



## Thermodynamical Properties of Transition Metal Diborides under Pressure†

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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. 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. 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 proposal aims to calculate the thermodynamic properties of various transition metal diborides under pressure using the quasi harmonic Debye model.

**Key Words:** Diborides, Transition metal,  $AlB_2$ .

### INTRODUCTION

Today, the transition metal diborides are of great interest because they have been found to possess unique physical and chemical properties such as high hardness, high melting point and oxidation, and have wide range of industrial applications. The diborides are members of a broad class of materials known as the boron-rich solids, which consist of extended networks of covalently bonded boron (B) atoms stabilized through donation of electrons from the metal atoms. The hexagonal  $AlB_2$  structure, into which these transition-metal diborides crystallize, is build up of hexagonal nets of pure transition-metal atoms and triangle nets of pure boron atoms. The crystal structure can hence be regarded as a layered structure. When considering the fact that the crystal structure can be regarded as a layered structure, physical properties are expected to be highly anisotropic and the extent of the anisotropy varies from diboride to diboride, depending on their  $c/a$  axial ratios. However, mainly because of the inherent difficulty in growing monocrystals of transition-metal diborides due to their high melting points<sup>1-3</sup>, almost nothing is known about how their physical properties vary with crystallographic directions (anisotropy) and how the extent of anisotropy varies from diboride to diboride for most of these transition-metal diborides.

The physical properties of these compounds have received less or none attention. To our best of knowledge, lattice

dynamical and thermodynamical properties, which are the important bulk properties for solids, have not been considered theoretically for these compounds so far. In the present paper, the thermodynamical properties of  $TMB_2$  ( $TM = Ti, Zr, Ru$ ) compounds have been investigated under pressure through the quasi harmonic Debye model.

### Quasi-Harmonic Debye model

The non-equilibrium Gibbs function  $G^*(V;P,T)$  can be written as reported by Francisco *et al.*<sup>4,5</sup>

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

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

$$A_{\text{vib}}(\Theta(V);T) = nKT \times \left( \frac{9\Theta}{8T} + 3 \ln(1 - e^{-\Theta/T}) - D(\Theta/T) \right)$$

where  $n$  is the number of atoms in the molecule, and the Debye integral  $D(\Theta/T)$  is defined as<sup>5</sup>

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

For an isotropic solid,  $\Theta$  is expressed by

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

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where  $M$  is the molecular mass per formula unit,  $B_s$  the adiabatic bulk modulus, which can be approximated by the static compressibility<sup>5</sup>

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

and the Poisson ratio  $\sigma$  and  $f(\sigma)$ <sup>4,6</sup> are given by the following forms:

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

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

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

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

The isothermal bulk modulus  $B_T$ , the heat capacity  $C_v$  and the thermal expansion coefficient ( $\alpha$ ) are expressed as<sup>5</sup>

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

$$C_v = 3nk \left( 4D(\Theta/T) - \frac{3\Theta/T}{e^{\Theta/T-1}} \right)$$

$$\alpha = \frac{\gamma C_v}{B_T V}$$

where  $\gamma$  is the Gruneisen parameter defined as

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

## RESULTS AND DISCUSSION

The experimental lattice parameters ratio<sup>7</sup>  $c/a$  is 1.0827. We have calculated a series of different  $c/a$  ratios from 1.077 to 1.084. For each  $c/a$ , a series of lattice constant  $a$  is set to calculate the total energy  $E$ . It is found that the most stable structure of HCP  $\text{AlB}_2$  corresponds to the ratio  $c/a$  of about 1.084. The calculated lattice constants  $a$  and  $c$ , compared with the experimental data<sup>7</sup> and other theoretical results<sup>7,8</sup> are given as under. The agreement among them is good.

