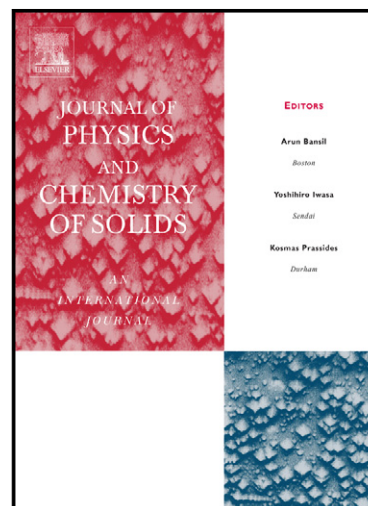


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Structural stability, electronic structure and mechanical properties of 4d Transition metal nitrides TMN (TM= Ru, Rh, Pd)

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Abstract: *Ab initio* calculations are performed to investigate the structural stability, electronic structure and mechanical properties of 4d transition metal nitrides TMN (TM=Ru, Rh, Pd) for five different crystal structures, namely NaCl, CsCl, zinc blende, NiAs and wurtzite. Among the considered structures, zinc blende structure is found to be the most stable one for all the three nitrides at normal pressure. A structural phase transition from ZB to NiAs phase is predicted at a pressure of 104 GPa, 50.5 GPa and 56 GPa for RuN, RhN and PdN respectively. The electronic structure reveals that these nitrides are metallic. The calculated elastic constants indicate that these nitrides are mechanically stable at ambient condition.

Keywords: Ab-initio calculations; Crystal structure; Phase transition; Electronic structure; Mechanical properties.

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1. Introduction

Transition metal mono nitrides have attracted increasing attention due to their importance in both fundamental and technological applications [1,2]. Many experimental and theoretical works have been focused on these materials due to their numerous technological applications [3-10]. Moreno-Armenta et.al [11] synthesized ruthenium nitride by the reactive pulsed laser (RPLD) method and analysed theoretically the possible structures of ruthenium nitride. On the theoretical side, structural stability, elastic and electronic properties of RuN polymorphs were investigated by Bannikov et.al [12] using first principles calculation with six different structures. Erjun Zhao et.al [13] analyzed the structural, mechanical and electronic properties of 4d transition metal mono nitrides. The elastic properties and the electronic structures of 4d and 5d transition metal nitrides have been investigated with NaCl and zinc blende structures by Chen et al. [14]. The influence of nitrogen vacancies on the magnetic and electronic properties of ruthenium mono nitride was studied [15]. Guillermet et al. [16] investigated the cohesive properties of 4d-transition metal nitrides in the NaCl-type structure; while de Paiva et al. [17, 18] analysed the atomic and electronic structures of 4d transition metal nitrides with zinc blende structure. Deligoz et al. [19, 20] studied the structural property of PdN and RhN in four different phases, namely NaCl, zinc blende (ZB), CsCl and wurtzite (WZ) structures. Linyan li [21] has performed the first principles calculation to study the electronic structure of noble metal nitrides with NaCl and zinc blende structures. Nikita Acharya et al. [22] analyzed the structural, electronic and elastic properties of PdN. To the best of our knowledge, the transition pressure, Debye temperature and the pressure dependence of elastic moduli of RuN, RhN and PdN are not yet reported. This has motivated us to study the high pressure properties of these materials.

In this paper, the structural, electronic and mechanical properties of 4d transition metal nitrides TMN (TM= Ru, Rh, Pd) are analyzed for five possible structures, namely NaCl, CsCl,

ZB, NiAs and WZ. In particular, the elastic constants, Young's modulus, bulk modulus, shear modulus, Poisson's ratio, Lamé constants, Kleinman parameter, Zener isotropy and micro hardness parameter are calculated to investigate the mechanical stability of these nitrides.

2. Theoretical framework

The *ab initio* calculations are performed using density functional theory within the local density approximation (LDA) [23] and generalized gradient approximation (GGA) [24-26] as implemented in the Vienna *ab initio* simulation package (VASP) [27,28]. The interaction between the ion and electron is described by the projector augmented wave method [29]. Ground state geometries are determined by minimizing stresses and Hellman-Feynman forces using the conjugate-gradient algorithm with force convergence less than 10^{-3} eV/Å. The Kohn-Sham orbitals are expanded using the plane wave energy cutoff of 600 eV. For accurate Brillouin zone integration, we use Monkhorst-Pack K-point mesh [30] with a grid size of 12x12x12 for structural optimization and total energy calculation. The valence electron configurations are Ru $4d^7 5s^1$, Rh $4d^8 5s^1$, Pd $4d^{10} 5s^0$ and N $2s^2 2p^3$ atoms. The crystal structure for the considered phases of transition metal nitrides RuN, RhN and PdN is shown in Fig.1.

3. Results and discussion

3.1 Structural properties

The structural stability of RuN, RhN and PdN is analysed among the five considered crystal structures: NaCl, CsCl, ZB, NiAs and WZ. The lattice constants are optimized and the total energy is calculated using both GGA and LDA for the ruthenium nitride (RuN), rhodium nitride (RhN) and palladium nitride (PdN) for various phases considered as a function of reduced volume and their plots are given in Fig.2 (a-b). It is observed that ZB structure is the most stable

for these nitrides at ambient condition. On further reducing the volume, all the three nitrides undergo a structural phase transition from ZB to NiAs phase.

