

# High pressure study on the phonon spectra and thermal properties in hafnium nitride and zirconium nitride

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**Abstract** We report ab initio calculations of the thermal properties for transition metal nitrides, hafnium and zirconium nitride at ambient and high pressures. The assessment of thermodynamical properties like lattice specific heat, vibrational energy, internal energy and entropy for two nitrides has been carried out. The basic calculations of ingredient phonon density of states for the determination of thermal properties have been done using density functional perturbation theory including external perturbations like strains and electric fields in periodic systems. The ground state properties such as equilibrium lattice constants and bulk modulus obtained for two nitrides are in good agreement with the available experimental value. The calculated pressure variation of the phonon density of states shows trend similar to the experimental pressure dependent Raman spectra. The lattice specific heat, internal energy, entropy and Helmholtz energy increases with pressure.

**Keywords** Density functional theory · Phonon density of states · High pressure · Thermal properties

## Introduction

The early transition metal mononitrides crystallize in the rock-salt structure and are known as refractory compounds. They exhibit extreme and unique physical properties of hardness, brittleness, high melting point, and in several of these compounds, a relatively high superconducting transition temperature [1]. Because of these properties, they

have technological applications in the area of hard coatings for cutting tools and magnetic storage devices. Recently, these compounds are also being investigated to understand their role in thermoelectric applications [2, 3]. The thermoelectric applications and high melting point of any material is the consequence of some special characteristics of phonon spectra and hence the phonon dispersion curves, thermal properties such as lattice specific heat, internal energy, entropy, etc. are of great importance. Recently, the phonon dispersion curves of HfN and ZrN have been obtained using inelastic neutron scattering which shows anomalous behaviour such as steep slopes of acoustic phonon branches near zone centre of Brillouin zone and a large gap between optic and acoustic phonon branches. This anomalous character of phonon dispersion leads to hardness and high melting point. Despite a direct correlation between the phonon spectra which enhance the thermal properties. Recently, there is a serious attention to the thermal properties and phonon spectra of these nitrides particularly at high pressure as it plays an important role in the synthesis of this group of the compounds [3]. The platinum nitride has been synthesized at high pressure and high temperature. Recently, there are few reports on the high pressure Raman spectra for HfN and ZrN [4, 5]. In this article, we report a systematic study on the pressure dependence of the phonon spectra and thermal properties of two transition metal nitrides using first principle calculations under the frame work of density functional theory (DFT).

## Computational method

Theory and computational aspects of our computational methods are based on the DFT. The first principles

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calculation is performed using the plane wave method within the generalised gradient approximation (GGA) implemented in the ABINIT code.<sup>1</sup> The cutoff energy for the plane wave basis set for both nitrides HfN and ZrN is 40 Ha. The thermal and phonon properties are subsequently obtained using the linear response approach which is based on the density functional perturbation theory. The basic ingredient phonon dispersions and phonon density of states for the thermal properties has been calculated using a  $8 \times 8 \times 8$   $\mathbf{q}$ -grid (29 force-constant matrices) [6]. The expressions are obtained from the second derivatives of the total energy with respect to the phonon displacement of atoms and an external electric field. The phonon density of states  $g(\omega)$  which is an essential quantity and vital for any thermodynamical calculation as it requires the calculations of phonons in whole Brillouin zone [7]. We use the root sampling (histogram) method on the phonon wavevectors  $\bar{q}$  for the calculation of  $g(\omega)$ . We then calculate the thermodynamic functions such as Helmholtz energy  $\Delta F$ , internal energy  $\Delta E$ , lattice specific heat  $C_v$  and vibrational entropy  $S$ , using the following relations [8].

$$\Delta F = 3nNk_{\beta}T \int_0^{\omega_L} \ln \left\{ 2 \sinh \frac{\hbar\omega}{2k_{\beta}T} \right\} g(\omega) d\omega \quad (1)$$

$$\Delta E = 3nN \frac{\hbar}{2} \int_0^{\omega_L} \omega \coth \left( \frac{\hbar\omega}{2k_{\beta}T} \right) g(\omega) d\omega \quad (2)$$

$$C_v = 3nNk_{\beta} \int_0^{\omega_L} \left( \frac{\hbar\omega}{2k_{\beta}T} \right)^2 \coth^2 \left( \frac{\hbar\omega}{2k_{\beta}T} \right) g(\omega) d\omega \quad (3)$$

$$S = 3nNk_{\beta} \int_0^{\omega_L} \left[ \frac{\hbar\omega}{2k_{\beta}T} \coth \frac{\hbar\omega}{2k_{\beta}T} - \ln \left\{ 2 \sinh \frac{\hbar\omega}{2k_{\beta}T} \right\} \right] g(\omega) d\omega \quad (4)$$

