

Experimental and Theoretical P-V-T Equation of State for Os₂B₃

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Abstract

Thermoelastic behavior of transition metal boride Os₂B₃ was studied under quasi-hydrostatic and isothermal conditions in a Paris-Edinburgh cell to 5.4 GPa and 1273 K. *In-situ* Energy Dispersive X-ray diffraction was used to determine interplanar spacings of the hexagonal crystal structure and thus the volume and axial compression. *P-V-T* data were fitted to a 3rd Order Birch-Murnaghan equation of state with a temperature modification to determine thermal elastic constants. The bulk modulus was shown to be $K_0 = 402 \pm 21$ GPa when the first pressure derivative was held to $K_0' = 4.0$ from the room temperature *P-V* curve. Under a quadratic fit $\alpha = \alpha_0 + \alpha_1 T - \alpha_2 T^{-2}$, the thermal expansion coefficients were determined to be $\alpha_0 = 1.862 \times 10^{-5} \text{ K}^{-1}$, $\alpha_1 = 0.841 \times 10^{-9} \text{ K}^{-2}$, and $\alpha_2 = -0.525 \text{ K}$. Density functional theory (DFT) with the quasi-harmonic approximation (QHA) were further employed to study Os₂B₃, including its *P-V-T* curves, phonon spectra, bulk modulus, specific heat, thermal expansion, and the Grüneisen parameter. A good agreement between the first-principle theory and experimental observations was achieved, highlighting the success of the Armiento-Mattsson 2005 generalized gradient approximation functional employed in this study and QHA for describing thermodynamic properties of Os₂B₃.

Introduction

There has been a renewed interest in the elastic properties and equation of state of incompressible transition metals like rhenium and osmium due to reported structural anomalies as well as due to their use as x-ray pressure standards in studies on materials under extreme conditions [1-4]. In addition, rhenium and osmium boride family of materials have shown unique mechanical properties with bulk moduli well into the multi-megabar region and high shear strength and thermal stability. The mechanical properties of transition metal borides have been attributed to a combination of high electron density and strong covalent bonding due to intercalated boron layers in the hexagonal structure [5]. Os₂B₃ has been studied recently with neutron diffraction technique and ambient temperature equation of state studies have been carried out to 358 GPa [6-7] exhibiting anisotropic compression to the highest pressure. However, effects of high temperatures on its volume and anisotropic compression of Os₂B₃ have not been investigated so far. Os₂B₃ is somewhat analogous to another transition metal boride ReB₂, as both have hexagonal structures and similar bulk moduli values, although ReB₂ has received more extensive electronic and thermal studies [8-10]. There is continued interest in Os₂B₃ being used for applications requiring strong deformation resistance and stability under high-pressure high-temperature environments.

In this paper, we study the thermoelastic behaviors of Os_2B_3 , including the elastic moduli and volume expansion/compression under simultaneous P - V - T conditions, via both high-pressure experiments and first-principles simulations. The Paris-Edinburgh press at the Advanced Photon Source, Beamline 16-BM-B, Argonne National Laboratory, can provide a robust method of *in-situ* X-ray diffraction, radiography, sound velocity measurements, and heating. X-ray diffraction allows for sample interplanar spacing and structure factor determination, and X-ray radiography can determine sample dimensions under compression in tandem with pulse-echo sound measurements. Our first-principles calculations based on density functional theory and the quasi-harmonic approximation also provide further validations and predictions of the experimental results.

Experimental Methods

High pressure and high temperature studies on Os_2B_3 were conducted at the Advanced Photon Source, Beamline 16-BM-B, Argonne National Laboratory. The bending magnet at Beamline 16-BM-B utilizes a white X-ray multi-angle energy dispersive X-ray diffraction (EDXD) for determination of sample interplanar spacing with X-ray energies ranging between 5-120 KeV. This can be combined with radiography imaging, heating, and ultrasonic measurements for a robust analysis into elastic constants and sample crystal structure under simultaneous pressure-temperature environments. Two tungsten carbide anvils were used in a Paris-Edinburgh (PE) large-volume press [Fig 1(a)] to compress a cylindrical pellet of Os_2B_3 with initial dimensions 0.9 mm in height and 1.5 mm in diameter [Fig 1(b)]. The sample pellet sits within a thermally insulating gasket comprised of an outer layer of boron epoxy and an inner layer of MgO, the latter of which is used for pressure calibration. Along the compression axis, an alumina (Al_2O_3) buffer rod is placed between the WC anvil and the sample. This allows for ease of radiography positioning to determine the size and shape of the sample during compression experiments. Zirconia (ZrO_2) caps are placed on the top and bottom of the sealing gasket to hold the alumina rod in place. A diagram of the PE press setup can be seen in Fig. 1(a) and in other relevant literature [11-13]. For temperature control, a graphite sleeve heater was fitted radially around the compression axis and the sample. Compression and heating experiments were done systematically by holding temperature constant and compressing in increasing steps of 400 psi, corresponding to about a 0.3 GPa increase per compression step. The PE cell would then be decompressed after maximum pressure was reached (3-5 GPa). This was repeated for temperatures at 298 K, 673 K, 873 K, 1073 K, and 1273 K. EDXD and radiography images of the sample were taken at each pressure step. 2θ angle was calibrated using 50-micron gold wire and held constant at 15.0167 ± 0.0012 degrees.