The cohesive energy (E_{coh}) determines the strength of the binding between the constituent atoms in a solid. The E_{coh} of a solid is the difference between the total energy per atom of the bulk material at ambient condition and the atomic energies of the atoms belonging to the unit cell of the material:

$$E_{\text{coh}}^{\text{TMN}} = [E_{\text{atom}}^{\text{TM}} + E_{\text{atom}}^{\text{N}} - E_{\text{total}}^{\text{TMN}}] \quad (1)$$

where $E_{\text{total}}^{\text{TMN}}$ is the total energy of the compound at the equilibrium lattice constant and $E_{\text{atom}}^{\text{TM}}$ and $E_{\text{atom}}^{\text{N}}$ are the atomic energies of the pure constituent atoms. The computed cohesive energies of transition metals (TMs) and their nitrides (TMNs) are shown in Fig.3. The cohesive energies of these nitrides are observed to be higher than those of the host elements. It is also observed that, RuN has the highest cohesive energy among the considered nitrides and hence it is the most stable one.

The formation enthalpy is calculated using the formula

$$\Delta H = [E_{\text{TMN}} - E_{\text{TM}} - \frac{1}{2}E_{\text{N}_2}] \quad (2)$$

and is plotted in Fig.4. It is found that the RuN, RhN and PdN have negative formation enthalpies. This suggests that these nitrides can be easily synthesized at ambient condition. The optimized lattice parameters of the 4d transition metal nitrides TMN (TM= Ru, Rh, Pd) are determined by computing the total energies for various volumes for all the five phases. The volume corresponding to the minimum energy is the equilibrium volume V_0 . These data are then fitted to the universal second order Birch-Murnaghan equation of state [31] to determine the bulk modulus B_0 and its first derivative B_0' at normal pressure. The calculated ground state properties like lattice constants a , c (\AA), cell volume V_0 (\AA^3), valence electron density ρ

(electrons/ Å³), bond length TM-N (Å), cohesive energy E_{coh} (eV), formation enthalpy ΔH (eV), bulk modulus B_0 (GPa) and its derivative B_0' for NaCl, CsCl, ZB, NiAs and WZ phases of RuN, RhN and PdN using both GGA and LDA are listed in Table 1-3 respectively along with the experimental and other available theoretical results [11-22]. It is found that our results are in agreement with the available data. There is a small deviation in bulk modulus values calculated using LDA and GGA because LDA usually underestimates the lattice constants and overestimates the bulk modulus, whereas the GGA overestimates the lattice constants and underestimates the bulk modulus.

In order to find the phase transition in a more accurate manner, we have calculated the enthalpy using the formula

$$H=E+PV \quad (3)$$

and the enthalpy values are plotted against pressure in Fig. 5 (a-b). A structural phase transition from ZB to NiAs phase is predicted at the pressures of 104 GPa, 50.5 GPa and 56 GPa with GGA (Fig 5(a)) for RuN, RhN and PdN respectively. Almost similar results are obtained with LDA (Fig. 5(b)) also.

3.2 Electronic Properties

The electronic structures of RuN, RhN and PdN are investigated by computing the band structures, total and partial density of states (DOS) with ZB structure. The calculated DFT-GGA band structures, at the equilibrium lattice constant are depicted in Fig.6, which are drawn along symmetry directions in the first Brillouin zone. For these systems, both LDA and GGA yield similar band structures. All the three nitrides in the ZB structure are observed to be metallic as there is a crossing of bands at the Fermi level. The energy bands crossing the Fermi level are

mainly formed due to the mixture of metal-4d (TM=Ru, Rh, Pd) and N-2p states. The band appears at the bottom of the valence band is due to the 2s state electrons of nitrogen atom. The other bands found just below the Fermi level are due to metal-4d (TM=Ru, Rh, Pd), metal-5s (TM=Ru, Rh, Pd) and N-2p states. The empty conduction bands above the Fermi level are due to metal-4d (TM=Ru, Rh, Pd), metal-p (TM=Ru, Rh, Pd) and N-3d states.

The total and partial density of states of RuN, RhN and PdN are shown in Fig.7 and 8. The feature lying lowest in the energy range of $\sim -10\text{eV}$ is N-2s derived state. The highest peak found just below the Fermi level is due to the d state electrons of the metal atoms and the N-2p state electrons. Above the Fermi level the peaks are due to metal-p states and N-3d states. The non-zero density of states in the Fermi level indicates the metallic behavior of these materials at normal pressure. The general features of the DOS are similar to the results obtained by Erjun Zhao et al [13], Chen et al. [14] and de Paiva et al. [17, 18].

Under high pressure all the three nitrides undergoes structural phase transition from cubic (ZB) to hexagonal (NiAs) phase. Hence, the high pressure electronic band structure and density of states are computed for RuN, RhN and PdN with NiAs structure and are plotted in Fig. 9-10 respectively. From Fig.9, it is seen that the band crossing the Fermi level is derived from metal-4d (TM=Ru, Rh, Pd) states and N-2p states. In Fig. 10, the lowest peak is due to 2s state electrons of the nitrogen atom and there is no energy gap, indicating that the 4d transition metal nitrides TMN (TM= Ru, Rh, Pd) have metallic nature at all pressures.

The covalent characteristics between transition metal TM and N atoms can be confirmed by the charge density distribution. The charge density distributions for cubic ZB–RuN, RhN and PdN are shown in Fig. 9. It is clearly seen that charge strongly accumulates between transition metal (TM) and N atoms, which means that a strong directional bonding exist between them. It is seen that for each material there is an increase in electron density near the nitrogen atoms

whereas decrease in electron density at the interstitial region between the metal atoms. The bonding nature of these materials is found to be covalent-like due to the hybridization of N and metal atoms. However, an ionic component with a significant charge transfer between metal and nitrogen atoms and metallic nature are also observed. Thus, the bonding is a mixture of covalent, metallic and ionic attribution.

