Pressure-induced structural transition and thermodynamic properties of RhN_2 and the effect of metallic bonding on its hardness*

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The elastic constant, structural phase transition, and effect of metallic bonding on the hardness of RhN_2 under high pressure are investigated through the first-principles calculation by means of the pseudopotential plane-wave method. Three structures are chosen to investigate for RhN_2, namely, simple hexagonal P6/mmm (denoted as SH), orthorhombic Pnnm (marcasite), and simple tetragonal P4/mbm (denoted as ST). Our calculations show that the SH phase is energetically more stable than the other two phases at zero pressure. On the basis of the third-order Birch–Murnaghan equation of states, we find that the phase transition pressures from an SH to a marcasite structure and from a marcasite to an ST structure are 1.09 GPa and 354.57 GPa, respectively. Elastic constants, formation enthalpies, shear modulus, Young's modulus, and Debye temperature of RhN_2 are derived. The calculated values are, generally speaking, in good agreement with the previous theoretical results. Meanwhile, it is found that the pressure has an important influence on physical properties. Moreover, the effect of metallic bonding on the hardness of RhN_2 is investigated. This is a quantitative investigation on the structural properties of RhN_2, and it still awaits experimental confirmation.

Keywords: phase transition, elasticity, hardness

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1. Introduction

Transition metal nitrides have attracted great attention from both experimental and theoretical studies for their excellent properties in both fundamental science and technological applications.[1−5] Recently, four noble metal nitrides, i.e., PtN_2,[6,7] OsN_2,[8] IrN_2,[7−9] and PdN_2[9] have been synthesized under high pressure and high temperature (at approximately 50 GPa∼60 GPa and 2000 K). The synthesized OsN_2, IrN_2, and PtN_2 (PdN_2) are reported to adopt the marcasite, $CoSb_2$-type, and pyrite structures, respectively.[7−16]

For rhodium nitride, only several theoretical studies have been reported. de Paiva *et al.*[17] carried out *ab initio* calculations for the zinc-blende structure of RhN. Wu and Zhao[18] investigated the structural stability and electronic properties of Rh_2N by using the first principles. According to the work by Yu *et al.*,[15] the marcasite (Pnnm) structure is the most stable phase for RhN_2. However, a simple hexagonal P6/mmm (denoted as SH) structure with N=N bonds, which could be more stable than the marcasite structure at low pressures, has been proposed by Li *et al.*[19] They also predicted an eight-coordinated simple tetragonal P4/mbm (denoted as ST) structure, which is energetically stable at high pressures. In addition, the elastic and thermodynamic properties of a crystal under high pressure, both experimentally and theoretically, have received considerable attention in recent years.[20,21] The reason is that the knowledge of physical and chemical properties of material at high pressure is important for a variety of scientific and technological applications. Li *et al.*[19] have calculated the elastic constants of SH–RhN_2 at zero pressure. However, the elastic constants and thermodynamic properties of RhN_2 under high pressure have not yet been well understood. Moreover, there are no detailed investigations on the effect of metallic bonding on the hardness of RhN_2.

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In the present paper, SH–RhN_2, marcasite–RhN_2, and ST–RhN_2 are considered. We describe a systematical investigation of the high-pressure behaviour and phase transition of RhN_2 by the first-principles quantum-mechanical calculations. The aim of the present work is threefold. Firstly, it is to give a comprehensive and complementary investigation on the structural and mechanical properties of RhN_2. Our second intention is to provide a further understanding of phase transition[22,23] among the three considered structures under high pressure. Thirdly, it is to provide powerful guidelines for future experimental investigations, hoping that such an investigation can contribute to some further understanding of the hardness of RhN_2 and its isomorphs.

