Debye Temperatures of Transition Metal Diborides TMB2 (TM= Ti, Zr, Os, Nb, Ru) Under Pressure

Tanveer Ahmad Wani

Department of Applied Science, Sagar Institute of Science & Technology, Gandhi Nagar Bhopal M.P. 462036
E-mail: *tanveerwani@sistec.ac.in

Abstract

The modern scientific and technical revolution is responsible for increasing interest and impetus in the search for materials possessing specific and desired properties. Today, the transition metal diborides (TMB$_2$) are of great interest because they have been found to possess unique physical and chemical properties. As an important physical quantity, the Debye temperature is closely related to the elastic constants, specific heat and melting point. Through the quasi harmonic Debye model, the dependency of Debye temperature on pressure P for various transition metal diborides is successfully obtained. The obtained results are consistent with the available theoretical results.

Keywords: TMB$_2$; Debye temperature; quasi harmonic Debye model

1. Introduction

One of the great keys in the advancement of technology is the development of materials that have the optimal combination of properties for the desired application. Materials therefore can become either enablers or bottlenecks for scientific and technological advancement. It is the primary work of material science engineers to understand the properties of matter and the processes that will combine those properties into synergistic materials with the overall material properties for a given application [1]. In order to understand the phenomena that govern material behavior scientists typically develop and perform countless experiments to determine the properties of interest such as mechanical strength, stiffness, resistance to heat, conductivity of electricity and many others. With recent advances in computer hardware and software the role of computer simulations in materials science is expanding and delivering many useful insights [2]. In particular, these 'virtual experiments' can provide understanding not only of what happens to a material but why it happens [3] based on understanding of microscopic phenomena.

The properties study of materials at high pressures and high temperature is always inevitable to extend our present understanding regarding the behaviour of the materials to these external influences as well as for the future technological developments. Research at elevated pressure and temperature provide a new insight into synthesis of materials with properties important for industrial, technical and scientific applications [4]. These include super hard materials, high-temperature superconductors, ferroelectrics, multiferroics, high energy density materials, nano-materials, materials for computers and communications and hydrogen-storage materials. Simulations of thermal or high pressure are useful to study the synthesis of novel materials, crystal growth etc [5]. High-pressure studies provide otherwise unattainable information about the phase diagrams, thermodynamic properties, and electronic structure which

can predict directions for search of materials with desirable properties.

Elastic properties, which are closely related to many fundamental solid-state properties, such as equation of state, specific heat, thermal expansion, Debye temperature, Gruneisen parameter, melting point, and so on, are important in fields ranging from geophysics to materials research, chemistry and physics. The knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid: load deflection, thermoelastic stress, internal strain, sound velocities and fracture toughness. From the elastic constants, one can obtain valuable information about the bonding characteristic between adjacent atomic planes and about the anisotropic character of the bonding and about the structural stability of a crystal.

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 [6], which consist of extended networks of covalently bonded boron (B) atoms stabilized through donation of electrons from the metal atoms. Most of the metal diborides have the AlB$_2$ structure in which layers of close-packed metal atoms alternate with planes of B atoms with a graphite-like geometric structure. The B sheets in the diborides of the AlB$_2$ structure would be isoelectronic with graphite [7] if the bonding involved a full transfer of two electrons to give $M^{2+}B_2^{-2}$. However, the fact that the B–B bond length in the diborides ranges from 1.7 to 1.8A˚, values typical of B–B single bonds, immediately suggests that there is an insignificant degree of p bonding between the B atoms. This conclusion is supported by recent electronic structure calculations and other data indicating that the metal–boron bonding is largely covalent in nature [8-9]. 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 [10]. The diborides are good electrical conductors

with resistivities that are often lower than those of the parent metal. They are attractive 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 Debye temperature of various TMB_2 (TM= Os, Nb, Ti, Zr and Ru) compounds have been investigated under pressure through the quasi harmonic Debye model.