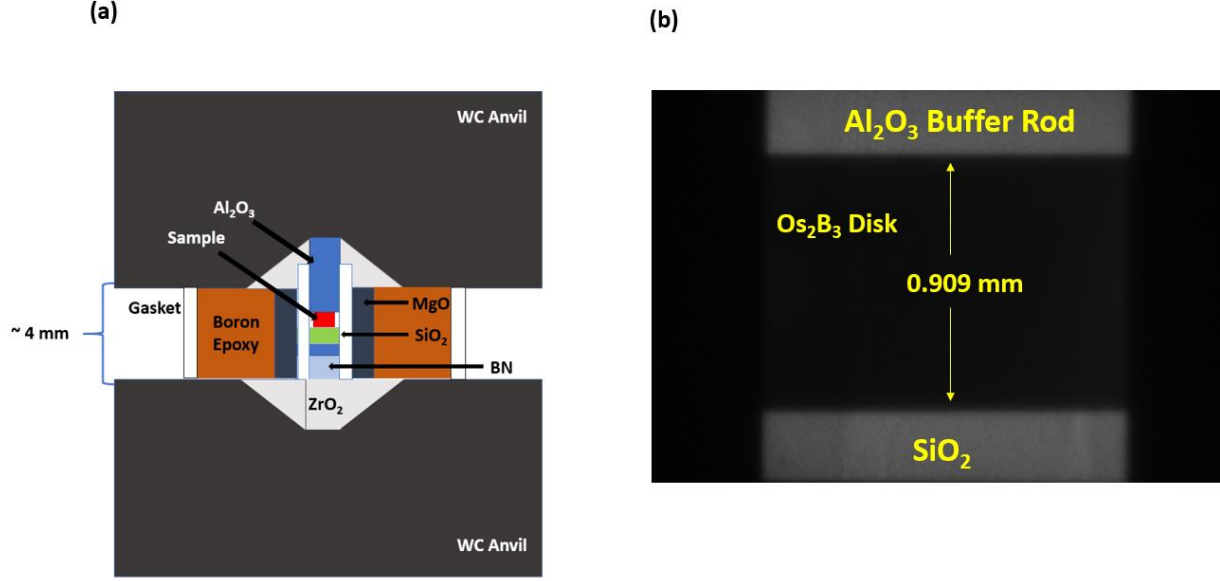


Figure 1: (a) Schematic diagram of the Paris-Edinburgh cell employed for high-pressure high-temperature measurements at the Advanced Photon Source, Beamline 16-BM-B, Argonne National Laboratory. (b) Radiography image of the initial Os_2B_3 sample before compression and temperature changes.

EDXD data was analyzed using hpMCA software to determine the observed d-spacings and structure factor (Q) values of the relevant hkl diffraction peaks for the Os_2B_3 sample. A sum of least squares fit was then used to determine the lattice parameters for the hexagonal Os_2B_3 crystal structure. Pressure was determined using MgO pressure calibrant taken from the P - V - T relations of MgO determined by Kono *et al.* 2010 [11]. The pressure measurements from MgO and the volume compression taken from the lattice parameters were employed in the 3rd order Birch-Murnaghan equation of state (BM EoS):

$$P(V) = \frac{3}{2} K_0 \left[x^{\frac{7}{3}} - x^{\frac{5}{3}} \right] \left[1 + \frac{3}{4} (K'_0 - 4) \left(x^{\frac{2}{3}} - 1 \right) \right] \quad (1)$$

where the bulk modulus is given by K_0 , the first pressure derivative by K'_0 , and $x = V_0/V$. The 3rd order BM EoS was given a temperature modification by Fei 1995 [14] thermal expansion model shown in Equation (2):

$$V_{0T} = V_{00} \exp \left(\alpha_0 (T - T_{ref}) + \frac{1}{2} \alpha_1 (T^2 - T_{ref}^2) - \alpha_2 \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right) \quad (2)$$

Here, the thermal expansion coefficients are labeled as α_0 , α_1 , and α_2 respectively. The thermal expansion is expressed in quadratic terms given by $\alpha = \alpha_0 + \alpha_1 T - \alpha_2 T^{-2}$, where the sign in front of α_2 is held negative to compare with theoretical models.

Computational Methods

First-principles calculations based on density functional theory (DFT) [15-16] and plane-wave pseudopotential method were performed using the Vienna Ab initio Simulation Package (VASP, version 5.4.4) [17-18]. The projector augmented wave (PAW) method [19-20] was

adopted for greater computational efficiency, and the cut-off energy for expanding the plane wave basis was set to 640 eV. The Armiento-Mattsson 2005 generalized gradient approximation (GGA-AM05) functional [21,22,23] was chosen for the DFT simulation, which provides a better theory-experiment agreement. The sampling integration of the Brillouin zone was performed by the Monkhorst-Pack Γ -centered method [24] with a $31 \times 31 \times 7$ (resolution = $0.01 \times 2\pi/\text{\AA}$) k-point mesh. The self-consistent convergence criterion of total energy was set to 10^{-6} eV/unit cell, and the structure relaxation convergence criterion of atomic force was set to 10^{-3} eV/ $\text{\AA}$.