2. Computational method

In the present work, all the calculations are performed using the CASTEP code,[24] based on the density functional theory. The Vanderbilt ultrasoft pseudopotential[25] is used with the same cutoff energy of 400 eV for the considered structures. The k point meshes of 10×10×6 for P6/mmm, 8×6×12 for Pnnm, and 6×6×9 for P4/mbm are generated using the Monkhorst–Pack scheme.[26] The conventional unit cells are used for the three structures in the geometry optimization process while the primitive cells are selected for calculating the electronic properties and elastic constants. The electronic exchange–correlation potentials are described within the generalized gradient approximation (GGA) parameterized by Perdew *et al.*[27] Formation enthalpies are calculated from $\Delta H = E(\mathrm{RhN_2}) - E(\text{solid Rh}) - E$ (solid molecular N_2). The solid molecular N_2 is from its α phase.[28] The bulk modulus, shear modulus, and Young's modulus are calculated in the Voigt–Reuss–Hill approximation.[29]

3. Results and discussion

3.1. Structural properties

The crystal structure is an important prerequisite for understanding the crystalline solid's properties.[30] The calculated parameters and bond length are listed in Table 1. For SH–RhN_2 and marcasite–RhN_2, the calculated lattice parameters and cell volume per formula unit are in excellent agreement with the previous theoretical values.[19,15] For an ST structure, there is no available data for comparison. The calculated total energy E_0 indicates that the SH phase is energetically more stable than the other two phases at low pressures. In Table 1, it is shown that the formation enthalpies of the three considered structures are positive, indicating that they are thermodynamically unstable. Therefore, these nitrides are metastable at zero pressure toward dissociation into their constituent elements.[31] Meanwhile, our calculation shows that the formation enthalpy of the ST structure is very large at 360 GPa. This implies that the ST structure is difficult to directly synthesize. However, we can obtain this structure through phase transition under high pressure.

For the SH structure, we find that the Rh–N bond length (1.915 Å, 1 Å=0.1 nm) is less than 2.102 Å in the marcasite structure. This indicates that there exists a stronger covalent Rh–N bond in the SH structure. The marcasite structure contains diatomic N–N units with the bond length 1.309 Å. This is in excellent agreement with the value 1.30 Å from previous work.[15] However, the N–N bond length value 1.309 Å is a little shorter than 1.40 Å (OsN_2), 1.42 Å (IrN_2 and PtN_2), indicating the presence of more "free" N_2 quasimolecules in RhN_2. The strong covalent N–N bonding provides a strengthening effect in the compounds, resulting in their high elastic moduli. This suggests a pathway to forming strong solids by employing strong N–N bonds instead of breaking them, as occurs in most nitrides.

Table 1. Formation enthalpy per formula unit ΔH (eV), lattice parameters a, b, c (Å), cell volume per formula unit V (Å^3), total energy E_0 (eV), nitrogen and nitrogen bond distance N–N (Å) and metal and nitrogen bond distance Rh–N (Å) from calculations in the GGA.

Structure	P/GPa		ΔH/eV	a/Å	b/Å	c/Å	V/Å	E_0/eV	N–N/Å	Rh–N/Å
SH	0	present	0.07	2.905	2.905	5.000	36.52	–1153.36	1.170	1.915
		theory[19]		2.907	2.907	4.954	36.27		1.142	1.906
Marcasite	0	present	0.12	3.944	4.899	2.972	28.72	–1153.30	1.309	2.102
		theory[15]		4.010	4.827	2.758			1.30	
ST	0	present	1.90	4.514	4.514	2.772	28.24	–1151.53	1.260	2.324
ST	360	present	–4.47	3.821	3.821	2.381	17.38		1.226	1.946

3.2. Phase transformation

In order to obtain a more detailed insight into the phase stability of RhN_2, we carry out the calculations of the Gibbs free energy G for the three structures. It is well known that at zero temperature, the Gibbs free energy G is equal to the enthalpy H for a solid. Therefore, the estimation of the zero-temperature transition pressure can be obtained from the usual condition of equal enthalpies. In other words at pressure P, the enthalpies calculated from the formula[32] $H = E + PV$ for both phases are the same. The enthalpies of RhN_2 with the SH, marcasite, and ST structures are calculated, and we obtain the phase transition pressures from the intersections in the enthalpy–pressure curves. The relationships of enthalpy versus pressure of RhN_2 in the SH, marcasite, and ST phases are presented in Fig. 1. According to the enthalpy criterion, it can be seen that the SH-to-marcasite and marcasite-to-ST phase transition pressures occur at 1.09 GPa and 354.57 GPa, respectively. The value 354.57 GPa is in good agreement with Li's result (325 GPa).[19] Unfortunately, as far as we know, there are no experimental data available related to the structural transition in the literature for our comparison. We hope that our results can serve as a prediction for future experimental investigation.