2. Quasi-harmonic Debye model

To investigate the thermodynamic properties of various diborides, we shall apply the quasi-harmonic Debye model, in which the non-equilibrium Gibbs function G*(V;P,T) can be written in the form of [11,12],

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

where E(V) is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, and A_{Vib} ($\Theta(V)$;T) is the vibrational term, which can be written as

$$A_{Vib}(\Theta(V); T) = nK \times [\frac{9}{8}T\frac{\Theta}{T} + 3\ln(1 - e^{-\Theta/T}) - D(\Theta/T)] \quad (2)$$

where n is the number of atoms in the molecule, and the Debye integral $D(\Theta/T)$ is defined as [12]

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

For an isotropic solid, Θ is expressed by

$$\Theta = \frac{h}{k}[6\pi^2 V^{1/2}n]^{1/3}f(\sigma)\sqrt{\frac{B_S}{M}} \quad (4)$$

where M is the molecular mass per formula unit, B_S the adiabatic bulk modulus, which can be approximated by the static compressibility [12]

$$B_S \sim B(V) = V(\frac{d^2E(V)}{dV^2}) \quad (5)$$

and the Poisson ratio σ and $f(\sigma)$ [11,13] are given by the following forms:

$$\sigma = \frac{3B - 2G}{6B + 2G}, \quad (6)$$

$$[f(\sigma)]^3 = 3[2(\frac{2}{3}\frac{1+\sigma}{1-2\sigma})^{3/2} + (\frac{1}{3}\frac{1+\sigma}{1-\sigma})^{3/2}]^{-1} \quad (7)$$

Therefore, the non-equilibrium Gibbs function G*(V;P,T) as a function of (V;P,T) can be minimized with respect to volume:

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

The isothermal bulk modulus B_T, the heat capacity C_V and the thermal expansion coefficient (α) are expressed as

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

$$C_V = 3nk[4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T}-1}] \quad (10)$$

$$\alpha = \frac{\gamma C_V}{B_T V} \quad (11)$$

where γ is the Gruneisen parameter defined as

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

3. Results and Discussion

As an important physical quantity, the Debye temperature is closely related to the elastic constants, specific heat and melting point. In this work, we have focused our attention on this physical quantity under high pressures using the quasi-harmonic Debye model. The Debye temperatures of various TMB_2 (TM= Os, Nb, Ti, Zr and Ru) compounds have been investigated. The Debye temperature for RuB_2 at various temperatures and pressures is given in Table 1 and presented in Figure 1.

Table 1. Static variation of Debye temperature with pressure for RuB_2.

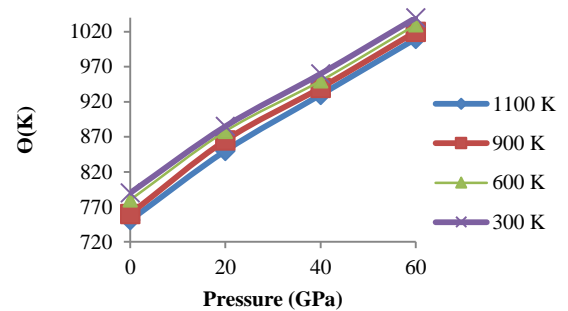| Pressure GPa	Θ (1100K)	Θ (900K)	Θ (600K)	Θ (300K)
0	751	760	780	790
20	850	865	878	885
40	930	940	950	960
60	1010	1020	1030	1040

Figure 1. Static variation of Debye temperature with pressure for RuB_2.

The calculated Debye temperature at T = 0 K is 796.2J/mol/K, which is in agreement with the result (780J/mol/K) from Hao et al [14]. From Figure 1, one can find: (a) When the temperature keeps constant, the Debye temperature almost linearly increases with applied pressures (b) When the pressure keeps constant, the Debye temperature decreases with the increasing temperatures; (c) The Debye temperature at the temperature of 1100K is lower than that at 300K, which shows that the vibration frequency of the particles in RuB_2 changes with the pressures and the temperatures. No experimental data for our calculated results are yet available for comparison.

The C_V and the Debye temperature as a function of pressure P are listed in Table 2 and shown in Figure 2 at the temperatures of 300 and 1500K for TiB_2.

Table 2. Static variations of thermodynamic parameters with pressure P for TiB₂.