In our calculation, we first performed full crystal structure relaxation to obtain the optimized equilibrium structure of Os_2B_3 at zero pressure and zero temperature. To study thermodynamic properties, we then computed the total energies for different unit cell volumes, ranging from -15% to +15% of the volume of the fully relaxed cell, with a step size of 3%. For each cell, we fixed the volume and fully relaxed the ionic positions and cell shape. Next, we used a $2 \times 2 \times 2$ supercell with the density functional perturbation theory (DFPT) method as implemented in VASP to compute the force constants, which were then used to compute the phonon spectra by the Phonopy package [25] for each cell volume. DFPT results usually converge better compared to the direct method of frozen-phonon (finite difference) approach using the same supercell size. The calculations were performed with a $61 \times 61 \times 61$ phonon q-point mesh.

Finally, the Phonopy-QHA (quasi-harmonic approximation) code [26,27] was utilized to evaluate thermodynamic quantities of Os_2B_3 , such as the pressure dependence of volume at various temperatures, heat capacity, thermal expansion, and the Grüneisen parameter. QHA is an efficient approach for accessing the P - T phase diagram and calculating thermodynamic properties at arbitrary pressures and temperatures [28]. Within QHA, the Gibbs free energy to be minimized is written as $G = E_0 + F_{\text{vib}} + PV = E_0 + F_{\text{zp}} + F_T + PV$. Here, E_0 is the static total internal energy, F_{zp} is the zero-point contribution from lattice vibration that is present at zero Kelvin, and F_T is the temperature dependence of the vibrational free energy, which can be expressed as

$$F_T(V, T) = k_B T \sum_{\mathbf{k}, \nu} \ln \left\{ 1 - \exp\left(-\frac{\hbar \omega_{\mathbf{k}\nu}}{k_B T}\right) \right\}, \quad (3)$$

where k_B is the Boltzmann's constant, $\hbar$ is the Plank's constant, and $\omega_{\mathbf{k}\nu}$ is the phonon frequency at wavevector $\mathbf{k}$. Therefore, F_T can be obtained by calculating the harmonic phonon modes $\omega_{\mathbf{k}\nu}$.

Results and Discussion

Figure 2 shows the representative EDXD spectra for pressure calibrant MgO and sample Os_2B_3 at high pressures and high temperatures. Two sample diffractions patterns are shown: The bottom one was taken at the lowest pressure during compression at room temperature, and the top one was taken at the highest pressure and highest temperature achieved (5.4 GPa and $T = 1273$ K, respectively). The Os_2B_3 is assigned a hexagonal crystal structure, which is evidenced in Fig. 2(b) by the hkl peaks labeled (101), (103), (006), (104), (105), (106), (107), (108), etc. The ambient pressure hexagonal phase of Os_2B_3 was found to be stable to 5.4 GPa and 1273 K. The pressure and temperatures of the two EDXD profiles in Fig. 2(b) correspond to the pressures and temperatures marked by the MgO peaks in Fig. 2(a). The red asterisks label an OsB_2 impurity found within the sample material.

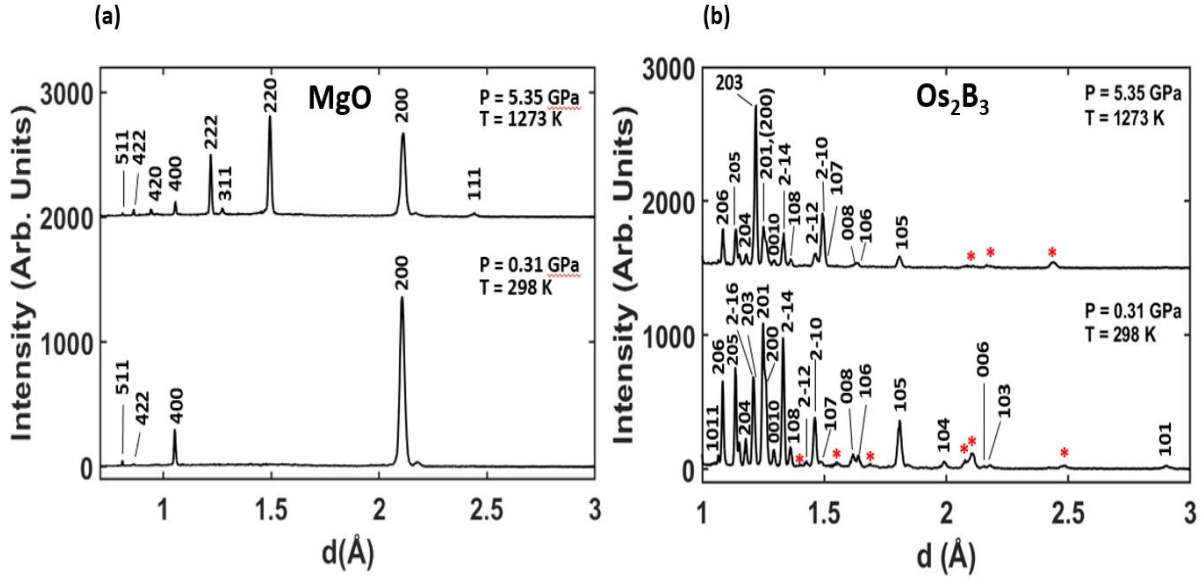


Figure 2. (a) EDXD patterns of MgO pressure marker at 0.31 GPa with ambient temperature (bottom), and 5.35 GPa at 1273 K (top). (b) EDXD patterns of Os_2B_3 with the corresponding pressures and temperatures from the MgO pressure marker in (a). Red asterisks (*) label a minor OsB_2 impurity phase present in the sample.