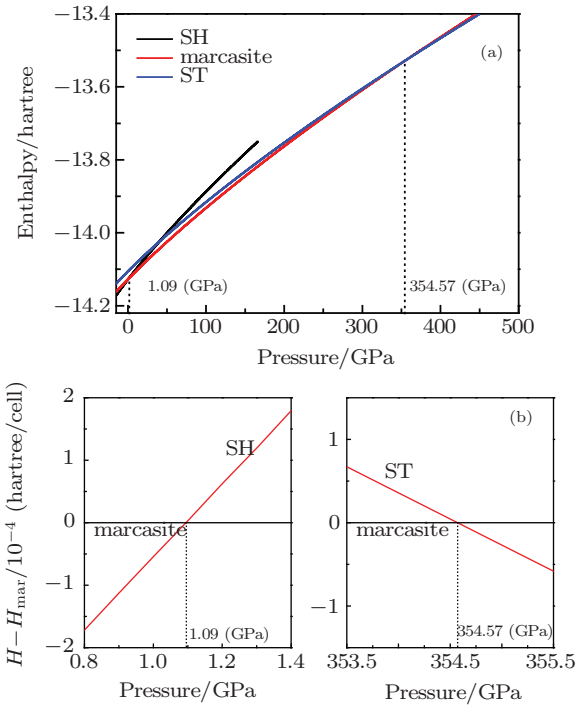


Fig. 1. (a) Plots of enthalpy versus pressure for RhN_2 in the SH, marcasite, and ST structures at $T = 0$ K. (b) plots of H–H_{mar} versus pressure, showing that the SH-to-marcasite and marcasite-to-ST phase transition pressures are 1.09 GPa and 354.57 GPa respectively, 1 hartree=27.21 eV.

3.3. Elastic properties

The calculated elastic constants, bulk modulus B, shear modulus G, Young's modulus E, Debye temperature Θ_D, and the ratio of B/G are listed in the Table 2. For the SH structure, the calculated elastic constants are comparable to the reported values.[19] In Table 2, it is shown that the SH and marcasite structures are mechanically stable except for the ST structure at 0 GPa. Since the C_{11} and C_{44} are negative in the ST structure, the mechanical stability criteria of tetragonal phase are disobeyed. When the pressure increases up to a certain value (high pressure), the ST structure becomes stable. It is interesting to note that there is an ultra-large C_{33} value in the SH structure, implying the high incompressibility along the c axis. This fact might be caused by the strong covalent N=N and Rh–N bonds along the c axis. We also note that abnormally large C_{11} and C_{33} occur in the ST structure at high pressures, indicating the orientationally incompressibility of these materials. The calculated ratios of B/G suggest that the considered structures are ductile. It is also worth noting that the ST structure has a very large bulk modulus of 1715 GPa at 360 GPa. The results suggest that RhN_2 may be a potential candidate for engineering hard material.

Table 2. Elastic constants C_{ij}, bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Debye temperature Θ_D, and the ratio of B/G.

Structure	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	B/GPa	G/GPa	E/GPa	Θ_D	B/G
SH (0 GPa)	122		1220	24		34	53	32		137	70	180	495	1.96
	129[a]		1085[a]	25[a]			50[a]	12[a]		84[a]				
Mar (0 GPa)	551	681	278	80	222	101	196	335	134	271	129	334	647	2.10
										286[b]				
ST (0 GPa)	–25		339	–190		159	400	61		148				
ST (360 GPa)	2201		2536	149		552	1486	1385		1715	300	851	922	5.72

[a]Ref. [19], [b]Ref. [15]