Pressure GPa	Θ (1500K)	Θ (300K)	C_v (1500K)	C_v (300K)
0	0	0	0	0
50	0.37	0.28	-0.05	-0.28
100	0.6	0.46	-0.07	-0.45
150	0.75	0.62	-0.1	-0.55
188	0.87	0.75	-0.12	-0.62

Note: The negative heat capacity is a true equilibrium phenomena occurring in small isolated systems and the negative heat capacity is a manifestation of the constancy of the system's total energy [15-18].
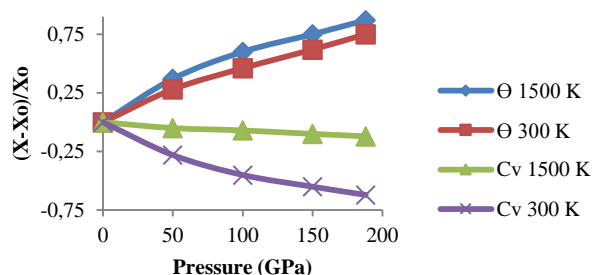

Figure 2. Variations of thermodynamic parameters (Debye temperature or specific heat) with pressure P. They are normalized by $(X–X_0)/X_0$ where X and X_0 are the Debye temperature or heat capacity under any pressure P and zero pressure P_0 at the temperatures of 300 and 1500 K.

It is shown that when the temperature is constant, the Debye temperature increases almost linearly with applied pressures. However, the Cv decreases with the applied pressures, as is due to the fact that the effect of increasing pressure on TiB₂ is the same as decreasing temperature of TiB₂.

The positive sign of the heat capacity reflects the fact that adding energy to a system results in an increment of its temperature. However, under special conditions certain specific systems behave in the opposite way [15-18]. The theoretical explanation of this apparent violation of the laws of thermodynamics is based on the differences between the microcanonical and canonical ensembles when the size of the system is small. The negative heat capacity is a true equilibrium phenomena occurring in small isolated systems. The microcanonical formalism is the appropriate theory for the treatment of isolated systems, and the negative heat capacity is a manifestation of the constancy of the system's total energy.

In Figure 3, we show the values of heat capacity C_V and the Debye temperature θ as a function of pressure P at the temperatures of 300 and 1800K for ZrB₂. The values are given in Table 3.

Table 3. Static variations of thermodynamic parameters with pressure P for ZrB₂.

Pressure GPa	Θ (1800K)	Θ (300K)	C_v (1800K)	C_v (300K)
0	0	0	0	0
20	0.2	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	-0.2

Note: The negative heat capacity is a true equilibrium phenomena occurring in small isolated systems. Under special conditions certain specific systems behave in this way [15-18].
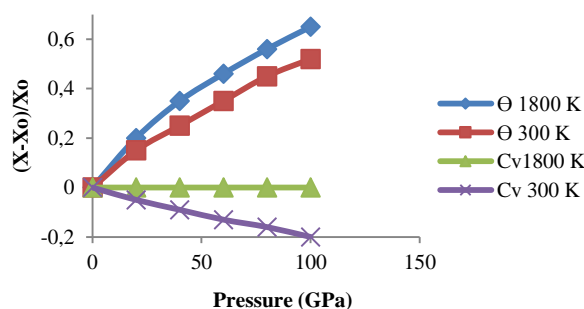

Figure 3. The static variations of thermodynamic parameters with pressure P. They are normalized by $(X-X_0)/X_0$, where X and X_0 are the Debye temperature or heat capacity under any pressure P and zero pressure P_0 at the temperatures of 300 and 1800K.

It is shown that when the temperature is constant, the Debye temperature increases non-linearly with applied pressures, indicating the change of the vibration frequency of particles under pressure. However, the heat capacity C_V decreases with the applied pressures, in which the increasing pressure might achieve the same result with decreasing temperature on ZrB₂. The variations of θ with temperature at different pressures for ZrB₂ are given in Table 4 and shown in Figure 4.

Table 4. Static variation of Debye temperature with temperature at different pressures for ZrB₂.