3.2 Mechanical Properties

The elastic constants of solids provide a link between the mechanical and dynamical behaviour of the crystal. In this work, to compute the elastic constants C_{ij} , we have used the total energy method [32-34]. It is noted that, cubic lattices have three independent elastic constants (C_{11} , C_{12} , C_{44}) and five (C_{11} , C_{12} , C_{44} , C_{13} , C_{33}) for hexagonal crystals [32]. The calculated elastic constants are given in Table 4-6 for RuN, RhN and PdN respectively. It is found that most of the calculated elastic constants are in agreement with the experimental and other available theoretical data [11-22]. Mechanical stability criteria for cubic crystal [35] at ambient conditions are $C_{44} > 0$, $C_{11} > |C_{12}|$, $C_{11} + 2C_{12} > 0$ and $C_{12} > 0$, $C_{33} > 0$, $C_{11} > C_{12}$, $C_{44} > 0$, $(C_{11} + C_{12})C_{33} > 2C_{13}^2$ for hexagonal crystal. The sign of the elastic constant C_{44} must always be positive for all possible structures; otherwise the crystal would be mechanically unstable. Our calculated elastic constants are positive for all the phases and obey the necessary mechanical stability conditions. Erjun Zhao et al. [13] and Chen et al. [14] reported that PdN in ZB phase is mechanically unstable due to the negative value of C_{44} , but our results suggest that PdN in ZB phase is mechanically stable and is in agreement with the Nikita Acharya et al. [22]. Therefore, RuN, RhN and PdN all are mechanically stable in all the phases considered. The bulk modulus (B) and shear modulus (G) for the cubic crystals and hexagonal crystals are determined using the Voigt-Reuss- Hill (VRH) averaging scheme [36-38].

The Voigt average for the bulk modulus of the cubic and hexagonal systems respectively is given by:

$$B_0 = \frac{(C_{11} + 2C_{12})}{3} \quad (4)$$

$$B_0 = \frac{2}{9}[C_{11} + C_{12} + 2C_{13} + (1/2)C_{33}] \quad (5)$$

The Voigt average for the shear modulus of the cubic and hexagonal systems respectively is given by:

$$G = \frac{3C_{44} + C_{11} - C_{12}}{5}$$

$$(\quad \quad \quad 6 \quad \quad \quad)$$

$$G = \frac{2(C_{11} + C_{33})}{15} - \frac{(C_{12} + 2C_{13})}{15} + \frac{3[2C_{44} + (1/2)(C_{11} - C_{12})]}{15} \quad (7)$$

The mechanical properties such as Young's modulus (E), shear modulus (G) and Poisson's ratio (ν) are important physical quantities, especially for engineering applications. The Zener anisotropy factor (A) measures the degree of anisotropy in the solid structure. The value of $A=1$, represents completely elastic isotropy, while values smaller or larger than 1 measure the degree of elastic anisotropy. The hardness of the polycrystalline material can be investigated by computing the Lamé constants (λ , μ), Kleinman parameter and micro hardness parameter (H). Physically, the first Lamé constant (λ) determines the compressibility of the material, while the second Lamé constant (μ) reflects its shear stiffness. These parameters are calculated using the following relations [39]:

$$\nu = \frac{C_{12}}{C_{11} + C_{12}} \quad (8)$$

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (9)$$

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)} \quad (10)$$

$$\mu = \frac{E}{2(1+\nu)} \quad (11)$$

$$\zeta = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}} \quad (12)$$

$$H = \frac{(1-2\nu)E}{6(1+\nu)} \quad (13)$$

The all calculated mechanical properties for RuN, RhN and PdN with considered structures using GGA and LDA are presented in Table 4-6 respectively. Bulk modulus (B_0) and shear modulus (G) can measure the resistance of a material to volume and shape change respectively. From Table (1-3) and Table (4-6), it is found that the bulk modulus values obtained from the EOS fit are close to the values calculated using the elastic constants. The results (Table 4-6) indicate that all the nitrides are more inclined to resist the volume change than shape change. Materials with high B and G are likely to be hard materials. As the calculated bulk modulus values of RuN, RhN and PdN are close to that of the superhard materials Hf_3N_4 [40, 41], Zr_3N_4 [41-44] and Si_3N_4 [45-47], the hardness of these nitrides are comparable to the superhard materials. It is also observed that the bulk modulus values of these nitrides are less than that of bimetallic interstitial nitrides Pt_2Mo_3N and Fe_3Mo_3N [48]. Therefore, these compounds are slightly more compressible than ultra-incompressible bimetallic interstitial nitrides [48]. Young's modulus is a measure of stiffness of a solid, i.e., larger the value of Young's modulus, stiffer is the material. The computed results indicate that RuN in NiAs phase, is the stiffest material among the three nitrides. The Poisson's ratio measures the degree of directionality of the covalent bonds. The value of the Poisson's ratio is small (≈ 0.1) for covalent materials, whereas it is greater than or equal to 0.25 [49] for ionic materials. Among the three

nitrides, the Poisson's ratio of WZ-PdN is the lowest, indicating that the TM–N bonding is more directional in nature. Also Poisson's ratio reflects the stability of the crystal against shear. The $\nu=0.25$ and 0.5 are the lower and upper limits, respectively, for central force in solids [50]. The obtained Poisson's ratio for NiAs-PdN and NaCl-RuN is close to the value of 0.25 , which indicates that PdN and RuN have central inter atomic forces.