Figure 3 shows the thermal equation of state (EoS) model given by Eqs. (1) and (2) fitted to the Os_2B_3 P - V - T plot. From the ambient temperature P - V data, the bulk modulus and its first pressure derivative were calculated to be $K_0 = 402 \pm 21$ GPa and $K_0' = 4.0$, respectively. When K_0' is allowed to freely vary, the bulk modulus was slightly lower at 358 ± 23 GPa with the first pressure derivative $K_0' = 3.3$. The somewhat large error and the difference in moduli values is likely attributed to the low pressures reached compared to the shear strength of the material. This results in the very linear P - V curves seen here and is attributed to the apparent disparity in K_0 derivation. It is inferred then that the real value of the bulk modulus lies somewhere between 358-402 GPa, which is agreeable with the previous non-hydrostatic study showing a $K_0 = 397$ GPa. The experimental ambient temperature initial volume V_0 was measured to be $95.133 \pm 0.004 \text{ \AA}^3$, which is slightly higher than the previously reported ambient volume of $95.076 \text{ \AA}^3$ [6]. This is seen in Table 1 along with the calculated bulk modulus and volume data for each temperature step. The first pressure derivative was held to $K_0' = 4.0$ for each calculation. Under a quadratic fit of thermal expansion $\alpha = \alpha_0 + \alpha_1 T - \alpha_2 T^{-2}$, the experimental thermal expansion coefficients were calculated to be $\alpha_0 = 1.862 \times 10^{-5} \text{ K}^{-1}$, $\alpha_1 = 0.841 \times 10^{-9} \text{ K}^{-2}$, and $\alpha_2 = -0.525 \text{ K}$.

Table 1: The fitted values of Bulk Modulus and ambient pressure Volume for Os_2B_3 at various temperatures

Temperature (K)	Bulk Modulus (GPa)	V/V_0
300K	402 ± 21	1.006 ± 0.004
673K	366 ± 11	1.008 ± 0.003
873K	328 ± 11	1.013 ± 0.004
1073K	287 ± 13	1.039 ± 0.004
1273K	255 ± 13	1.024 ± 0.005