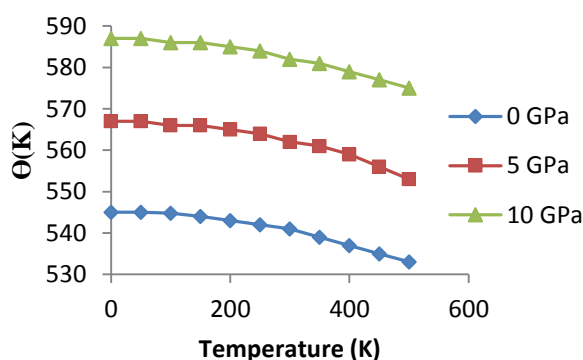| Temperature K	Θ (0GPa)	Θ (5GPa)	Θ (10GPa)
0	545	567	587
50	545	567	587
100	544	566	586
150	544	566	586
200	543	565	585
250	542	564	584
300	541	562	582
350	539	561	581
400	537	559	579
450	535	556	577
500	533	553	575

Figure 4. Static variation of Debye temperature with temperature at different pressures for ZrB₂.

We can see that at low pressure, the Debye temperature decreases significantly when the temperature changes from 0 to 500K. It can be noted that as the pressure goes higher, the decreased magnitude of θ becomes small. When the pressure approaches to 10GPa, the variation of θ is very small in the whole changed temperature range from 0 to 500K. Therefore, it can be concluded that the effect of the temperature on the Debye temperature is not as important as that of the pressure on θ. And the higher the pressure is, the smaller the effect of the pressure on the Debye temperature is.

The obtained Debye temperatures of the orthorhombic OsB_2 under pressure are given in Table 5 and shown in Figure 5. At zero pressure and zero temperature, we obtain θ= 601.09K, consistent with other results, such as θ= 601, 591 [14] and 550K [19]. It is noted that the Debye temperature of OsB_2 tend to increase with increasing pressure.
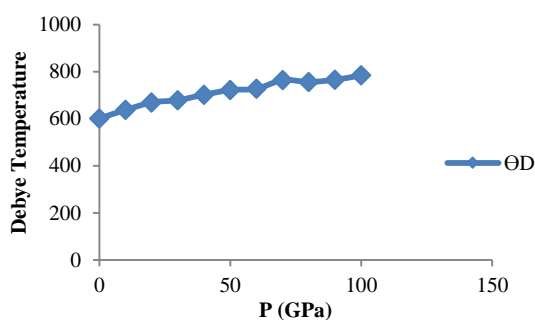

Figure 5. Static variation of Debye temperature with pressure for OsB_2.

Table 5. Static variation of Debye temperature with pressure for OsB_2.

Pressure (GPa)	Θ_D
0	601.09
10	637.49
20	669.13
30	679.38
40	702.15
50	722.05
60	727.64
70	764.08
80	756.39
90	765.69
100	784.26

The Debye temperatures of NbB_2 are given in Table 6 and also exhibited at various pressures in Figure 6.

At P = 0 GPa and T = 0 K, θ = 861.5 K, which is higher than the theoretical value of 753.3 K calculated from the elastic constants by Islam et al [20,21]. From Figure 6, it is shown that the Debye temperature increases monotonically with increasing pressure.
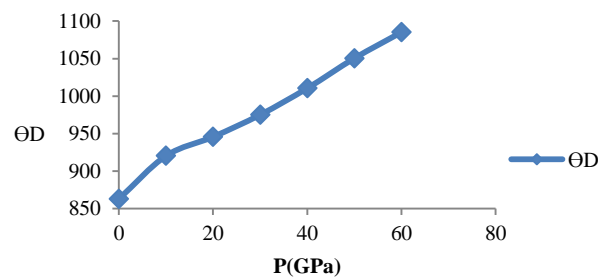

Figure 6. Static variation of Debye temperature with pressure for NbB_2.

Table 6 -Static variation of Debye temperature with pressure for NbB_2.

Pressure (GPa)	Θ_D
0	861.5
10	920.3
20	945.7
30	975.1
40	1010.5
50	1050.4

Conclusion

As an important physical quantity, the Debye temperature is closely related to the elastic constants, specific heat and melting point. In this work, we have focused our attention on this physical quantity under high pressures using the quasi-harmonic Debye model. The Debye temperatures of various TMB_2 (TM= Os, Nb, Ti, Zr and Ru) compounds have been investigated. It is found that the Debye temperature increase monotonically and the anisotropy is weakened with pressure. Furthermore, the high temperature leads to a smaller Debye temperature. But the high pressure gives birth to a larger Debye temperature, in the wide range of pressures and temperatures.

