



## Pressure induced structural phase transition of OsB<sub>2</sub>: First-principles calculations

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### ABSTRACT

Orthorhombic OsB<sub>2</sub> was synthesized at 1000 °C and its compressibility was measured by using the high-pressure X-ray diffraction in a Diacell diamond anvil cell from ambient pressure to 32 GPa [R.W. Cumberland, et al. (2005)]. First-principles calculations were performed to study the possibility of the phase transition of OsB<sub>2</sub>. An analysis of the calculated enthalpy shows that orthorhombic OsB<sub>2</sub> can transfer to the hexagonal phase at 10.8 GPa. The calculated results with the quasi-harmonic approximation indicate that this phase transition pressure is little affected by the thermal effect. The calculated phonon band structure shows that the hexagonal *P* 6<sub>3</sub>/*mmc* structure (high-pressure phase) is stable for OsB<sub>2</sub>. We expect the phase transition can be further confirmed by the experimental work.

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### 1. Introduction

Hard materials are of great scientific interest due to numerous industrial applications. Therefore, great efforts have been devoted on synthesizing superhard materials. A main design principle of synthesizing hard materials is of combining small and light covalent elements with large and electron-rich transition metals [1,2]. Recently, five transition-metal nitrides and borides, i.e., OsB<sub>2</sub> [1], PtN<sub>2</sub> [3,4], IrN<sub>2</sub> [4,5], OsN<sub>2</sub> [5], ReB<sub>2</sub> [6] were synthesized under high pressure (ambient pressure for OsB<sub>2</sub>, ReB<sub>2</sub>) and at high temperature. The experimental results show that both OsB<sub>2</sub> and ReB<sub>2</sub> are ultra-incompressible (bulk modulus of 365–395 GPa) and hard compounds. Meanwhile, lately theoretical studies [7–12] also show that they are ultra-incompressible and metallic. Interestingly, OsB<sub>2</sub> and ReB<sub>2</sub> form different lattice structures: OsB<sub>2</sub> has an orthorhombic RuB<sub>2</sub>-type structure (space group *P*<sub>mmm</sub>, no. 59) [1,13], and ReB<sub>2</sub> crystallizes with the hexagonal ReB<sub>2</sub>-type structure [6] (space group *P* 6<sub>3</sub>/*mmc*, no. 194).

Since Os and Re are two neighboring 5*d* transition metals elements, it is desirable to investigate phase stability, electronic structure, and elastic properties of OsB<sub>2</sub> with the ReB<sub>2</sub>-type hexagonal structure. Our calculated hexagonal structure is only 0.048 eV higher in energy with the generalized gradient approximation (GGA) than the orthorhombic one at zero pressure. Because the two structures are so close in energy and the

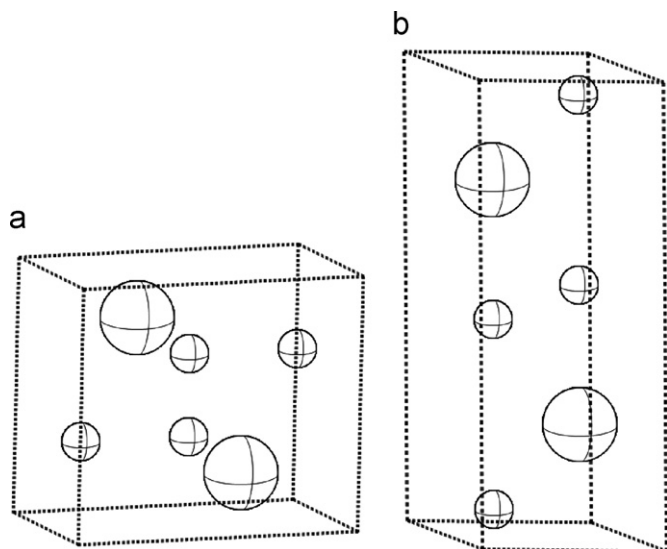
compressibility of OsB<sub>2</sub> is measured by using high-pressure X-ray diffraction in a Diacell diamond anvil cell from ambient pressure to 32 GPa [1], it is very interesting to explore whether the pressure-induced phase transition exists. Chen et al. [14] reported that the orthorhombic phase was found to transform into the hexagonal one for OsB<sub>2</sub> at 2.5 GPa with the local density approximation (LDA). However, common experience favors GGA for such estimates. On the other hand, OsB<sub>2</sub> was synthesized at 1000 °C [1]. Thus, it is necessary to consider thermal effect on the phase transition. However, to our knowledge, there is no report about it. With such motivations, we perform herein first-principles calculation and the quasi-harmonic approximation with the frozen phonon dynamical matrix method to study the phase transition behavior of OsB<sub>2</sub>. The phase stability, electronic structure, elastic properties, and the thermal effect of OsB<sub>2</sub> are compared and analyzed in detail.