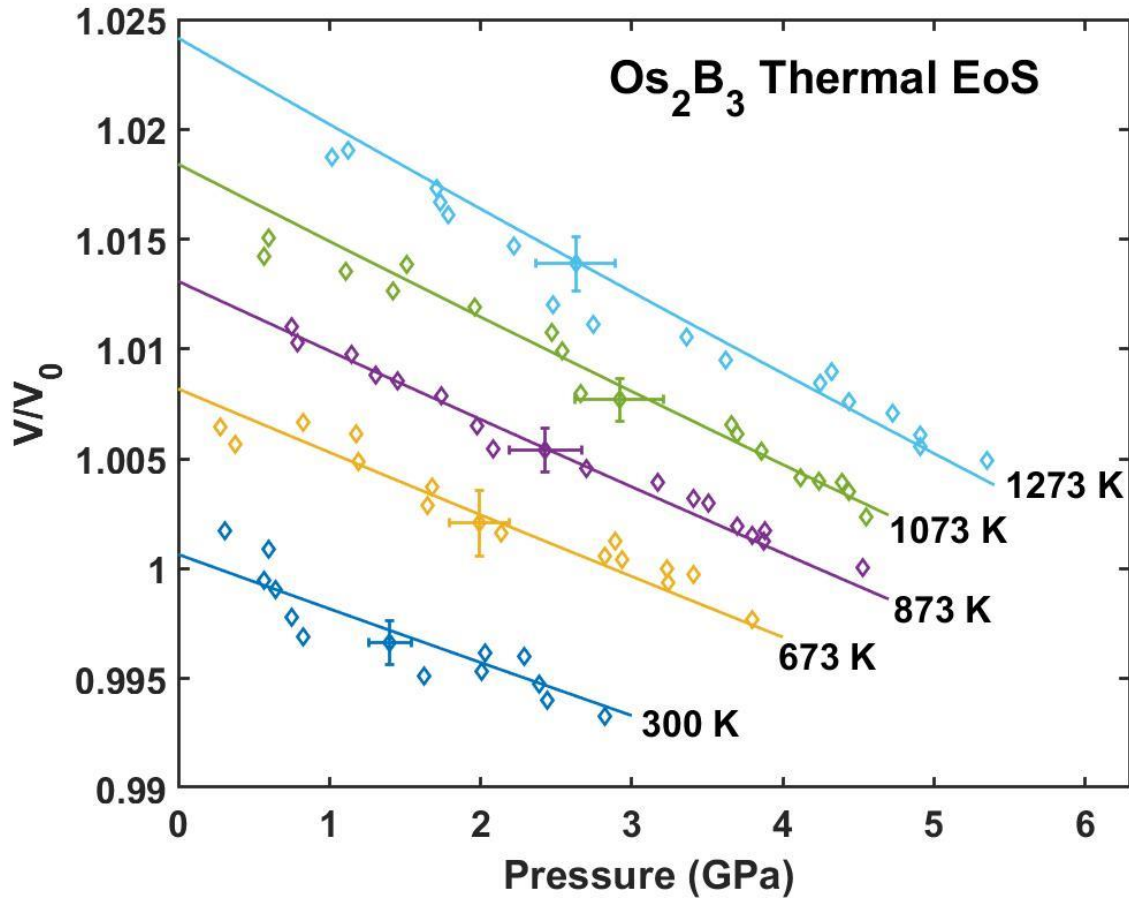


Figure 3: The measured isothermal equation of state of Os_2B_3 at various temperatures. The solid lines are fits to the experimental data to a thermal equation of state described in the text.

The large volume PE cell at Beamline 16 BM-B allows for a quasi-hydrostatic compression of sample materials by utilizing the cylindrical shape of the concentric gasket materials indicated in Fig. 1(a). In the x-ray diffraction studies on Os_2B_3 to ultrahigh pressure to 358 GPa in a diamond anvil cell, it was observed that the hexagonal a -axis was more compressible than the hexagonal c -axis [6]. As a result of this anisotropic compression, axial ratio (c/a) was observed to increase with increasing pressure and this trend was observed to the highest pressure of 358 GPa. Figure 4 shows

the measured c/a axial ratio for Os₂B₃ to pressures of 5.4 GPa and temperatures of 1273 K. In this pressure-temperature range, we did not document any discernible trends in the c/a axial ratio indicating isotropic behavior is likely due to the limited compression achieved in the present series of experiments.

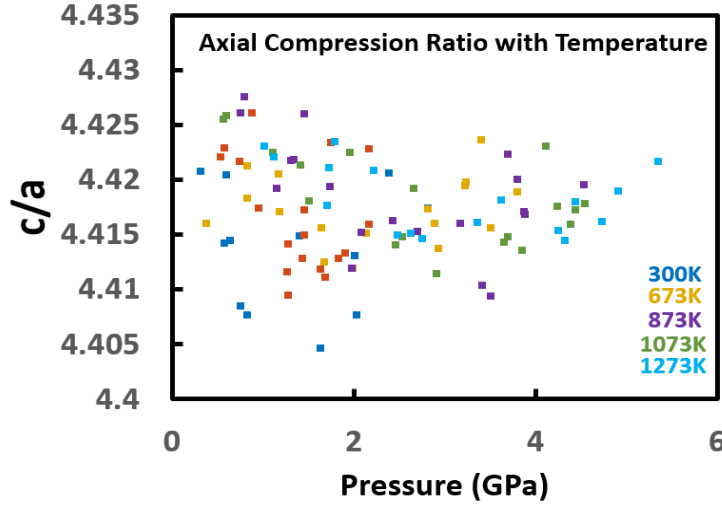


Figure 4: The measured c/a axial ratio for Os₂B₃ as a function of pressure at various temperatures. In the pressure-temperature range studied; the axial ratio does not show any discernible trend showing a nearly isotropic compression behavior.

We now shift our discussion to computational results obtained by the AM05 functional [21,22,23]. Figure 5 shows DFT calculations for the P - V - T curves of Os₂B₃ along with the experimental data. The calculations utilized the default Vinet EoS in Phonopy-QHA [26,27]. The overall computed trends as functions of pressure and temperature agree with the experiments. In our calculation, the equilibrium lattice parameter and volume (at zero pressure and zero temperature) are $a = 2.914 \text{ \AA}$, $c = 12.860 \text{ \AA}$, and $V_0 = 94.55 \text{ \AA}^3$, respectively, which are consistent with the experimental values and theoretical results in the literature [29,30]. We note that the discrepancy between DFT calculations and experimental data shown in Fig. 5 is at most 0.5%. Therefore, the AM05 functional with the quasi-harmonic approximation (QHA) can reasonably describe the P - V - T equation of states of Os₂B₃. We also have performed similar calculations using the Ceperley-Alder-Perdew-Zunger local density approximation (LDA) functional [31] and the Perdew-Burke-Ernzerhof GGA (PBE-GGA) functional [32]. As expected, the simulations [not shown] revealed that the lattice parameters were underestimated by LDA while overestimated by PBE-GGA. On the other hand, the AM05 functional – which considers uniform electron gas for local region and Airy gas for edge or surface region – was shown systematically to be capable of obtaining more accurate lattice parameters for solids [33]. AM05 also exhibits greater computational efficiency compared to other more advanced DFT functionals beyond GGA. Therefore, in our calculations, we focus on using the AM05 functional to compute other thermodynamic properties and the phonon spectra.