The ratio of bulk modulus to shear modulus (B/G) is used to estimate the brittle or ductile behaviour of materials. A high B/G value is associated with ductility, while a low B/G value corresponds to the brittle nature. The critical value which separates ductile and brittle materials is about 1.75 . The calculated values of B/G predict that RuN, RhN and PdN are ductile in nature in the stable cubic ZB phase. Also all the three nitrides are elastically anisotropic at ambient pressure. The calculated H values indicate that RuN in NiAs phase is the hardest material among the considered nitrides and it is close to the hardness of ultra-incompressible bimetallic interstitial nitrides [48].

In order to investigate the pressure dependence behaviour of the elastic properties of 4d transition metal nitrides TMN (TM= Ru, Rh, Pd), the calculations are carried out for the pressure ranging from 0 GPa to 100 GPa with stable ZB phase. The variation of elastic moduli with pressure for RuN, RhN and PdN is shown in Fig.10. It is seen that the elastic constants C_{44} and C_{12} increase monotonically with increase in pressure. It is worth to notice that C_{11} increases rapidly with pressure. The elastic constant C_{11} represents the elasticity in length. A longitudinal strain produces a change in C_{11} . The elastic constants C_{12} and C_{44} are related to the elasticity in shape, which is a shear constant. A transverse strain causes change in shape without change in volume. Therefore, C_{12} and C_{44} are less sensitive to pressure as compared to C_{11} . It is also observed that the pressure has an important influence on Young's modulus, bulk modulus and shear modulus.

The Debye temperature (θ_D) is the important parameter closely related to many physical properties of materials, such as specific heat, elastic constants and melting temperature. The Debye temperature is calculated from the elastic constants data using average sound velocity v_m by the following common equation [51]:

$$\theta_D = \frac{\hbar}{k_B} \left[6\pi^2 n \frac{N_A \rho}{M} \right]^{1/3} v_m \quad (14)$$

with $\hbar = h/2\pi$, h is Planck's constant, k_B is Boltzmann's constant, N_A is the Avogadro's number, ρ is density, M is molecular weight, n is the number of atoms in the molecule and

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (15)$$

where

$$v_l = \left(\frac{B + 0.75G}{\rho} \right)^{1/2} \quad (16)$$

and

$$v_t = \left(\frac{G}{\rho} \right)^{1/2} \quad (17)$$

are the velocities of longitudinal and transverse sound waves respectively. The calculated longitudinal, transverse, average sound velocities and Debye temperature values for RuN, RhN and PdN using GGA and LDA along with other available theoretical data [13, 19] are listed in Table 7. The high value of the Debye temperature for NiAs-RuN implies that its thermal conductivity is more when compared with other nitrides. The variation of Debye temperature and the sound velocities with pressure is shown in Fig. 11. It is found that the Debye temperature and sound velocities increases slightly as the pressure increases.

4. Conclusion

In this work, we have performed ab initio calculations using density functional theory to investigate the structural, electronic and mechanical properties of 4d transition metal nitrides TMN (TM= Ru, Rh, Pd). The calculated ground state properties are in good agreement with the experimental and other available theoretical results. Our results suggest that all the three nitrides are stable in ZB structure at ambient pressure. A pressure-induced structural phase transition from ZB to NiAs phase is predicted in RuN, RhN and PdN at a pressure of 104 GPa, 50.6 GPa and 56 GPa respectively. The electronic band structure and density of states of 4d transition metal nitrides TMN (TM= Ru, Rh, Pd) confirm their metallic nature. The computed elastic constants obey the necessary mechanical stability conditions suggesting that all the nitrides are mechanically stable. The hardness of these nitrides is comparable to the superhard materials Hf_3N_4 , Zr_3N_4 and Si_3N_4 . Moreover, the pressure dependence of elastic constants, bulk modulus, Young's modulus, shear modulus and Debye temperature are also investigated. It is found that the pressure has an important influence on the physical properties of these metal nitrides.

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TABLE CAPTIONS

Table 1 Calculated lattice parameters a, c (Å), equilibrium volume V_0 (Å³), valence electron density ρ (electrons/ Å³), Bond length TM-N (Å), cohesive energy E_{coh} (eV), formation enthalpy ΔH (eV), bulk modulus B_0 and its derivative B_0' for RuN.

Table 2 Calculated lattice parameters a, c (Å), equilibrium volume V_0 (Å³), valence electron density ρ (electrons/ Å³), Bond length TM-N (Å), cohesive energy E_{coh} (eV), formation enthalpy ΔH (eV), bulk modulus B_0 and its derivative B_0' for RhN.

Table 3 Calculated lattice parameters a, c (Å), equilibrium volume V_0 (Å³), valence electron density ρ (electrons/ Å³), Bond length TM-N (Å), cohesive energy E_{coh} (eV), formation enthalpy ΔH (eV), bulk modulus B_0 and its derivative B_0' for PdN.

Table 4 Calculated elastic constants C_{11}, C_{12}, C_{44} (GPa), Young's modulus E (GPa), shear modulus G (GPa), B/G ratio, Poisson's ratio ν , Zener isotropy (A), Lamé constants (λ, μ), Kleinman parameter (ζ) and micro hardness parameter (H) for RuN.

Table 5 Calculated elastic constants C_{11}, C_{12}, C_{44} (GPa), Young's modulus E (GPa), shear modulus G (GPa), B/G ratio, Poisson's ratio ν , Zener isotropy (A), Lamé constants (λ, μ), Kleinman parameter (ζ) and micro hardness parameter (H) for RhN.