where  $k_{\beta}$ ,  $n$ ,  $N$ ,  $\omega_L$ , and  $g(\omega)d\omega$  are the Boltzmann constant, number of atoms per unit cell, numbers of the unit cell, largest phonon frequency, fractional number of phonon frequencies, respectively. The thermodynamic functions presented in Eqs. 1–4 are calculated using the rectangular formula for integration from the functional values at the mid points of each frequency channel. Here the convergence of thermodynamical quantities achieved better than 0.1% by fixing the width of the frequency channel as  $1 \text{ cm}^{-1}$  and keeping the  $30 \times 30 \times 30$  Monkhorst–Pack grids [6] homogeneous sampling of the phonon wave vector in the Brillouin zone at all studied temperature.

<sup>1</sup> The ABINIT Code is a Common Project of Universite Catholique de Louvain, Corning Incorporated and Other Contributors ([www.abinit.org](http://www.abinit.org)).

## Results and discussion

All calculations are performed at equilibrium lattice constant obtained using the methodology discussed above. The equilibrium lattice constant, bulk modulus and pressure derivative of bulk modulus value for both transition metal nitrides HfN and ZrN are presented in Table 1 together with available experimental and other theoretical pressure derivative and bulk modulus data. There is a reasonably good agreement between present theoretical and available experimental data within the experimental error and limitations of pseudopotentials. The predicted lattice constants are slightly higher but it is justified due to the use of GGA pseudo potential and exchange correlation functional which is known to overestimates the lattice constant.

To calculate the thermal properties of two nitrides HfN and ZrN at high pressure, we first calculated the phonon dispersion curves (not presented) and phonon density of states (DOS) at ambient condition and up to the pressure of 32 GPa. We report the phonon DOS only up to 32 GPa as the experimental data on Raman spectra is available up to this pressure. The calculated pressure dependent phonon density of states along with the measured high pressure Raman spectra for HfN and ZrN are presented in Fig. 1a and b, respectively. These figures reveal that there is an excellent agreement between the Raman spectra and calculated phonon DOS. They also reveal a wide gap separating the low frequency and high frequency region which corresponds to acoustic and optical parts, respectively of the phonon spectra. It is to be pointed that the above two quantities, phonon DOS and Raman spectra is in principle an uncomparable quantitatively as experimental Raman

**Table 1** Equilibrium lattice parameter, bulk modulus and derivative of the bulk modulus for HfN and ZrN crystals

System B1 structure	acell/Å	Bulk modulus/GPa	B'
HfN	4.602	253.9	4.33
	4.52 <sup>a</sup>	294.0 <sup>a</sup>	4.26 <sup>c</sup>
	4.54 <sup>b</sup>	278.0 <sup>b</sup>	
	4.54 <sup>c</sup>	269.0 <sup>c</sup>	
	4.52 <sup>d</sup>		
ZrN	4.60	278.19	4.37
	4.59 <sup>a</sup>	281.3 <sup>a</sup>	4.28 <sup>c</sup>
	4.57 <sup>b</sup>	264.0 <sup>b</sup>	
	4.583 <sup>c</sup>	250 <sup>c</sup>	
	4.537 <sup>d</sup>		

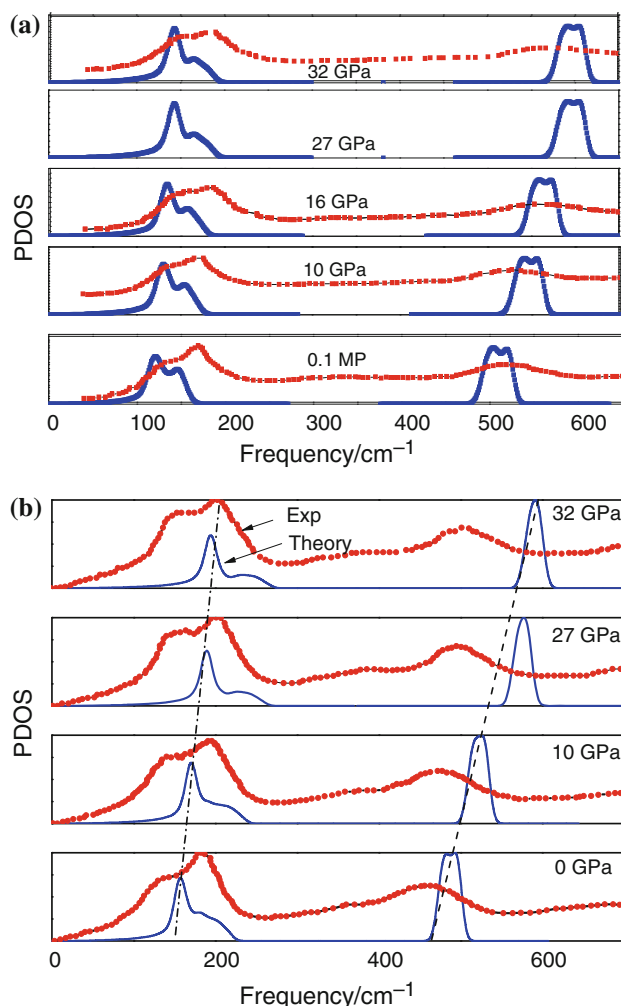
<sup>a</sup> [14]