Present work	Ref [8]	Exp [7]
$a=3.005$	$a=3.009$	$a=3.0062$
$b=30257$	$b=3.262$	$b=3.2548$
$c/a=1.084$	$c/a=1.084$	$c/a=1.0827$

The thermodynamic properties of  $\text{RuB}_2$  are obtained by the quasi-harmonic Debye model, in which the phonon effects are considered. The Debye temperature is a fundamental parameter of a material, linked to many physical properties such as specific heat, elastic constants and melting point<sup>9</sup>. The Debye temperature and the Gruneisen parameter at various temperatures and pressures are presented in Figs. 1 and 2. Our calculated Debye temperature at  $T = 0$  K is 796.2 J/mol/K,

which is in agreement with the result (780 J/mol/K) from Hao *et al.*<sup>10</sup>. From Figs. 1 and 2, one can find: (a) When the temperature keeps constant, the Debye temperature almost linearly increases with applied pressures, while the Gruneisen parameter decreases smoothly with pressures. (b) When the pressure keeps constant, the Debye temperature decreases with the increasing temperatures; while the Gruneisen parameter increases with the increasing temperatures, in virtue of the fact that the effect of increasing pressure on the material is the same as decreasing temperature on the material. (c) The Debye temperature 1100 K is lower than that at 300 K, which shows that the vibration frequency of the particles in  $\text{RuB}_2$  changes with the pressures and the temperatures.

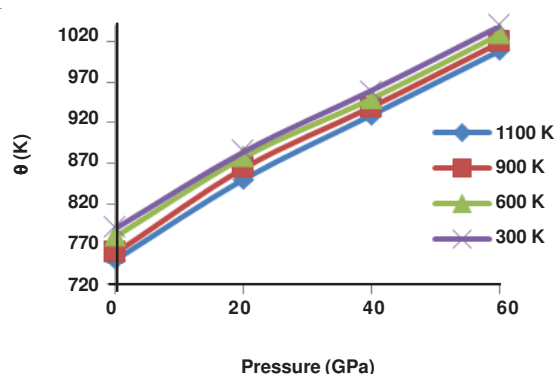


Fig. 1. Static variation of Debye temperature with pressure

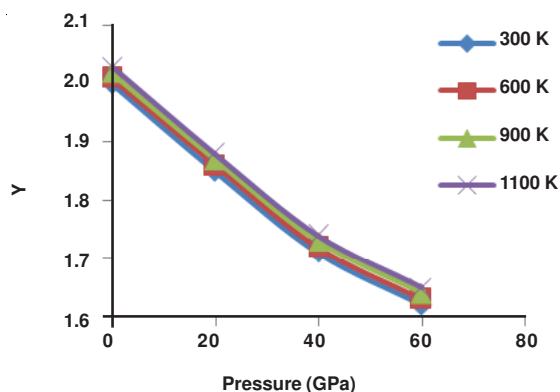


Fig. 2. Static variation of Gruneisen parameter with pressure

The thermal expansion coefficient ' $\alpha$ ' with pressure for  $\text{RuB}_2$  is presented in Fig. 3. The effects of pressure on the thermal expansion coefficient are very small at low temperatures. The effects are increasing obviously as the temperature increases. As pressure increases, the thermal expansion coefficient decreases rapidly and the effects of temperature become less and less pronounced, resulting in linear high temperature behaviour. It can be found that the thermal expansion coefficient converges to a constant value at high pressures. However, as the pressure increases, the thermal expansion coefficient decreases almost exponentially and the lower the temperature is, the faster the thermal expansion coefficient decreases. This shows that the effect of temperature is much greater than that of pressure on the thermal expansion coefficient. The  $C_v$  and the Debye temperature as a function of pressure  $P$  are shown in Fig. 4 at 300 and 1500 K for  $\text{TiB}_2$ . It is shown that when the

temperature is constant, the Debye temperature  $\theta$  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 on  $TiB_2$  is the same as decreasing temperature of  $TiB_2$ .