Table 6 Calculated elastic constants C_{11}, C_{12}, C_{44} (GPa), Young's modulus E (GPa), shear modulus G (GPa), B/G ratio, Poisson's ratio ν , Zener isotropy (A), Lamé constants (λ, μ), Kleinman parameter (ζ) and micro hardness parameter (H) for PdN.

Table 7 Density ρ (g/cm³), longitudinal velocity v_l (m/s), transverse velocity v_t (m/s), average velocity v_m (m/s) and Debye temperature (K).

FIGURE CAPTIONS

Figure 1. Crystal structure of different phases of transition metal nitrides TMN (TM= Ru, Rh, Pd).

Figure 2. Total energy (in eV) versus reduced volume for the different structures of transition metal nitrides TMN (TM= Ru, Rh, Pd): (a) Using GGA (b) Using LDA.

Figure 3. Cohesive energies of transition metals (TM) and the corresponding nitrides in their stable structure

Figure 4. Formation enthalpy of transition metals nitrides in their stable structure

Figure 5. Enthalpy versus pressure curve of transition metal nitrides TMN (TM= Ru, Rh, Pd): (a) Using GGA (b) Using LDA.

Figure 6. Electronic band structure of transition metal nitrides TMN (TM= Ru, Rh, Pd) at normal pressure.

Figure 7. Total density of states (DOS) of transition metal nitrides TMN (TM= Ru, Rh, Pd) at normal pressure.

Figure 8. Partial density of states (DOS) of transition metal nitrides TMN (TM= Ru, Rh, Pd) at normal pressure.

Figure 9. Electronic band structure of transition metal nitrides TMN (TM= Ru, Rh, Pd) under high pressure (NiAs structure).

Figure 10. Total density of states (DOS) of transition metal nitrides TMN (TM= Ru, Rh, Pd) under high pressure (NiAs structure).

Figure 11. Charge density distribution of transition metal nitrides TMN (TM= Ru, Rh, Pd) in the ZB structure.

Figure 12. Pressure dependence of elastic constants of transition metal nitrides TMN (TM= Ru, Rh, Pd).

Figure 13. Pressure dependence of longitudinal velocity v_l (m/s), transverse velocity v_t (m/s), average velocity v_m (m/s) and Debye temperature (K)

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Table 1

	NaCl		CsCl		ZB		NiAs		WZ	
	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA
a	4.32	4.25	2.69	2.64	4.58	4.52	2.73	2.61	2.51	2.47
	4.32 ^a	4.22 ^d	2.675 ^b		4.555 ^b	4.47 ^d	2.948 ^b			
	4.313 ^b	4.056 ^f			4.53 ^d	4.47 ^g	2.94 ^c			
	4.29 ^c					4.47 ^h				
	4.29 ^d									
	4.326 ^e									
c							4.99	4.89	4.16	4.09
							5.272 ^b			
							5.24 ^c			
V ₀	20.16	19.19	19.47	18.4	24.02	23.09	22.36	20.78	22.72	21.65
	20.15 ^a						19.6 ^c			
	19.7 ^c									
ρ	0.644	0.677	0.667	0.706	0.541	0.563	0.5813	0.625	0.572	0.601
TM-N	1.89	1.94	2.09	2.02	1.88	1.89	1.91	1.93	1.82	2.00
	2.14 ^c						2.14 ^c			
E _{coh}	7.565	8.016	7.125	7.630	8.961	9.208	7.415	7.552	6.261	6.539
ΔH	-8.003	-8.271	-7.555	-7.878	-9.309	-9.453	-7.848	-7.801	-6.68	-6.785
B ₀	312	312.4	248	250	298	297	212	223	210.2	228
	335.6 ^a	361 ^d			265 ^d	305 ^d	307 ^c			
	307 ^c					307.3 ^g				
	305 ^d					307.3 ^h				
	298 ^e									
B ₀ '	4.45	4.41	4.20	4.23	4.31	4.02	4.03	4.20	3.98	3.81

^a Ref-11-Exp.^b Ref-12- GGA.^c Ref-13- GGA.^d Ref-14- GGA & LDA.^e Ref-15- LAPW.^f Ref-16- LSDA.^g Ref-17- LSDA.^h Ref-18- LSDA.

Table 2

	NaCl		CsCl		ZB		NiAs		WZ	
	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA
a	4.339	4.301	2.731	2.70	4.629	4.54	3.16	2.90	2.52	2.50
	4.34 ^a	4.30 ^b			4.63 ^b	4.58 ^b	3.04 ^a			
	4.35 ^b	4.080 ^c				4.51 ^d				
						4.51 ^e				
c							5.056	4.785	4.158	4.125
							5.17 ^a			
V ₀	20.42	19.88	20.37	19.68	24.80	23.39	21.57	25.43	23	22.45
	20.5 ^a						20.7 ^a			
ρ	0.685	0.704	0.687	0.711	0.564	0.598	0.649	0.550	0.608	0.623
TM-N	2.10	1.92	2.08	2.01	1.89	1.78	1.91	2.03	1.90	1.95
	2.17 ^a						2.18 ^a			
E _{coh}	7.439	8.476	6.722	7.765	8.336	9.296	7.731	7.725	6.884	7.081
ΔH	-6.32	-6.48	-5.60	-5.66	-7.21	-7.51	-6.61	-5.98	-5.14	-5.26
B ₀	307	309	298	299	251	266	254	259	234	232
	291 ^a	333 ^b			234 ^b	267 ^b	298 ^a			
	286 ^b					267 ^d				
						310 ^c				
B ₀ '	3.98	3.87	3.88	4.41	4.01	4.20	4.21	4.20	4.11	4.45

^a Ref-13- GGA.^b Ref-14- GGA & LDA.^c Ref-16- LSDA.^d Ref-18- LSDA.^e Ref-17- LSDA.

