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Ab initio study of phase transition and thermodynamic properties of PtN

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Abstract

The transition phase of PtN from zincblende (ZB) structure to rocksalt (RS) structure is investigated by *ab initio* plane-wave pseudopotential density functional theory method, and the thermodynamic properties of the ZB and RS structures under high pressure and temperature are obtained through the quasi-harmonic Debye model. The transition phase from the ZB structure to the RS structure occurs at the pressure of 18.2 GPa, which agrees well with other calculated values. Moreover, the dependences of the relative volume V/V_0 on the pressure P, the Debye temperature Θ and heat capacity C_V on the pressure P, together with the heat capacity C_V on the temperature T are also successfully obtained.

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Transition metal nitrides are attracting considerable interest in the synthesis of new nitrides due to their technological and fundamental importance [1–7]. Owing to their outstanding physical and chemical properties, they have been widely used as corrosion resistants and optical coatings, electrical contacts, and diffusion barriers, and in many other technological applications [8–11]. So, great theoretical and experimental efforts have been made to study the early transition metal nitrides [12–18].

Recently, the synthesis of platinum nitride was succeeded by Gregoryanz et al. [19] using laser-heated diamond anvil-cell techniques at pressures up to 50 GPa and temperatures exceeding 2000 K. The synchrotron X-ray diffraction experiment revealed PtN to be face-centered cubic but was unable to distinguish between zincblende (ZB) and rocksalt (RS) structures due to a much stronger Pt signal caused by the large difference between masses of Pt and N. But PtN had a first-order Raman spectrum and hence RS structure was discarded. Nevertheless, several theoretical investigations of platinum nitride have now also been carried out [1–7], and the consensus appears to be that the compound does not crystallize in the proposed ZB structure, because this arrangement would violate the requirement of positive strain energy [1,2,4,6]. Yu and Zhang [1,4] have furthermore suggested that platinum nitride is instead stable in the fluorite structure, an arrangement in which the nitrogen atoms occupy all the tetrahedral interstitial sites of the face-centered cubic metal lattice and which necessitates a stoichiometry of PtN_2. Most recently, the experiment contributed by Crowhurst et al. [20] reveals that the platinum nitride is of the pyrite structure and indicates that both ZB and fluorite structures are highly unstable at both ambient pressure and 50 GPa. The pyrite structure was also confirmed later by Yu et al. [21] with first-principles calculations.

Although there exists numerous theoretical calculations on the stability, bulk modulus and electronic structures of any form of PtN, few works focus on the thermodynamic properties of PtN under high pressure and temperature. In this work, the transition phase of PtN from the ZB

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structure to the RS structure is investigated. All calculations are performed based on the plane-wave pseudopotential density-function theory (DFT) [22,23] method. Vanderbilt-type ultrasoft pseudopotentials (USPP) [24] are employed to describe the electron–ion interactions. The effects of exchange–correlation interaction are treated with the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) [25]. Moreover, the thermodynamic properties of PtN in the ZB and RS structures under high pressure and temperature are successfully obtained through the quasi-harmonic Debye model [26–28] from energy–volume data. In the structure calculation, a plane-wave basis set with energy cut-off 480.00 eV is used. Pseudo-atomic calculations are performed for N $2s^2 2p^3$ and Pt $5d^9 6s^1$. For the Brillouin-zone sampling, we adopted the $10\times10\times10$ Monkhorst–Pack mesh [29], where the self-consistent convergence of the total energy is at 10^{-7} eV/Atom and the maximum force on the atom is blow 10^{-4} eV/Å. All the total energy electronic structure calculations are implemented through the CASTEP code [30,31].

For both the ZB and RS structures of PtN, a series of different values of lattice constant a are set to calculate the total energy E and the corresponding primitive cell volumes V. The calculated energies as a function of the primitive cell volume for PtN are shown in Fig. 1, together with the information concerning the static equations of state (EOS) and the phase stability data. Here, we fit the calculated E–V points to both the Birch–Murnaghan EOS [32] and the natural strain EOS [33].