### 2. Computation details

The present calculations were performed within the density functional theory, using the projector-augmented wave (PAW) method [15,16]. Computations were done using the Vienna *ab initio* simulation package (VASP) [17–19]. It is empirically known that GGA [20] can predict accurately the structural phase transition, so that GGA is used with PAW potential. The experimental structure data of orthorhombic OsB<sub>2</sub> with symmetry *Pmmn* were used as initial parameters. In the orthorhombic unit cell, two Os atoms are placed at the Wyckoff position of

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**Fig. 1.** Crystal structures of  $\text{OsB}_2$ : (a) the orthorhombic [space group  $Pmmn$ , no. 59] and (b) the hexagonal [space group  $P6_3/mmc$ , no. 194] structures. The large and small spheres represent the Os and B atoms, respectively.

$2a(\frac{1}{4}, \frac{1}{4}, z)$  and  $4f(u, \frac{1}{4}, v)$  for B atoms [13,21]. Hexagonal  $\text{OsB}_2$  has the same symmetry with  $\text{ReB}_2$  [11]. The hexagonal unit cell contains two  $\text{OsB}_2$  chemical formula unit (f.u.), two Os atoms are placed in  $2c(\frac{1}{3}, \frac{1}{3}, \frac{1}{4})$  and four B atoms in  $4f(\frac{1}{3}, \frac{2}{3}, z)$  positions, with  $z = 0.548$ . The size of the  $k$  mesh is chosen to be  $11 \times 15 \times 12$  and  $14 \times 14 \times 10$  for the orthorhombic structure and the hexagonal one, respectively. A plane wave cutoff energy of 500 eV is employed throughout to assure convergence. The structures are fully relaxed with the conjugate-gradient algorithm method and the force on each ion is smaller than 5 meV/Å. A three-dimensional drawing of the optimized hexagonal structure and the orthorhombic one is shown in Fig. 1. The frozen phonon dynamical matrix method is used to determine the normal-mode frequencies of ionic vibrations within the quasi-harmonic approximation.

### 3. Results and discussions

Table 1 lists the calculated structural parameters and relative total energy of  $\text{OsB}_2$ . Meanwhile, the available theoretical and experimental data are also tabulated in same table for comparison. From this table, it can be seen that our calculated equilibrium lattice parameters of the orthorhombic structure are in excellent agreement with the previous theoretical results and the experimental ones. Moreover, the hexagonal structure is only 0.048 eV higher in energy than the orthorhombic one at zero pressure. Since so small difference in energy between the two structures, it is valuable to explore the possibility of the structural phase transition between the orthorhombic structure and the hexagonal one under pressure. Consequently, the orthorhombic structure and the hexagonal one of  $\text{OsB}_2$  are optimized with increasing pressure (from  $-20$  to 40 GPa in 5 GPa steps). The results are summarized in Fig. 2. As seen in the figure, the equilibrium volume for the hexagonal structure is smaller, but the total energy is higher than those for the orthorhombic one. Furthermore, at smaller volumes, i.e., higher pressures, the cross of the total energy curves for the two structures indicates that, upon compression, the orthorhombic structure can transform into the hexagonal one. The pressure value for the transition from the orthorhombic phase to the hexagonal one can be estimated by calculating the dependence of the enthalpy