Table 3

	NaCl		CsCl		ZB		NiAs		WZ	
	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA
a	4.446	4.35	2.78	2.718	4.747	4.653	3.145	2.62	2.6	2.505
	4.39 ^a	4.33 ^b	2.77 ^d	2.70 ^d	4.71 ^b	4.64 ^b	3.01 ^a		3.40 ^d	3.37 ^d
	4.40 ^b	4.33 ^c		2.71 ^e	4.739 ^c	4.630 ^c				3.3 ^e
	4.436 ^c	4.34 ^d			4.75 ^d	4.65 ^d				
	4.43 ^d	4.38 ^e				4.67 ^c				
		4.14 ^f				4.62 ^g				
c							5.052	4.292	4.29	4.185
							5.41 ^a		5.28 ^d	5.19 ^d
										5.2 ^e
V ₀	21.97	20.58	21.48	20.08	26.74	25.18	21.99	23.06	25.26	22.59
	21.2 ^a						21.2 ^a			
ρ	0.682	0.728	0.698	0.747	0.560	0.595	0.684	0.650	0.593	0.664
TM-N	2.16	2.13	1.80	1.97	1.86	1.81	1.83	2.01	1.96	1.94
	2.20 ^a						2.20 ^a			
E _{coh}	4.404	6.082	4.274	5.390	5.216	6.230	4.778	4.636	4.379	4.791
ΔH	-4.17	-5.01	-3.39	-3.89	-4.33	-4.96	-3.91	-3.88	-4.08	-4.39
B ₀	254.8	272	231	256	199	220	196	228	180	194
	229 ^a	287 ^b	221 ^d	284 ^d	181 ^b	228 ^b	229 ^a		164 ^d	210 ^d
	234 ^b	273 ^c		251 ^e	170.6 ^c	218 ^c				171 ^e
	209 ^c	283 ^d			174 ^d	221 ^d				
	216.9 ^d	297 ^e				192 ^f				
						217.1 ^g				
B ₀ '	3.99	3.97	4.21	4.43	4.5	4.53	4.32	4.21	4.01	3.97
	5.0 ^c	5.1 ^c	5.39 ^d	5.64 ^d	5.38 ^d	4.8 ^c			5.03 ^d	4.90 ^d
	5.23 ^d	5.26 ^d		4.0 ^e	4.9 ^c	5.22 ^d				4.6 ^e
		4.15 ^e				4.7 ^e				

^a Ref-13- GGA.^b Ref-14- GGA & LDA.^c Ref-21- GGA & LDA.^d Ref-22- GGA & LSDA.^e Ref-19- LDA.

^f Ref-16- LSDA.^g Ref-17- LSDA.

Table 4

	NaCl		CsCl		ZB		NiAs		WZ	
	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA
C ₁₁	521 317 ^a 285 ^b 263.7 ^c 263.8 ^d	541 421 ^a	385	407	473 289 ^a 280 ^d	501 320 ^a	420 118 ^b	444	352	399
C ₁₂	201 299 ^a 318 ^b 314.4 ^c 314 ^d	192 330 ^a	157	152	192 252 ^a 258 ^d	198 298 ^a	192 504 ^b	171	207	211
C ₄₄	97 -155 ^a -167 ^b -66.1 ^c -66.2 ^d	101 -191 ^a	82	87	66 104 ^a 168 ^d	71 104 ^a	82.7 105 ^b	97	85	81
C ₁₃	-	-	-	-	-	-	62 270 ^b	65	97	88
C ₃₃	-	-	-	-	-	-	507 620 ^b	582	427	444
B ₀	307.6 305 ^a 307 ^b 298 ^c 297.5 ^d 335 ^e	308.3 361 ^a	233	237	286 265 ^a 265.9 ^d	299 305 ^a 307 ^f 307.3 ^g	219.8 307 ^b	230	214.7	224
G	122	130	95	103	96 61 ^a	103 58 ^a	142 144 ^b	163	108	122

					168 ^d					
E	323	341	250	269	259	277	350	395	277	309
							376 ^b			
λ	149	146	124	125	128	137	217	182	287	267
μ	127	135	98	105	101	108	133	155	101	114
ζ	0.52	0.49	0.53	0.51	0.54	0.53	0.58	0.52	0.69	0.65
ν	0.27	0.26	0.28	0.27	0.28	0.28	0.31	0.27	0.37	0.35
	0.49 ^a	0.44 ^a			0.47 ^a	0.48 ^a	0.30 ^b			
B/G	2.51	2.36	2.45	2.30	2.97	2.90	1.54	1.41	1.98	1.83
A	0.61	0.58	0.71	0.68	0.47	0.46	0.72	0.71	1.17	0.86
H	19.49	21.65	14.32	16.23	14.83	15.86	16.92	23.84	8.76	11.44

^a Ref-14- GGA & LDA.^b Ref-13- GGA.^c Ref-15- LAPW.^d Ref-12- GGA.^e Ref-11-Exp.^f Ref-17- LSDA.^g Ref-18- LSDA.