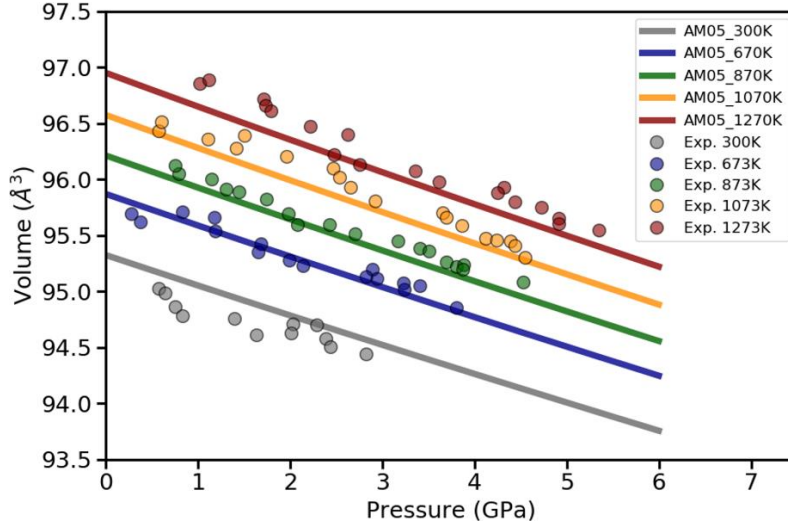


Figure 5: Comparison of theoretical P - V - T curves and experimental data of Os_2B_3 . The calculations were performed using the AM05 DFT functional and the quasi-harmonic approximation (QHA), together with the Vinet EoS in Phonopy-QHA. The theoretical temperature under consideration ranges from 300 K to 1270 K, and the maximal pressure is 6 GPa.

Figure 6 shows the theoretical phonon density of states (DOS) and dispersion for Os_2B_3 under different pressure and temperature conditions: 0 GPa and 300 K for panel (a), 3 GPa and 800 K for panel (b), as well as 6 GPa and 1300 K for panel (c). Overall, the phonon spectra show two clusters respectively in the energy ranges ~ 0 -7 THz and 14-23 THz, and they are well-separated by a gap of ~ 10 THz (or ~ 0.04 eV). As also shown in Fig. 6, there does not exist any negative phonon mode. These results confirmed that the Os_2B_3 structures for the temperature and pressure ranges under consideration are all dynamically stable.

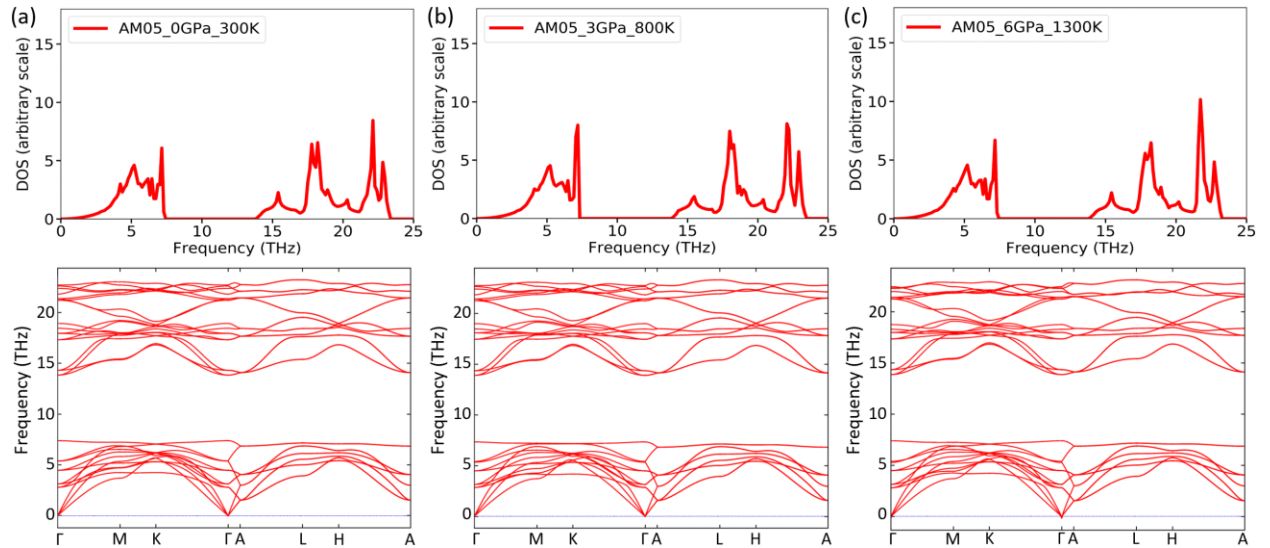


Figure 6: The phonon density of state (DOS) and corresponding phonon dispersion curves along high-symmetry directions in the Brillouin zone at different pressure and temperature: (a) 0 GPa and 300 K, (b) 3 GPa and 800 K, and (c) 6 GPa and 1300 K. The calculations were performed using the AM05 functional. All phonon modes are positive, indicating that all structures under study are dynamically stable.