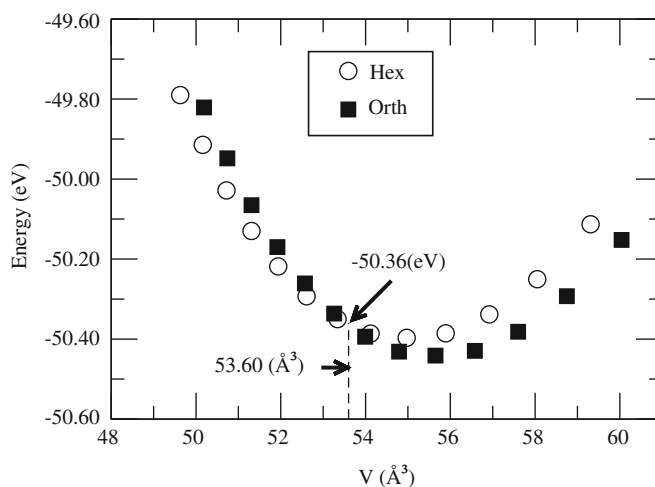
**Table 1**

Equilibrium volume  $V_0$  (in Å<sup>3</sup>), relative total energy  $\Delta E_0$  (in eV) per unit cell, equilibrium lattice constants (in Å) for  $\text{OsB}_2$ .

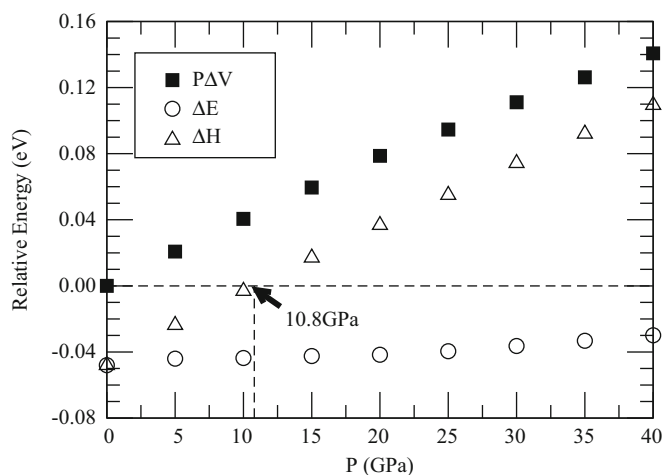
	This work		Theory <sup>a</sup>	Expt. <sup>b</sup>
	Orth	Hex	Orth	Orth
$a$	GGA 4.703	GGA 2.941	GGA 4.705	4.684
$b$	2.890		2.895	2.872
$c$	4.094	7.338	4.096	4.076
$V_0$	55.64	54.97	55.78	54.80
$\Delta E_0$	0	0.048		

<sup>a</sup> Ref. [10].

<sup>b</sup> Ref. [13].



**Fig. 2.** Dependence of total energy  $E_{tot}$  with cell volume  $V$  per formula unit cell for the orthorhombic structure and the hexagonal one.



**Fig. 3.** Enthalpy difference  $\Delta H$  (triangle up), the total energy difference  $\Delta E$  (circles) and the product of cell volume and pressure difference  $P\Delta V$  (square) for the orthorhombic phase relative to the hexagonal one of  $\text{OsB}_2$  as a function of the applied pressure with GGA.