Since all the known crystals are essentially elastically anisotropic, the description of such an anisotropic behaviour is important in both engineering science and crystal physics. In the present work, we focus on investigating the elastic anisotropy of RhN_2 in the ST structure under high pressures. The anisotropy for ST–RhN_2 is measured by A_- and A_+ coefficients calculated for each symmetry plane and axis. In order to quantify the elastic anisotropy of the ST–RhN_2, we calculate the anisotropy factor by use of the following expressions:[33]

$$A_-^{(010)\text{ or }(100)} = \frac{C_{44}\left(C_{11}+2C_{13}+C_{33}\right)}{\left(C_{11}C_{33}-C_{13}^2\right)},$$
$$A_-^{(1\bar{1}0)} = C_{44}\left(C_L+2C_{13}+C_{33}\right)/\left(C_LC_{33}-C_{13}^2\right),$$
$$A_-^{(001)} = 2C_{66}/\left(C_{11}-C_{12}\right),$$
$$A_+^{[100],\,(010)} = 2C_{44}/\left(C_{11}-C_{13}\right),$$
$$A_+^{[001],\,(010)} = 2C_{44}/\left(C_{33}-C_{13}\right),$$
$$A_+^{[110],\,(1\bar{1}0)} = 2C_{44}/\left(C_L-C_{13}\right),$$
$$A_+^{[001],\,(1\bar{1}0)} = 2C_{44}/\left(C_{33}-C_{13}\right),$$
$$A_+^{[100],\,(001)} = 2C_{66}/\left(C_{11}-C_{12}\right),$$

where $C_L = C_{66} + (C_{11}+C_{12})/2$.

The calculated values of the anisotropic for ST structure under high pressures are given in Table 3. It is shown that RhN_2 is elastic anisotropic. It is interesting to note that most of the anisotropy factors first increase and then decrease. However, the anisotropy factors of the crystal in symmetry plane (001) gradually decrease.

Table 3. Anisotropy factors A_-, A_+ of ST–RhN_2 for, respectively, symmetry plane (ijk) and $[ijk]$ symmetry axis with symmetry plane (ijk) each as a function of pressure.

P/GPa	A_-			A_+				
				[100]	[001]	[110]	[001]	[100]
	(010)	$(1\bar{1}0)$	(001)	(010)	(010)	$(1\bar{1}0)$	$(1\bar{1}0)$	(001)
354.5	0.2982	0.2694	1.5574	0.3548	0.2540	0.2862	0.2540	1.5574
360	0.3060	0.2768	1.5430	0.3661	0.2595	0.2958	0.2595	1.5430
370	0.3098	0.2806	1.5240	0.3709	0.2626	0.3004	0.2626	1.5240
380	0.3287	0.2982	1.5083	0.3907	0.2804	0.3177	0.2804	1.5083
390	0.3262	0.2960	1.5038	0.3907	0.2767	0.3174	0.2767	1.5038
400	0.3160	0.2869	1.4960	0.3759	0.2693	0.3063	0.2693	1.4960

3.4. Pressure dependence of structural, elastic, and thermodynamic properties

In order to investigate the pressure-dependence behaviours of the structural, elastic, and thermodynamic properties[34] of RhN_2, we focus our investigations on the pressure range 150 GPa–210 GPa for the marcasite phase and 354.57 GPa–400 GPa for the ST phase. In Figs. 2(a) and 2(b), we describe the dependences of elastic constants on hydrostatic pressure for marcasite and ST structures, respectively. From Fig. 2(a), for the marcasite structure, we can see that C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, and C_{23} increase monotonically with pressure increasing. It is obvious that C_{11} and C_{33} change largely under the effect of the pressure compared with others. It is interesting to note that C_{55} and C_{66} have no remarkable changes with the increase of pressure. It is noticeable that C_{44} gradually decreases with pressure increasing. From Fig. 2(b), for the ST structure, we note that all of the elastic constants increase monotonically with the increase of pressure. Moreover, the C_{11} and C_{33} increase rapidly whereas C_{12}, C_{13}, C_{44}, and C_{66} increase slowly with pressure increasing. In Figs. 3(a) and 3(b), we plot the variations of bulk modulus, shear modulus, Young's modulus, and Debye temperature with pressure for marcasite and ST structures, respectively. We can also observe that the pressure has an important influence on these four quantities. Furthermore, we find that the variation tendencies of Young's modulus E and Debye temperature $\Theta_{\rm D}$ are, to some extent, similar. The above results are of significant importance for a better understanding of the high-pressure behaviour of RhN_2 crystal.