Table 5

	NaCl		CsCl		ZB		NiAs		WZ	
	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA
C ₁₁	502	510	498	501	348	392	439.6	448	301	322
	462 ^a	498 ^a			251 ^a	287 ^a	429 ^b			
	466 ^b									
C ₁₂	209.6	214	201	197	191	212	249	221	185	197
	198 ^a	251 ^a			226 ^a	258 ^a	226 ^b			
	204 ^b									
C ₄₄	83	95	78	85	41	49	101	97	83	69
	56 ^a	13 ^a			39 ^a	44 ^a	68 ^b			
	41 ^b									
C ₁₃	-	-	-	-	-	-	110	121	171	158
							188 ^b			
C ₃₃	-	-	-	-	-	-	566	601	405	431
							700 ^b			
B ₀	306	312	300	298	243	272	264	269.2	229	233
	286 ^a	333 ^a			234 ^a	267 ^a	298 ^b			
	291 ^b					267.8 ^c				
						267.9 ^d				
G	108	116	106	111	56	65	142	151	86	92
	94 ^a	68 ^a			26 ^a	29 ^a	102 ^b			
	66 ^b									
E	289	309	284	296	156	180	361	381	229	243
	344 ^a	331 ^a					275 ^b			
	185 ^b									

λ	154	178	141	147	134	155	341	278	262	252
μ	112	118	110	115	57.7	66.6	132	143	82.9	88.6
ζ	0.55	0.56	0.54	0.53	0.66	0.65	0.68	0.62	0.72	0.71
ν	0.29	0.30	0.28	0.28	0.35	0.35	0.36	0.33	0.38	0.37
	0.30 ^a	0.33 ^a			0.47 ^a	0.47 ^a	0.35 ^b			
	0.39 ^b									
B/G	2.83	2.68	2.83	2.68	4.33	4.18	1.85	1.78	2.66	2.53
A	0.56	0.64	0.52	0.56	0.52	0.54	1.06	0.85	1.43	1.10
H	15.68	15.84	16.27	16.95	5.77	6.66	12.38	16.23	6.63	7.68

^a Ref-14- GGA & LDA.^b Ref-13- GGA.^c Ref-17- LSDA.^d Ref-18- LSDA.

Table 6

	NaCl		CsCl		ZB		NiAs		WZ	
	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA
C ₁₁	335	372	351	389	383	427	397	395	384	424
	345 ^a	435 ^a			163 ^a	201 ^a	318 ^b			
	306 ^b				151 ^d	243 ^c				
						195 ^d				
C ₁₂	200	248	151	168	143	174	139	142	115	128
	178 ^a	213 ^a			190 ^a	242 ^a	180 ^b			
	191 ^b				184 ^d	166 ^c				
						235 ^d				
C ₄₄	58	49	18	37	91	102	99.2	107	51.2	60.5
	50 ^a	46 ^a			-30 ^a	-16 ^a	-20 ^b			
	48 ^b				41.15 ^d	8.22 ^c				
						81.83 ^d				
C ₁₃	-	-	-	-	-	-	78	81	71	65
							155 ^b			
C ₃₃	-	-	-	-	-	-	445.8	468	371.07	452
							507 ^b			
B ₀	245	289	217	241	223	258	203	207	183.6	201.7
	234 ^a	287 ^b	221 ^d	284 ^d	181 ^b	228 ^b	229 ^a		164 ^d	210 ^d
	229 ^b	283 ^d		251 ^f	174 ^d	221 ^d				171 ^f
	216.9 ^d	273 ^e			170.6 ^e	218 ^e				
	209 ^e	297 ^f				192 ^f				
						217.1 ^g				
G	61	54	51	66	102	112	137	141	121	140

	67 ^a	79 ^a				16.16 ^c				
	51 ^b									
E	169	152	142	181	265	293	335	344	297	342
	224 ^a	294 ^a				47 ^c				
	143 ^b									
λ	175	217	82	104	122	156	134	147	102	118
						146 ^c				
μ	62	54	55	70	104	113	134	136	120	139
						16.26 ^c				
ζ	0.70	0.76	0.57	0.56	0.51	0.55	0.49	1050	0.45	0.44
						0.77 ^c				
ν	0.37	0.40	0.30	0.30	0.27	0.29	0.25	0.26	0.23	0.23
	0.34 ^a	0.33 ^a			0.54 ^a	0.55 ^a				
	0.40 ^b					0.45 ^c				
B/G	4.01	5.35	4.25	3.65	2.18	2.31	1.48	1.46	1.51	1.43
A	0.86	0.79	0.18	0.33	0.76	0.81	0.76	0.85	0.38	0.41
H	5.34	3.62	7.28	9.28	15.99	15.88	22.3	21.84	8.60	7.28

^aRef-14- GGA & LDA.^bRef-13- GGA.^cRef-19- LDA.^dRef-22- GGA & LSDA.^eRef-21- GGA & LDA.^fRef-18- LSDA.^gRef-17- LSDA.