Table 1
Lattice constants, bulk modulus and pressure derivative of bulk modulus of the ZB and RS structures of PtN at zero pressure

Structure	a_0 (Å)	B_0 (GPa)	B'
ZB			
Present	4.805	193[a] 191[b]	5.22[a] 5.23[b]
Patil et al.[c]	4.794	192	
Patil et al.[c]	4.781	178	
Yu et al.[d]	4.780	194	
Kanoun et al.[e]	4.690		
Sahu et al.[f]	4.804	185.5	
Uddin et al.[g]	4.801	186.5	5.06
Experimental[h]	4.804	186	5.26
RS			
Present	4.504	234[a] 231[b]	5.31[a] 5.21[b]
Patil et al.[c]	4.504	226	
Patil et al.[c]	4.496	233	
Sahu et al.[f]	4.518	215.5	
Uddin et al.[g]	4.521	219	5.02

[a] From the Birch–Murnaghan EOS.
[b] From the natural strain EOS.
[c] Ref. [2] DFT–GGA.
[d] Ref. [1] DFT–GGA.
[e] Ref. [7].
[f] Ref. [3] DFT–GGA.
[g] Ref. [5] DFT–GGA.
[h] Ref. [19].

Table 2
Elastic constants (GPa) of PtN at various pressures P (GPa)

Structure	Pressure	C_{11}	C_{12}	C_{44}
ZB	0	184.9	191.7	42.0
	5	208.5	217.9	33.1
	10	232.0	244.8	34.2
	15	254.3	270.4	30.6
RS	0	265.9	210.9	37.8
	20	433.5	282.3	36.5
	40	590.9	347.5	34.3
	60	743.5	409.7	32.5
	80	892.4	468.7	30.8
	100	1042.9	522.0	28.2

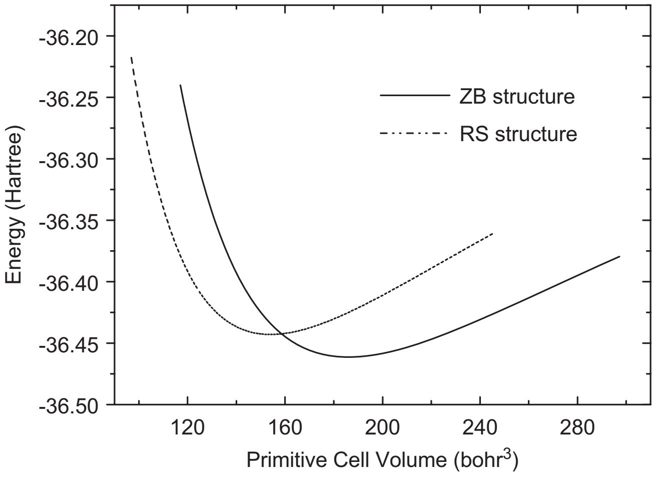

Fig. 1. Energy as a function of primitive cell volume for PtN.

The obtained lattice constant a_0, the bulk modulus B_0 and the pressure derivative of bulk modulus B_0' in the ZB and RS structures of PtN at zero pressure are listed in Table 1. It is obvious that the calculated results are consistent with other calculated values [1–3,5,7] and the experimental data [19]. Moreover, it is also found that when compared to experiment [19], the results from the natural strain EOS seem to be better than those from the Birch–Murnaghan EOS. So, the results from the natural strain EOS are adopted in the following calculations. We also calculate the elastic constants of PtN listed in Table 2. For cubic crystal structures such as those of ZB–PtN or RS–PtN, the necessary conditions for mechanical stability are given by [34]

$$C_{11} - C_{12} > 0, \quad C_{11} + 2C_{12} > 0, \quad C_{11} > 0, \quad C_{44} > 0. \tag{1}$$

It can be found that the numerical values of our computation of all the elastic constants of ZB–PtN satisfy all the stability conditions of Eq. (1) except the condition that $C_{11} - C_{12} > 0$. Thus, we conclude that the ZB–PtN is mechanically unstable which contradicts the experimental data [19].