<sup>b</sup> [11]

<sup>c</sup> [12]

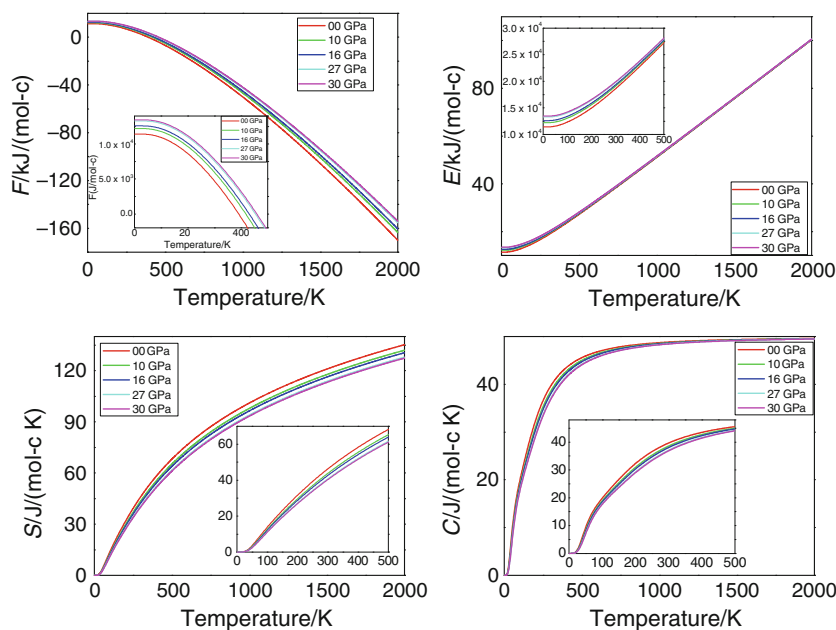
<sup>d</sup> [15]

<sup>e</sup> [16]



**Fig. 1** **a** Calculated phonon density of states for HfN at various pressures. **b** Calculated phonon density of states for ZrN at various pressures

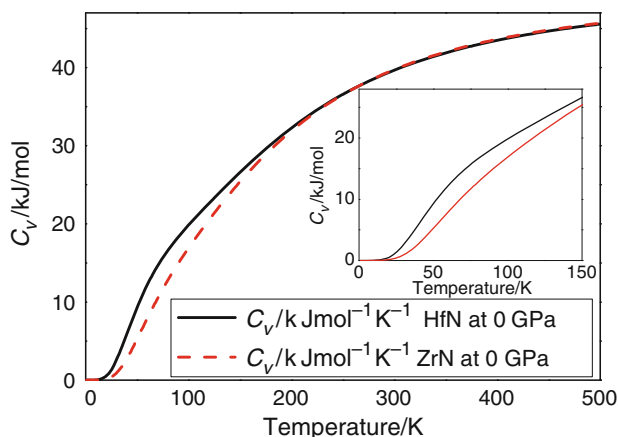
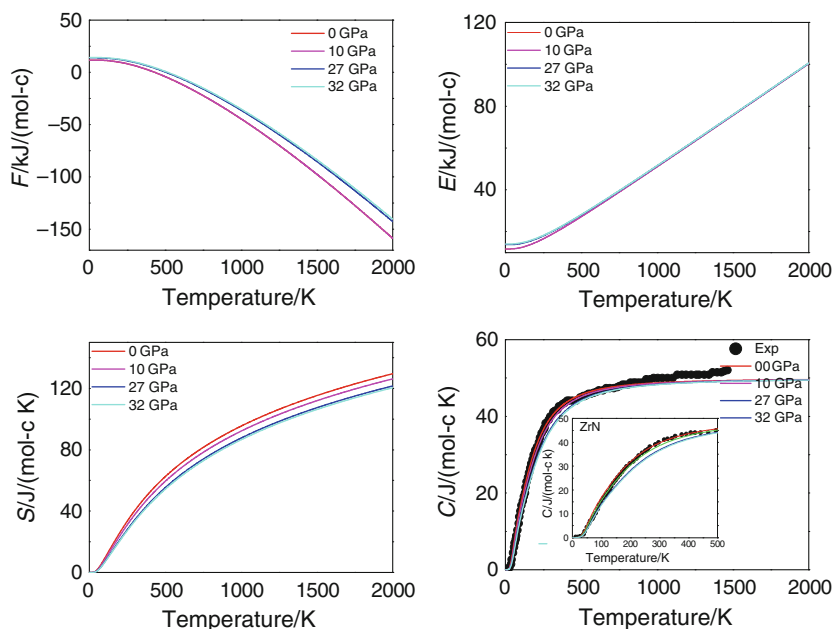
**Fig. 2** Calculated thermal properties of HfN at various temperature and pressure