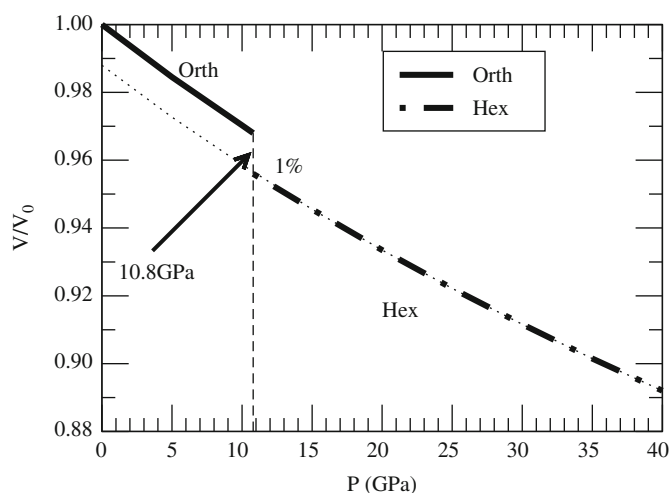
(defined as  $H = E + PV$ , where  $E$  is the total energy for the particular pressure  $P$  at volume  $V$ ) difference ( $\Delta H = H_{orth} - H_{hex}$ ) as a function of the applied pressure with GGA (as shown Fig. 3). Apparently at 10.8 GPa, it can be seen in this figure that a pressure-induced phase transition takes place from the orthorhombic phase to the hexagonal one. In order to check the

convergency of the cutoff energy for the transition pressure, we performed same calculations with 600 eV of cutoff energy and find that the phase-transition pressure does not change. Chen et al. [14] also reported that the orthorhombic phase was found to transform into the hexagonal one for OsB<sub>2</sub> at 2.5 GPa with LDA. While the phase transition was not observed even at 32 GPa in the experiment, which is the most likely due to a high kinetic barrier. We have tried to calculate the kinetic barrier, unfortunately, because the path of pressure-induced phase transition in OsB<sub>2</sub> is so complicated that the calculation cannot go on smoothly. We expect it can be further confirmed by the experimental work.

Our calculated enthalpy shows that the orthorhombic–hexagonal structural phase transition can occur at 10.8 GPa with GGA. Moreover, the structures reported for other 5d transition-metal diborides TM B<sub>2</sub> (TM = Hf, Ta, W, Re, Ir) have been also selected to check the possibility phase transition among them. The calculated results show that their enthalpies are always larger than that of the orthorhombic one with increasing pressure (up to 50 GPa).

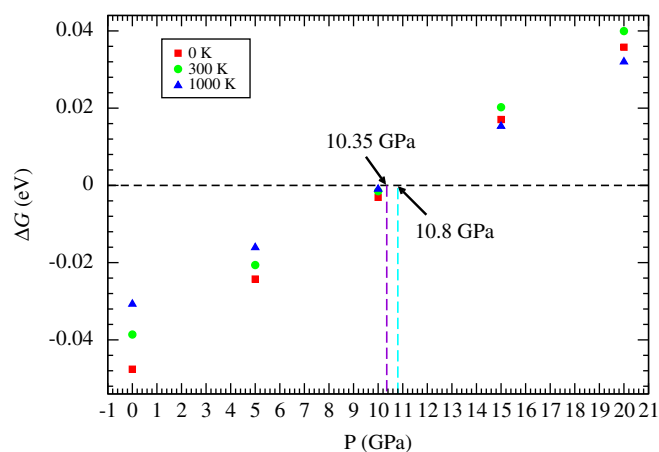
In order to further understand the phase transition behavior of OsB<sub>2</sub>, we also plotted the total energy difference ( $\Delta E$ ) and the product of cell volume and pressure difference ( $P\Delta V = P(V_{hex} - V_{orth})$ ) in Fig. 3. As seen in this figure, with increasing pressure, there is no noticeable change in  $\Delta E$ , while the value of  $P\Delta V$  increases monotonously with the same  $\Delta H$ . Thus the change of  $\Delta H$  is mainly due to the change of  $P\Delta V$ , which can be understood from the higher bulk modulus of the hexagonal phase (presented in Table 2). The higher bulk modulus of the hexagonal structure means that its volume less reduces with increasing pressure than the orthorhombic one. Consequently, we conclude that the pressure induced structural phase transition of OsB<sub>2</sub> is originated from the less compressibility of the hexagonal phase than the orthorhombic one. In addition, the calculated relationship between the pressure and volume for the two phases is shown in Fig. 4. It is clear to see in this figure that during the transition region, there is a volume collapse of 1%, which is usually accompanied with the structural phase transition by breaking and transformations of chemical bonds between atoms and reconstructions of anion and cation sublattices.