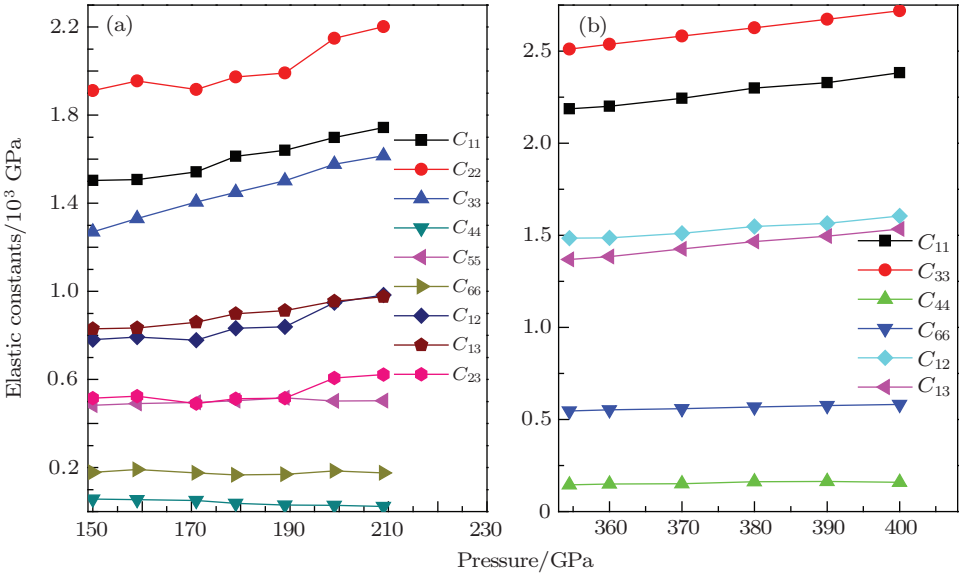


Fig. 2. (colour online) Pressure dependences of elastic constants in both the marcasite (a) and ST (b) structures of RhN_2.

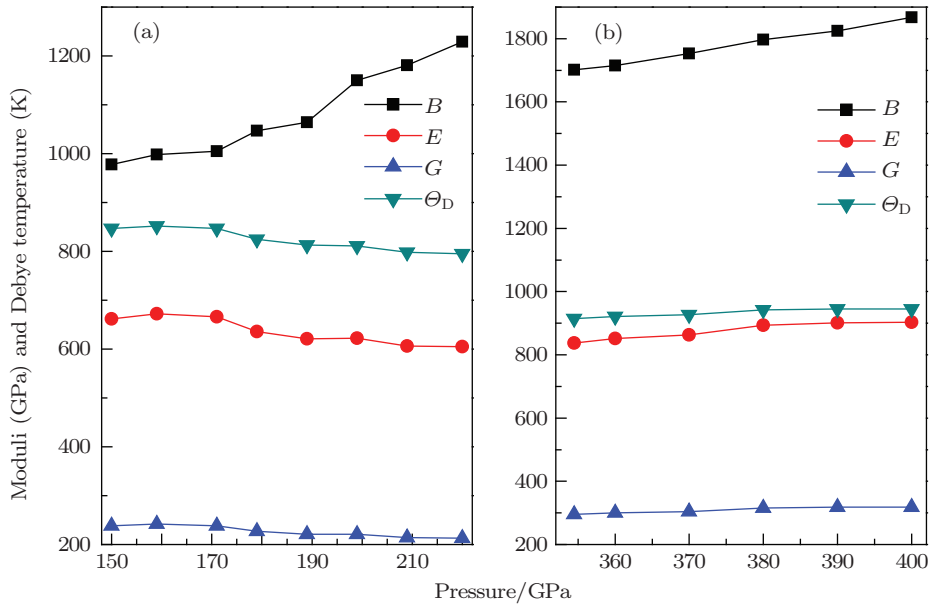


Fig. 3. (colour online) Pressure dependences of bulk modulus B, shear modulus G, Young's modulus E, and Debye temperature Θ_D in both the marcasite (a) and ST (b) structures of RhN_2.