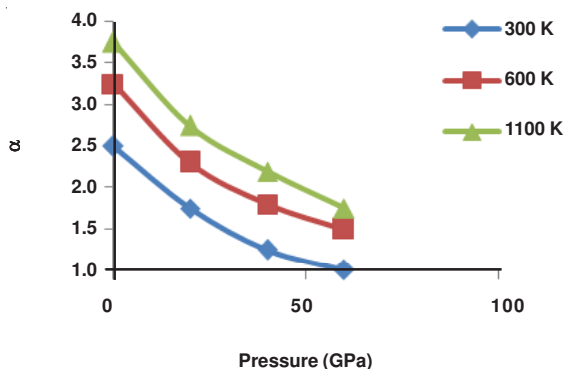


Fig. 3. Variation of thermal expansion coefficient with pressure

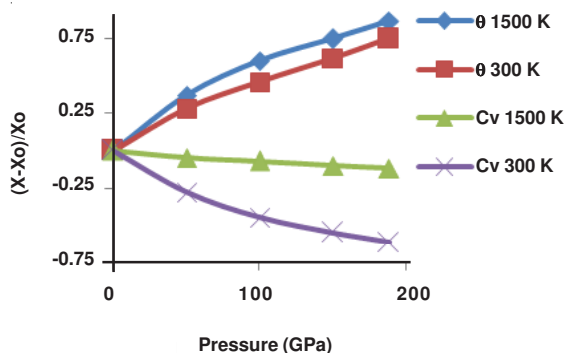


Fig. 4. Static variations of thermodynamic parameters with pressure P. They are normalized by  $X-X_0/X_0$

Fig. 5 showed the ratios of heat capacity  $C_v$  and the Debye temperature  $\theta$  as a function of pressure P at the 300 and 1800 K for  $ZrB_2$ . 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  $ZrB_2$ . The variations of  $\theta$  with pressure P are plotted in Fig. 6. We can see that at low pressure, the Debye temperature decreases significantly when the temperature changes from 0 to 500 K. It can be noted that  $\theta$  decreases by 2.69, 2.00 and 1.63 % at the pressures of 0, 5, 10 Gpa when the used temperature is from 50 to 450 K, respectively. As the pressure goes higher, the decreased magnitude of  $\theta$  becomes small. When the pressure approaches to 10 GPa, the variation of  $\theta$  is very small in the whole changed temperature range from 0 to 500 K. 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  $\theta$ . And the higher the pressure is, the smaller of the effect of the pressure on the Debye temperature is. The Gruneisen parameter  $\gamma$  is thought to be described the alteration in a frequency of the crystal lattice vibration based on the lattice's increase or decrease in

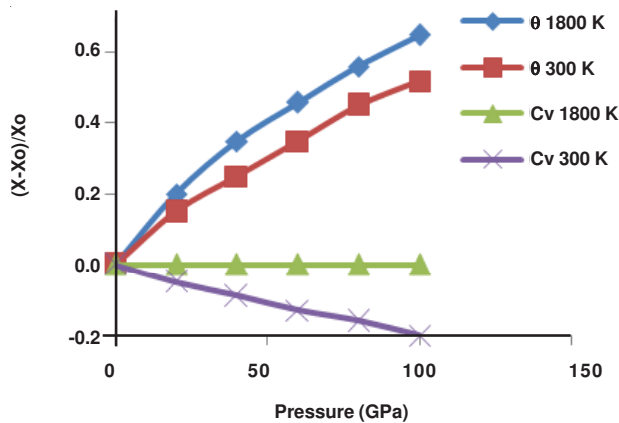


Fig. 5. Static variations of thermodynamic parameters with pressure P. They are normalized by  $X-X_0/X_0$