The C_v and the Debye temperature as a function of pressure P for TiB_2 and ZrB_2 have been investigated. It is shown that when the temperature is constant, the Debye temperature increases almost linearly with applied pressures. However, the C_v decreases with the applied pressures, as is due to the fact that the effect of increasing pressure is the same as decreasing temperature. The obtained results are consistent with the available theoretical results. No experimental data for our calculated results are yet available for comparison.

References

[1] W. D. Callister, *Materials Science and Engineering: An Introduction, 7th Ed.* New York: Wiley & Sons, 2007.

[2] V. de Walle, G. Ceder, "The effect of lattice vibrations on substitutional alloy thermodynamics," *Rev. Mod. Phys.*, *74*, 11–45, 2002.

[3] J. Hafner, "Atomic-scale computational materials science,'' *Acta Materialia., 48*, 71–92, 2000.

[4] J. V. Badding, "High-pressure synthesis, characterization, and tuning of solid state materials,'' *Annual Review of Material Science, 28*, 631-658, 1998.

[5] S. L. Chaplot, "Synthesis and properties of novel materials at high pressure and temperature—molecular dynamics simulation studies,'' *Bull. Mater. Sci., 22*, 279-285, 1999.

[6] J.L. Hoard, R.E. Hughes, *in: E.L. Muetterties Ed. The Chemistry of Boron and its Compounds,* New York: Wiley, 1967.

[7] W. N. Lipscomb, D. Britton, "Valence structure of the higher borides," *J. Chem. Phys., 33*, 275-280, 1960.

[8] X. B. Wang, D. C. Tian, L. L. Wang, "The electronic structure and chemical stability of the AlB_2-type transition-metal diborides,'' *J. Phys.: Condens. Matter, 6*, 10185, 1994.

[9] K. Lie, R. Huier, R. Brydson, "Theoretical site- and symmetry-resolved density of states and experimental eels near-edge spectra of AlB_2 and TiB_2," *Phys. Rev. B, 61*, 1786-1794, 2000.

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

[11] E. Francisco, J. M. Recio, M. A. Blanco, A. Martín Pendás, "Quantum-mechanical study of thermodynamic and bonding properties of MgF_2,'' *J. Phys. Chem., 102*, 1595-1601, 1998.

[12] M. A. Blanco, E. Francisco, V. Luana, "GIBBS: isothermal-isobaric thermodynamics of solids from energy curves using a quasi-harmonic debye model,'' *Comput. Phys. Commun., 158*, 57-72, 2004.

[13] E. Francisco, G. Sanjurjo, M. A. Blanco, "Atomistic simulation of SrF_2 polymorphs,'' *Phys. Rev. B, 63*, 09410-7, 2001.

[14] X. Hao, Y. Xu, Z. Wu, D. Zhou, X. Liu, J. Meng, "Elastic anisotropy of OsB_2 and RuB_2 from first-principles study,'' *J. Alloys Compd., 453*, 413-417, 2008.

[15] M. Schmidt, R. Kusche, T. Hippler, J. Donges, W. Kronmuller, B. von Issendor, H. Haberland, "Negative heat capacity for a cluster of 147 sodium atoms,'' *Phys. Rev. Lett., 86*, 1191-1194, 2001.

[16] D. Lynden-Bell, Negative specific heat in astronomy, physics and chemistry,'' *Physica A, 263*, 293, 1999.

[17] T. Padmanabhan, "Statistical mechanics of gravitating systems,'' *Phys. Rep., 188*, 285-362, 1990.

[18] D.H.E. Gross, "Microcanonical thermodynamics and statistical fragmentation of dissipative systems. The topological structure of the n-body phase space,'' *Phys. Rep., 279*, 119, 1997.

[19] B. J. Suh, X. Zong, Y. Singh, A. Niazi, D. C. Johnston, "B NMR in the layered diborides OsB_2 and RuB_2,'' *Phys. Rev. B, 76*, 144511, 2007.

[20] A. K. M. A. Islam, A. S. Sikder, F. N. Islam, "NbB_2: A density functional study,'' *Phys. Lett. A, 350*, 288-292, 2006.

[21] A. S. Sikder, A. K. M. A. Islam, M. Nuruzzaman, F. N. Islam, "Superconducting NbB_2: an ab initio study of elastic constants,'' *Solid State Commun., 137*, 252-256, 2006.