3.5. Density of states

The calculated total densities of states (DOSs) shown in Fig. 4 indicate that the three structures are metallic because of the finite DOS at the Fermi level. As shown in Figs. 4(a) and 4(b), the DOSs for SH and marcasite phases can be separated into three energy ranges: (I) the range from −14.0 eV to −5.0 eV, in which the DOS is primarily composed of N 2p orbitals; (II) the range from −5.0 eV to 6.0 eV, in which N 2p orbitals have a strong hybridization with Rh 4d orbitals, indicating the covalent bonding between N and Rh; (III) the range higher than 6.0 eV, in which the DOS is contributed from both N 2p orbitals and Rh 4p orbitals. From Fig. 4(c), the DOS of the ST phase at 360 GPa is composed of two main parts. We can see that N 2p orbitals have a strong hybridization with Rh 4d orbitals in a wide energy range of −14.0 eV–7.0 eV, leading to the formation of the strong covalent

Rh–N bonds. In a range of 10.0 eV–15.0 eV, the DOS is contributed mainly from both N 2p orbitals and Rh 4p orbitals.

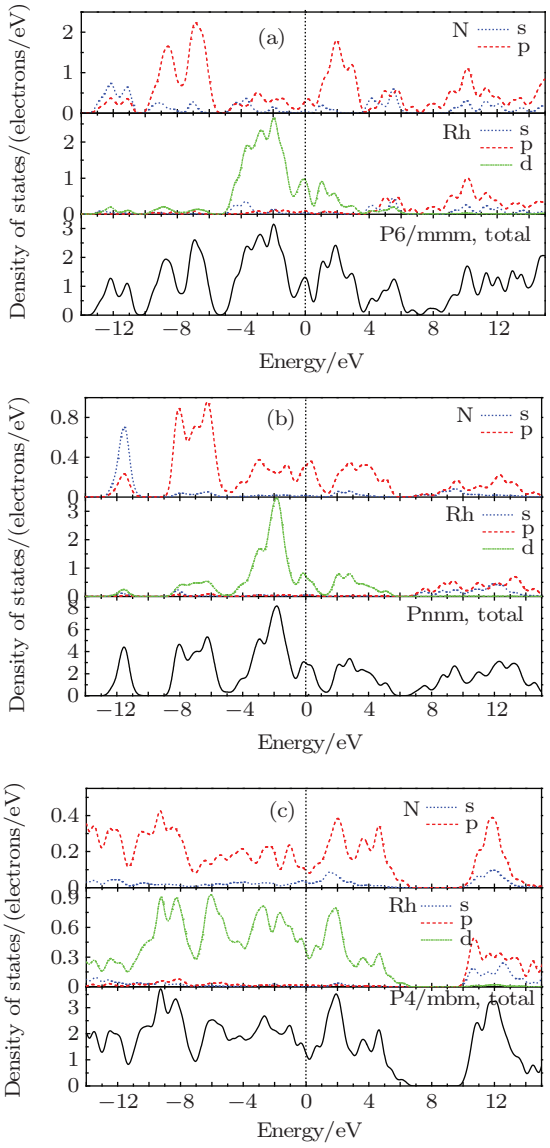


Fig. 4. (colour online) Calculated total and partial densities of states (DOSs) of RhN_2: (a) the SH structure at 0 GPa, (b) the marcasite structure at 0 GPa, (c) the ST structure at 360 GPa. Vertical dotted lines indicate the Fermi energy.

From Fig. 4, we note that there is a deep valley above the Fermi level in each of the three phases, which is termed pseudogap. It is caused by the strong hybridization between Rh 4d orbitals and N 2p orbitals. This suggests that not all the bonding states are filled and some extra electrons are required to reach maximal stability in this compound.