As we know, OsB<sub>2</sub> was synthesized at 1000 °C and its compressibility was measured by using high-pressure X-ray diffraction in a Diacell diamond anvil cell from ambient pressure to 32 GPa [1]. However, there is no phase transition was observed experimentally. So, we doubt that the disagreement between the

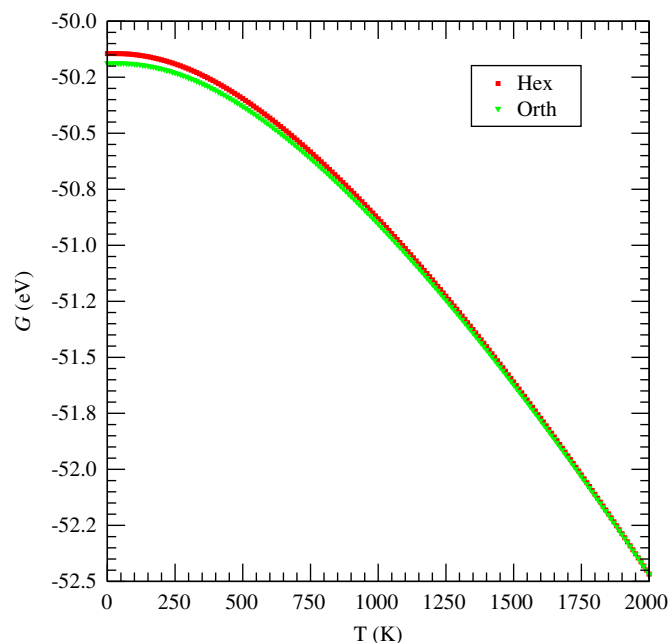


**Fig. 4.** Cell volume of OsB<sub>2</sub> in the hexagonal phase and the orthorhombic one as a function of pressure with GGA. The lines in this figure are obtained by fitting the volume–pressure data points to the third-order Birch–Murnaghan equation of states.

theory and experiment is mainly due to the thermal effect. Here, we employ the quasi-harmonic Debye model to calculate the Gibbs free energy  $G$  ( $G = E + PV + F_{phonon}$ ,  $F_{phonon}$  is Helmholtz free energy of phonon system which is calculated by VASP) of the hexagonal structure and the orthorhombic one of OsB<sub>2</sub> with increasing pressure (from 0 to 40 GPa) and temperature (from 0 to 2000 K). The Gibbs energy difference ( $\Delta G = G_{orth} - G_{hex}$ ) between the hexagonal structure and the orthorhombic one of OsB<sub>2</sub> at 0, 300, and 1000 K as a function of pressure is shown in Fig. 5. Under zero pressure (shown in Fig. 6), there are no intersection between the two phases and  $\Delta G$  is negative in the whole considered temperature range, which means that the temperature phase transition from the orthorhombic structure to the hexagonal one does not occur within this range of temperature. As shown in Fig. 5, at  $T = 300$  and 1000 K the pressure-induced phase transition takes place at 10.35 GPa. (The calculated phase transition pressure is also 10.35 GPa at other temperature,

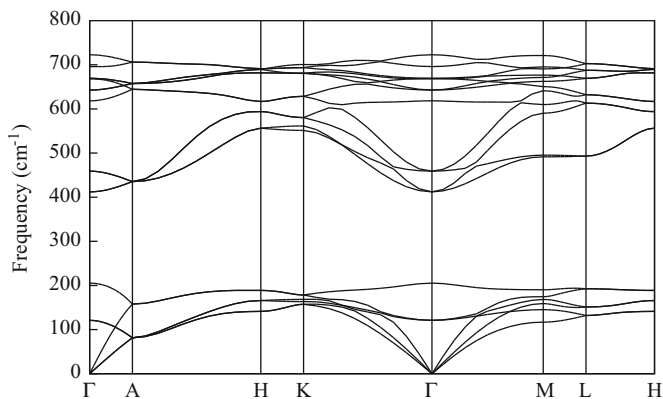


**Fig. 5.** (Color online) The Gibbs energy difference  $\Delta G$  for the orthorhombic phase relative to the hexagonal one of OsB<sub>2</sub> as a function of the applied pressure with GGA at 0, 300, and 1000 K.