spectra involves matrix element for the interaction of light with phonons. However, a qualitative description of Raman spectra can be made through phonon DOS. Moreover, our motive here for the comparison of lower and higher frequency region at which the phonon DOS exhibits features related to the acoustic and optical modes, respectively have to gain the information about the presence of acoustic and optic regions as well as its pressure dependence. Figures depict that the lower and higher frequencies increases with pressure.

Using the phonon density of states, pressure dependent thermodynamic functions for HfN and ZrN are presented in Figs. 2 and 3, respectively. The thermodynamical functions Helmholtz free energy  $\Delta F$ , the internal energy  $\Delta E$ , constant volume specific heat  $C_v$ , and entropy  $S$  have been calculated using expressions presented in Eqs. 1–4, within harmonic approximations [8]. Figures show that the shape of plots is similar with slight different range. As temperature increases the calculated for both compounds decrease gradually, the calculated  $\Delta E$  and  $S$  increases continuously and the constant volume lattice specific heat ( $C_v$ ) tend to asymptotic limit of 50 J/(mol-c K). The zero temperature values  $\Delta F_0$  and  $\Delta E_0$  do not vanish due to the zero point motion [8] and can be calculated from asymptotic expressions of Eqs. 1 and 2 at zero temperature. The value of  $\Delta F_0$  and  $\Delta E_0$  is 11.41 and 11.72 kJ/mol, respectively. It is to be noted that the comparison between theoretical and experimental [9, 10, 13] could only be made in the case of ZrN. The comparison between constant volume specific heat  $C_v$  and experimental constant pressure lattice specific heat, is not a serious drawback as at lower temperature there is not much difference in both specific heats. Furthermore, the lattice dynamical calculations give the constant volume

**Fig. 3** Calculated thermal properties of ZrN at various temperature and pressure



**Fig. 4** The pressure effect of the phonon contribution to the entropy energies of Hafnium nitrides (*solid lines*) and Zirconium nitrides (*dashed lines*)

specific heat. The figure depicts that there is a good match between the experimental and calculated specific heat with minor discrepancies which are quite obvious due to above facts. The specific heat plots from Fig. 4 reveal that the  $C_v$  in the case of HfN has more value than ZrN at low temperatures. This can be understood from lower frequency region of the phonon density of states presented earlier. The acoustic phonons of ZrN are softer than HfN due to the fact that the same is derived from Zr displacements which has smaller mass compared to Hf. In addition, the specific heat at low temperature is dominated by acoustic phonons and is inversely proportional to the cube of the velocity of sound; the specific heat of HfN is more than the ZrN (Fig. 4). At high temperature, there are large discrepancies

between the calculated and experimental specific heats as the lattice undergoes the thermal expansion and harmonic interactions. As far as the pressure effect on the temperature dependent lattice specific heat for HfN and ZrN is concerned, the pressure causes a decrease in the specific heat and entropy in contrast to the temperature effect. This is in accord with the second law of thermodynamics. This is due to the fact that the acoustic phonon becomes harder and hence the sound velocity harder with the increases of pressure. However, at high temperature it is readily seen that the  $C_v$  values for all pressures approaches approximately to the classical Dulong–Petit values and are identical for both compounds. It is seen that when  $T < 1500$  K, the heat capacity  $C_v$  is dependent on both temperature  $T$  and pressure  $P$ . This is due to the anharmonic approximations of Debye model. However, at higher pressures and temperatures, the anharmonic effect on  $C_v$  is suppressed and is very close to the Dulong–Petit limit  $6 NK$ , where  $N$  represents Avogadro's number.

## Conclusions

We have performed an ab initio calculation of the phonon properties and thermal properties such as Helmholtz free energy, internal energy, entropy and constant volume specific heat in the frame work of the DFPT for HfN and ZrN at high pressure and temperature hydrostatic pressure. The calculated phonon densities of states at both ambient and high pressures are in reasonable qualitative agreement with Raman spectra measured at various pressures up to 32 GPa. There is a red shift of the both peaks presented in lower and higher frequency region. With the application of

pressure HfN has more specific value than ZrN at ambient condition. The specific heat increases with pressure for both nitrides similar to other thermodynamical variable. The equilibrium lattice constants and bulk modulus are in good agreement with experimental data.

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