3.6. Hardness

In fact, bulk modulus measures resistance to volume change, which has little direct connection with hardness as is well known from dislocation theory.[35] It is difficult to describe hardness quantitatively only by macroscopic physical properties of E and G. So the prediction of hardness is of great potential interest. A formula for estimating the hardness of nonmetallic materials has been developed by Mulliken population in first-principles techniques.[36] The overlap population is a convenient way to quantify the strength of bonding. Since metallic bonding is delocalized and not directly related to hardness,[35] for hardness calculation of crystals with partial metallic bonding such as NbN and RhN_2, a correction of metallic bonding in the formula should be considered. Here the screening effect of the metallic component is described by introducing a correction factor $\exp(-\beta f_{\rm m}^n)$, where β and n are two constants, and $f_{\rm m}$ is the metallicity of chemical bond. The exponential regression equation of hardness can be written as[37]

$$H_\nu({\rm GPa}) = 746 P v_{\rm b}^{-5/3} \exp(-1.359 f_{\rm m}^{0.9256}), \qquad (1)$$

where $v_{\rm b}$ is the bond volume, and P is the Mulliken bond overlap population. For complex multi-band compounds, such as pyrite-PtN_2 and marcasite-RhN_2, the hardness can be expressed as an average of hardness of all hypothetical binary system in the complex compound,[38] i.e., $H_\nu = \left[\prod^{\mu}(H_\nu^\mu)^{n^\mu}\right]^{1/\sum n^\mu}$, where n^μ is the number of μ-type bonds in the complex compound. The bond volume is expressed as[38] $v_{\rm b}^\mu = (d^\mu)^3 / \sum_\nu [(d^\nu)^3 N_{\rm b}^\nu]$, and the metallicity can be estimated with $f_{\rm m}^\mu = P'(N_{MA} + N_{MB})/(P_A N_{MA} + P_B N_{MB})$, where $N_{\rm b}^\nu$ is the bond number of type ν per unit cell, N_{MA} (or N_{MB}) is the number of the chemical bonds with the metallic component around atom A (or B), and is metallic population.[37,39] Using Eq. (1), we calculate the hardness of RhN_2. It can be seen from Table 4, at zero pressure, the hardness is 12.8 GPa for marcasite-RhN_2, and under high pressure, the hardness is 9.2 GPa for ST–RhN_2. These results indicate that RhN_2 is a hard material but not a superhard one. Our investigation should be useful for searching superhard materials of transition metal nitrides.

Table 4. Calculated bond parameters and Vickers hardness of marcasite–RhN_2 and ST–RhN_2, where d is the bond length, P is the Mulliken bond overlap population, f_m is the metallicity of the chemical bond, v_b is the bond volume, and $H_{\nu\ \mathrm{calc}}$ (GPa) is the calculated Vickers hardness.

	Bond	d/Å	P	f_m	v_b/Å^3	$H_{\nu\ \mathrm{calc.}}$
Marcasite (0 GPa)	N–N	1.309	0.87	0	1.099	12.8
	Rh–N(1)	2.102	0.12	0.214	4.554	
	Rh–N(2)	2.126	0.29	0.214	4.709	
ST (360 GPa)	N–N	1.226	0.86	0	0.668	9.2
	Rh–N	1.946	0.02	0.327	2.674	

4. Conclusion

From the above investigations, we draw the following conclusions.

(i) From our calculations, the formation enthalpies of RhN_2 at different phases are found to be positive, indicating that the compound is in principle thermodynamically unstable at zero pressure. Meanwhile, the SH–marcasite and marcasite–ST structural phase transitions are investigated.

(ii) The structural parameters and mechanical properties for the three structures of RhN_2 are derived. The calculated values are found to be in good agreement with the available data. Moreover, the pressure dependences of elastic properties, bulk modulus, Young's modulus, shear modulus, Poisson's ratio, and Debye temperature are also investigated. It is found that the pressure has an important influence on physical properties.

(iii) The electronic structures of RhN_2 are calculated. The results show that the three phases are metallic. The bonding nature of RhN_2 can be described as being covalent-like due to hybridization of N and Rh states, but there is also obvious metallic character.

(iv) Based on first-principles calculations, the hardnesses of RhN_2 for different structures are calculated. The calculation results suggest that RhN_2 is a hard material but not a superhard one. Our investigation should be useful for searching superhard materials of transition metal nitrides.

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