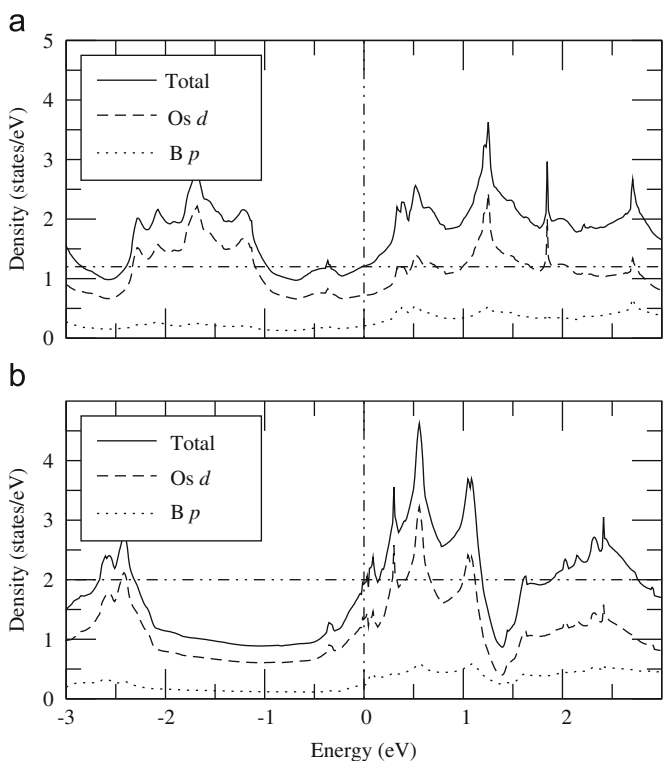


**Fig. 6.** The Gibbs free energy  $G$  for the orthorhombic phase and the hexagonal one of OsB<sub>2</sub> as a function of the applied temperature with GGA at 0 GPa.

which is not given in this manuscript.) These results mean that the phase transition pressure is little affected by the thermal effect and it is a pure pressure-induced structural phase transition.



**Fig. 7.** Calculated phonon band structure of the hexagonal OsB<sub>2</sub>. The special k points A, H, K, M, and L in this figure represent the points  $(0, 0, \frac{1}{2})$ ,  $(-\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ ,  $(-\frac{1}{3}, \frac{2}{3}, 0)$ ,  $(0, \frac{1}{2}, 0)$ , and  $(0, \frac{1}{2}, \frac{1}{2})$ , respectively.



**Fig. 8.** Total and partial DOS of OsB<sub>2</sub> at zero pressure: (a) the orthorhombic and (b) hexagonal phases. The Fermi level is at zero.

To our knowledge, there is no experimental report about the existence of hexagonal OsB<sub>2</sub>. Thus, it is necessary to check its stability. Its phonon frequencies along symmetric lines in hexagonal Brillouin zone were computed by the ABINIT code [22] and the result is shown in Fig. 7. The calculations for the phonon dispersion were performed by the PWP method with GGA (Fritz–Haber–Institute pseudopotentials). The optimized cell volume by the ABINIT code is 55.67 Å<sup>3</sup> and is very close to that by VASP, 55.64 Å<sup>3</sup>, which proves the reliability of ABINIT code. The calculated phonon band structure shows no soft phonon induced instability, further confirming the stability of OsB<sub>2</sub> with the hexagonal *P* 6<sub>3</sub>/*mmc* structure.