We next discuss other thermodynamic quantities obtained within the quasi-harmonic approximation (QHA) as a function of temperature T (up to 2000K) and at zero pressure, using the Vinet EoS in Phonopy-QHA [26,27]. Figure 7(a) shows the computed volume $V(T)$, which can be expressed in a general form

$$V(T) = V_0 \exp \left(\int_{T_0}^T \alpha(T) dT \right), \quad (4)$$

where V_0 is unit cell volume at temperature T_0 , and α is the coefficient of thermal expansion. Above the room temperature, the volume increases $\sim$ linearly with temperature, indicating that the thermal expansion is dominated by the 3rd-order anharmonic effect. In QHA, the harmonic phonon model still holds for each given volume, but the phonon frequencies become volume-dependent, so the equilibrium volume at different temperature changes, which is the underlying cause of thermal expansion in QHA. Once $V(T)$ is known, mechanical properties can be computed as well. Figure 7(b) shows the temperature dependence of bulk modulus $K(T)$. Above room temperature, $K(T)$ is decreased $\sim$ linearly with increasing temperature, and $\left(\frac{\partial K}{\partial T}\right)_P$ is about -0.03 GPa/K. The computed $K(T = 0 \text{ K})$ bulk modulus value of 354 GPa is also comparable to the experimental data.

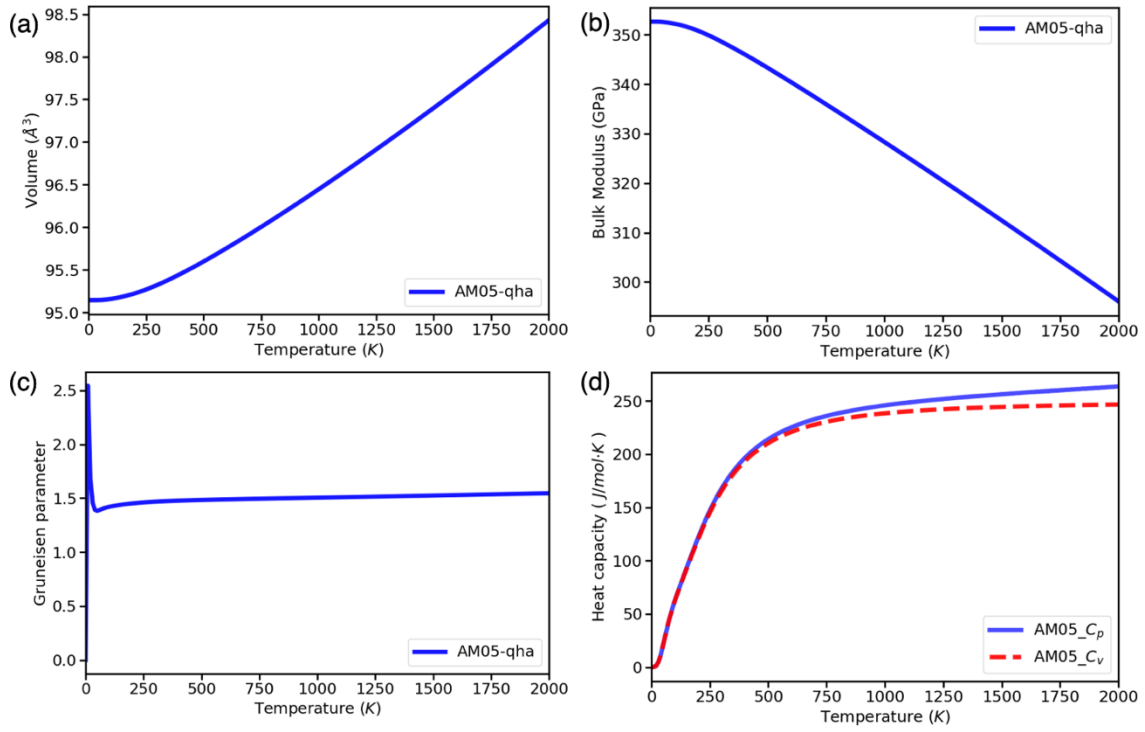


Figure 7: Temperature dependences of (a) volume, (b) bulk modulus, (c) thermal Grüneisen parameter, and (d) heat capacity for Os_2B_3 . The calculations were performed using the AM05 DFT functional and the quasi-harmonic approximation (QHA) at zero external pressure.

Based on the volume dependences of phonon frequencies $\omega_{kv}(V)$, we also can evaluate the Grüneisen parameters (or mode gammas) $\gamma_{kv} = -\frac{d \ln \omega_{kv}}{d \ln V}$, which in turn can be utilized to compute the thermal Grüneisen parameter γ . Another way to compute γ is by using the relation $\gamma = \frac{V \alpha K}{C_v}$,

which is used in Phonopy-QHA. Here, C_v is the constant-volume specific heat. Figure 7(c) shows that the computed thermal Grüneisen parameter has very weak temperature dependence, and the value remains at around 1.50 above $T = 200$ K. We note that if each mode gamma has the same value, then it is equal to the thermal Grüneisen parameter. In the Debye model [34], $\gamma = -\frac{1}{6} + 0.5 \frac{dK/dP}{K}$ (which is also called the Slater gamma [35]). If the experimental value of $K_0' = 3.26$ for Os_2B_3 is used, the Debye-Slater model then leads to a thermal Grüneisen parameter of 1.46, which is fairly close to our QHA calculation.