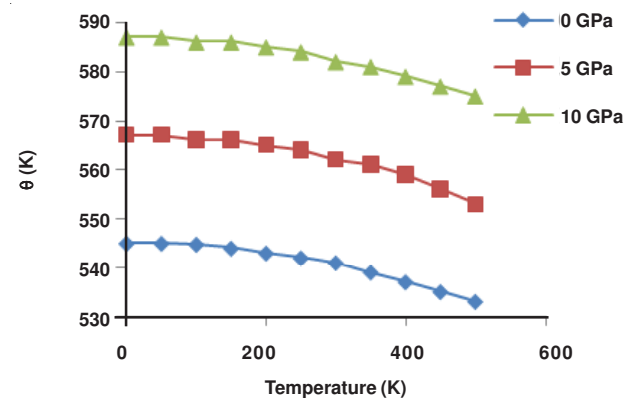


Fig. 6. Static variation of Debye temperature with temperature at different pressures

volume as the temperature changes. It is directly related to the equation of state (EOS). We have determined the pressure dependence of  $ZrB_2$  (Figs. 7 and 8). It can be observed that at given pressure, the  $\gamma$  increases dramatically with the temperature T when  $T > 500$  K varies almost monotonously with temperature T; while at fixed temperature, the decreases dramatically with pressure and that as the temperature goes higher, the  $\gamma$  decreases more rapidly with the increase of pressure P as displayed in Fig. 8. These results are due to the fact that the effect of temperature T on the ratio  $\gamma$  is not as significant as that of pressure P, and there will be a large thermal expansion at a low pressure P.

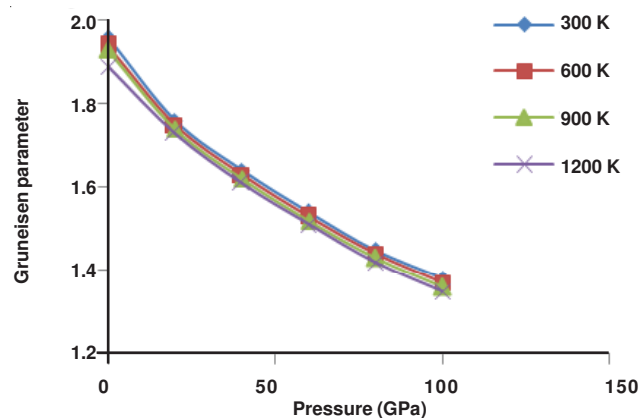


Fig. 7. Static variation of Gruneisen parameter with pressure

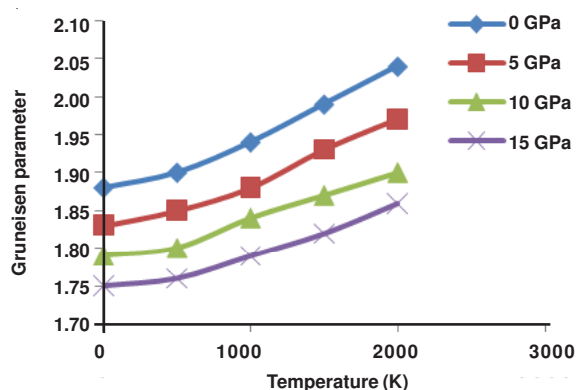


Fig. 8. Static variation of Gruneisen parameter with temperature

## Conclusion

In this work, we have focused our attention on the thermodynamic properties of various  $TMB_2$  under high pressures using the quasi-harmonic Debye model. First, the high temperature leads to a smaller Debye temperature and a larger Gruneisen parameter at constant pressure for  $ZrB_2$ . Second, the high pressure gives birth to a larger Debye temperature and a smaller Gruneisen parameter at constant temperature. The pressure dependences of heat capacity are also obtained for  $RuB_2$ . It is found that the ratios of elastic constants and the Debye temperature increase monotonically and the anisotropy is weakened with pressure. Furthermore, the high temperature leads to a

smaller Debye temperature, a larger heat capacity, Gruneisen parameter and a bigger thermal expansion coefficient. But the high pressure gives birth to a larger Debye temperature, a smaller heat capacity, a smaller Gruneisen parameter and thermal expansion coefficient in the wide range of pressures and temperatures.

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