Now we turn to study the electronic structure of hexagonal OsB<sub>2</sub>. The total and partial density of states (DOS) of OsB<sub>2</sub> in the orthorhombic and the hexagonal phases were calculated with GGA and are plotted in Fig. 8. As seen in Fig. 8(a) and (b), at zero pressure, DOS near the Fermi level in the orthorhombic phase is much lower than the hexagonal one, which is beneficial for lowering the total energy of the orthorhombic phase. Therefore, the orthorhombic structure is more stable than the hexagonal one at zero pressure.

The elastic constants can provide useful information of the stability and stiffness for materials. We calculated the elastic constants of hexagonal OsB<sub>2</sub> and list them in Table 2. For comparison, the calculated elastic constants of the orthorhombic structure with the same method are also listed in same table. The elastic constants were estimated via the strain–stress method. The bulk and shear moduli in this table were calculated with the Voigt–Reuss–Hill approximation [23]. It can be observed in Table 2 that our obtained elastic constants of orthorhombic OsB<sub>2</sub> compare well with the previous theoretical results. Moreover, the calculated eigenvalues of the elastic constants matrix of the two structures are all positive, which confirms that the hexagonal and orthorhombic structures of OsB<sub>2</sub> are both mechanically stable. It is interesting to note that the hexagonal structure of OsB<sub>2</sub> has a higher bulk modulus than the orthorhombic one, which implies that hexagonal OsB<sub>2</sub> is also incompressible. From Table 1, it can be found that the optimized cell volume of the hexagonal structure is smaller than that of the orthorhombic one, which actively contributes to its higher bulk modulus. We find that both the hexagonal and orthorhombic structures have unusually high incompressibility along the *c* axis, as demonstrated by the extremely large *C*<sub>33</sub> values (as seen Table 2). Also, it is interesting to note that the shear elastic constant *C*<sub>44</sub> of the hexagonal structure (209 GPa) is much larger (by about 129 GPa) than that of the orthorhombic one (80 GPa). The large elastic constant *C*<sub>44</sub> means the strong ability of resisting the monoclinic shear distortion in (100) plane. The high shear modulus of hexagonal OsB<sub>2</sub> partially results from its large *C*<sub>44</sub>.

#### 4. Conclusions

The possibility of the structural phase transition of OsB<sub>2</sub> has been investigated by the first-principles calculations. The calcu-

**Table 2**  
Elastic constants (in GPa), bulk modulus *B* (in GPa), shear modulus *G* (in GPa), Young's modulus *E* (in GPa), Poisson's ratio *ν*, and *G/B* for OsB<sub>2</sub>.

		<i>C</i> <sub>11</sub>	<i>C</i> <sub>12</sub>	<i>C</i> <sub>13</sub>	<i>C</i> <sub>22</sub>	<i>C</i> <sub>23</sub>	<i>C</i> <sub>33</sub>	<i>C</i> <sub>44</sub>	<i>C</i> <sub>55</sub>	<i>C</i> <sub>66</sub>	<i>B</i>	<i>G</i>	<i>E</i>	<i>ν</i>	<i>G/B</i>
This work	Orth	565	181	184	539	136	759	80	198	195	314	183	461	0.26	0.58
	Hex	461	177	236			873	209		142	326	207	513	0.24	0.63
Theory <sup>a</sup>	Orth	597	198	206	581	143	825	70	212	201	344	194	490	0.26	

<sup>a</sup> Ref. [10].

lated enthalpy and the Gibbs energy as a function of pressure and temperature show that there is a pressure induced phase transition at 10.8 GPa with GGA between the orthorhombic phase and the hexagonal one. Our calculated results show that the phase transition pressure is little affected by the thermal effect. Lack of soft mode at any wavevectors of the phonon band structure indicates that hexagonal OsB<sub>2</sub> is stable. The hexagonal structure has higher bulk and shear moduli than the orthorhombic one. It is the less compressibility of the hexagonal structure that supplies the driving force for the pressure induced phase transition of OsB<sub>2</sub>. We hope that our calculations will further stimulate the more experimental and theoretical research on the pressure induced phase transition of the 5d transition-metal nitrides and borides.

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