The computed constant-volume and constant-pressure heat capacities (C_v and C_p) of Os_2B_3 are shown in Fig. 8(d). Since $C_p = C_v(1 + \alpha\gamma T)$, the difference between C_v and C_p is negligible at low temperature, where the specific heat is known to be proportional to T^3 . At high temperature (compared to the Debye temperature ~ 600 K in our calculation), C_v is expected to saturate in accord with the Dulong-Petit law, while C_p continues to increase monotonically with temperature. Since the phonon DOS in Fig. 6 show two well-separated branches, this implies that the Debye model would tend to underestimate C_v at lower temperature T , and overestimate C_v at higher T .

Finally, we discuss the temperature dependence of the thermal expansion coefficient α . We first note that the thermal expansion can be related to other thermodynamic quantities via $\alpha = \frac{\gamma C_v}{V K}$. Since γ is near constant and T has an opposite effect on V and K , the temperature variation of α is expected to be dominant by C_v , as shown in Fig. 8(a). Therefore, α is proportional to $\sim T^3$ at low T and approaches constant (or shows weak temperature dependence) at T much higher than the Debye temperature. Also, since α is small at low T , C_v and C_p are expected to be similar below the Debye temperature. To compare the theoretical result with experiment, we also fitted the thermal expansion using a quadratic form $\alpha = \alpha_0 + \alpha_1 T - \alpha_2 T^{-2}$. As shown in Fig. 8(b), the fitted values of the theory curve are $\alpha_0 = 1.636 \times 10^{-5} \text{ K}^{-1}$, $\alpha_1 = 2.974 \times 10^{-9} \text{ K}^{-2}$, and $\alpha_2 = 0.4767 \text{ K}$, which are comparable to the experimental ones. It is also noted that the fitting (especially for the higher-order terms) can largely depend on the temperature range.

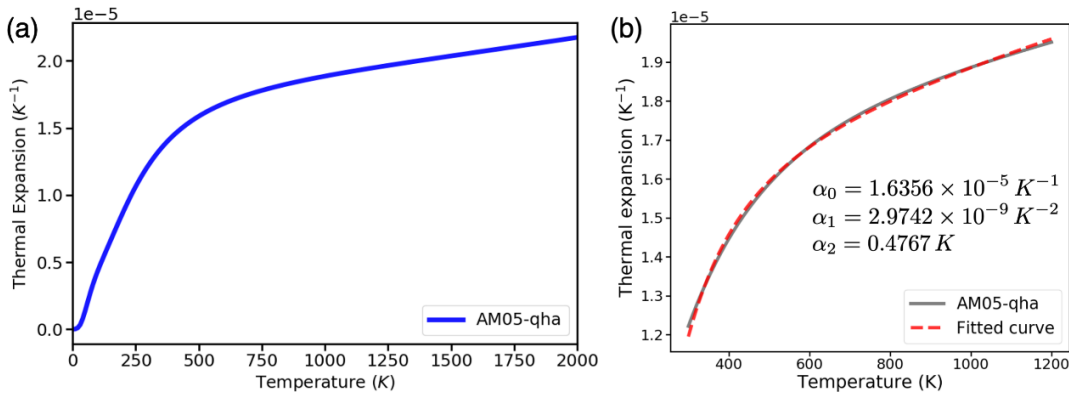


Figure 8: (a) Temperature dependence of thermal expansion for Os_2B_3 . The calculations were performed using the AM05 DFT functional and the quasi-harmonic approximation (QHA) at zero external pressure. (b) Fitting of the thermal expansion in the temperature range 300 K - 1200 K, using a quadratic formula $\alpha = \alpha_0 + \alpha_1 T - \alpha_2 T^{-2}$.

Conclusions

Quasi-hydrostatic compression measurements were conducted under isothermal conditions on the highly incompressible transition metal boride Os_2B_3 to a pressure of 5.4 GPa and temperatures up to 1273 K. The ambient pressure hexagonal phase of Os_2B_3 is observed to be stable to the highest pressures and temperatures achieved in this study. The compression of the hexagonal phase of Os_2B_3 was found to be nearly isotropic as evidenced by the measured c/a axial ratio. The bulk modulus was shown to be $K_0 = 402$ GPa with a fixed value of pressure derivative $K'_0 = 4.0$ by fitting with a 3rd-order Birch Murnaghan equation of state (BM EoS). The thermal expansion coefficients were also obtained by applying a Fei 1995 temperature modification to the 3rd-order BM EoS. These values were given as $\alpha_0 = 1.862 \times 10^{-5} \text{ K}^{-1}$, $\alpha_1 = 0.841 \times 10^{-9} \text{ K}^{-2}$, and $\alpha_2 = -0.5254 \text{ K}$, using a quadratic thermal expansion form $\alpha = \alpha_0 + \alpha_1 T - \alpha_2 T^{-2}$. Density functional theory calculations using the GGA-AM05 functional and the quasi-harmonic approximation also have shown good agreements with the experimental data on bulk modulus, pressure derivative, and thermal expansion coefficients. Our results suggest that Os_2B_3 can be a promising material for applications in extreme temperature and pressure conditions where high shear strength is desired while maintaining structural stability.

Acknowledgments

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