544	566	586
200	543	565	585
250	542	564	584
300	541	562	582
350	539	561	581
400	537	559	579
450	535	556	577
500	533	553	575

to a larger Debye temperature in the wide range of pressures and temperatures. It is also shown that when the temperature is constant, the Debye temperature increases almost linearly with increasing pressures. However, the heat capacity decreases with the increasing pressures, as is due to the fact that the effect of increasing pressure is the same as decreasing temperature. It has been observed that at given pressure, the Grüneisen parameter increases dramatically with the temperature; while at fixed temperature, the Grüneisen parameter decreases dramatically with pressure, however, as the temperature goes higher, the Grüneisen parameter decreases more rapidly with the increase of pressure. These results are due to the fact that the effect of temperature on the ratio Grüneisen parameter (γ) is not as significant as that of pressure, and there will be a large thermal expansion at a low-pressure.

Received 14 February 2017

References

[1] HOARD J.L., HUGHES R.E.: In: *The Chemistry of Boron and its Compounds* (E.L. Muetterties (Ed.)). Wiley, New York 1967.

[2] Samsonov G.V., Vinitskii I.M.: *Handbook of Refractory Compounds.* Plenum Press, New York 1980.

[3] Blanco M.A., Francisco E., Luana V.: *GIBBS: isothermal-isobaric thermodynamics of solids from energy curves using a quasi-harmonic Debye model.* Comput. Phys. Commun. **158**(2004), 57–72.

[4] Francisco E., Recio J.M., Blanco M.A., Martín Pendás A.: *Quantum-mechanical study of thermodynamic and bonding properties of MgF_2.* J. Phys. Chem. **102**(1998), 1595–1601.

[5] Perdew J.P., Zunger A.: *Self-interaction correction to density-functional approximations for many-electron systems.* Phys. Rev. B **23**(1981), 5048.

[6] Ceperley D.M., Alder B.J.: *Ground state of the electron gas by a stochastic method.* Phys. Rev. Lett. **45**(1980), 566.

[7] Hartwingsen C., Goedecker S.: *Relativistic separable dual-space Gaussian pseudopotentials from H to Rn.* J. Hutter, Phys. Rev. B **58**(1998), 3641.

[8] Segall M.D., Lindan P.L.D., Probert M.J., Pickard C.J., Hasnip P.J., Clark S.J., Payne M.C.: *First-principles simulation: ideas, illustrations and the CASTEP code.* J. Phys. Condens. Matter **14**(2002), 2717–2744.

[9] Milman V., Winkler B., White J.A., Packard C.J., Payne M.C., Akhmatskaya V.E., Nobes R.H.: *Electronic structure, properties, and phase stability of inorganic crystals: A pseudopotential plane-wave study.* Int. J. Quantum Chem. **77**(2000), 895.

[10] Loa I., Kunc K., Syassen K., Bouvier P.: *Crystal structure and lattice dynamics of AlB_2 under pressure and implications for MgB_2.* Phys. Rev. B **66**(2002), 134101.

[11] Vajeeston P., Ravindran P., Ravi C., Asokamani R.: *Electronic structure, bonding, and ground-state properties of AlB_2-type transition-metal diborides.* Phys. Rev. B **63**(2001), 045115.

[12] Mahmud S.T., Islam A.K.M.A., Islam F.N.: *VB_2 and ZrB_2: a density functional study.* J. Phys. Condensed Matter **16**(2004), 2335.

[13] Hongzhi Fu, Min Teng, Xinhua Hong, Ying Lu, Tao Gao: *Elastic and thermodynamic properties of ZrB_2: First principle study.* Physica B **405**(2010), 846–851.

[14] Shein I.R., Ivanovskii A.L.: *Band structure of ZrB_2, VB_2, NbB_2 and TaB_2 hexagonal diborides: Comparison with the superconducting MgB_2.* Phys. Solidr State **44**(2002), 10, 1833–1839 (see also cond-mat super-con (2001) 0109445).

[15] Samsonov G.V., Vinitskii I.: *Refractory Compounds.* Metallurgia. Moscow 1976 (in Russian).

[16] Gasparov V.A., Sidorov N.S., Zverkova I.I., Kulakov M.P.: *Electron transport in diborides: Observation of superconductivity in ZrB_2.* JETP Lett. **73**(2001), 532.

[17] Epelbaum V.A., Gurevich M.A.: *On Zr-B phase diagram: Formation of ZrB_2 phase.* Zh. Fiz. Khim. **32**(1958), 2274.

[18] Wang J., Yip S., Phillpot S.R., Wolf D.: *Mechanical instabilities of homogeneous crystals.* Phys. Rev. B **52**(1995), 12627.

[19] WALLACE D.C.: *Thermodynamics of Crystals*, Wiley, New York 1972.

[20] KARKI B.B., ACKLAND G.J., CRAIN J.: *Elastic instabilities in crystals from ab initio stress-strain relations.* J. Phys.: Condens. Matter **9**(1997), 8579.

[21] BARRON T.H.K., KLEIN M.L.: *Second-order elastic constants of a solid under stress.* Proc. Phys. Soc. **85** (1965), 523–532.

[22] BORN M.: *On the stability of crystal lattices.* Proc. Cambridge Philos. Soc. **36**(1940), 160.