Table 7

Compound			P	v_l	v_t	v_m	θ_D
RuN	NaCl	GGA	9.475	7045	3588	4020	554
		LDA	9.867	6984	3629	4062	569
	CsCl	GGA	9.725	6081	3125	3500	488
		LDA	10.291	6031	3163	3538	502
	ZB	GGA	8.752	6877	3311	3723	498
		LDA	8.200	7294	3543	3982	524
	NiAs	GGA	8.468	6943	4094	4537	604
		LDA	9.112	7006	4229	4675	638
							598 ^a
		WZ	GGA	8.334	6553	3599	4012
		LDA	8.746	6649	3734	4155	559
RhN	NaCl	GGA	9.177	7002	3430	3852	528
		LDA	9.427	7035	3507	3935	545
							411 ^a
	CsCl	GGA	9.200	6925	3394	3812	523
		LDA	9.523	6843	3414	3830	532
	ZB	GGA	7.954	6319	2653	3000	390
		LDA	8.012	6690	2848	3219	422

PdN	NiAs	GGA	8.688	7223	4042	4499	606
		LDA	7.369	7988	4526	5033	642
	WZ	GGA	8.148	6494	3248	3644	480
		LDA	8.348	6527	3319	3720	494
	NaCl	GGA	8.898	6055	2618	2957	396
		LDA	9.506	6162	2383	2702	370
	CsCl	GGA	9.072	5604	2370	2680	361
		LDA	9.705	5822	2607	2941	406
	ZB	GGA	7.475	6929	3693	4126	517
		LDA	7.739	7254	3804	4254	544
	NiAs	GGA	8.862	6596	3931	4352	582
		LDA	8.451	6836	4084	4520	595
	WZ	GGA	7.701	6686	3963	4389	561
		LDA	8.612	6709	4031	4459	591

^a Ref-13- GGA.

^b Ref-19- LDA.

Research Highlights

- ▶ Electronic, structural and mechanical properties of RuN, RhN, PdN are investigated.
- ▶ A pressure induced structural phase transition is predicted under high pressure.
- ▶ Electronic structure reveals that these materials exhibit metallic behavior.
- ▶ Computed elastic moduli obey traditional mechanical stability condition.
- ▶ Among these nitrides RuN is found to be the hardest material.
- ▶ The Debye temperature values are computed for RuN, RhN, PdN.

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Fig.1

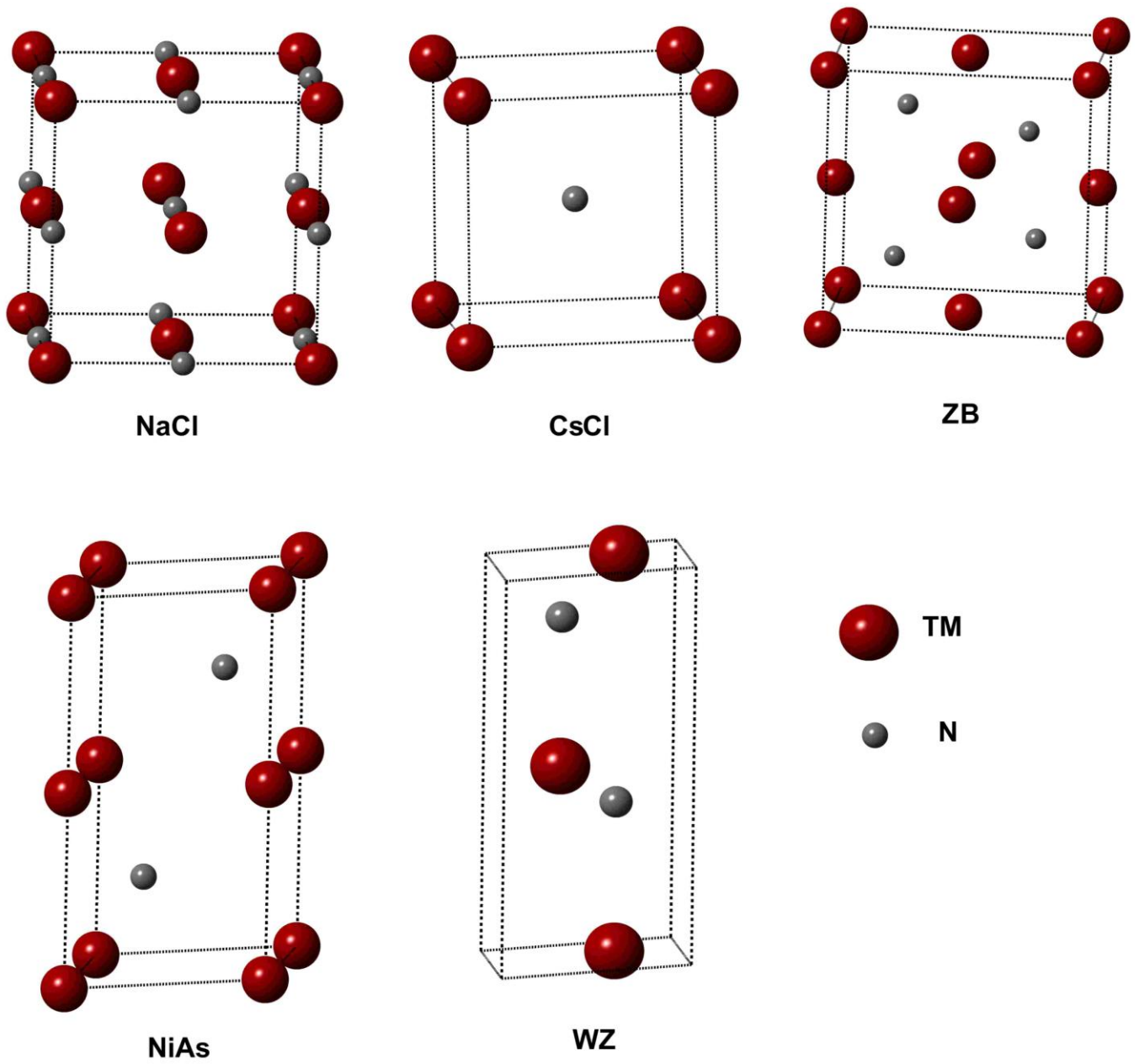


Fig.2(a)

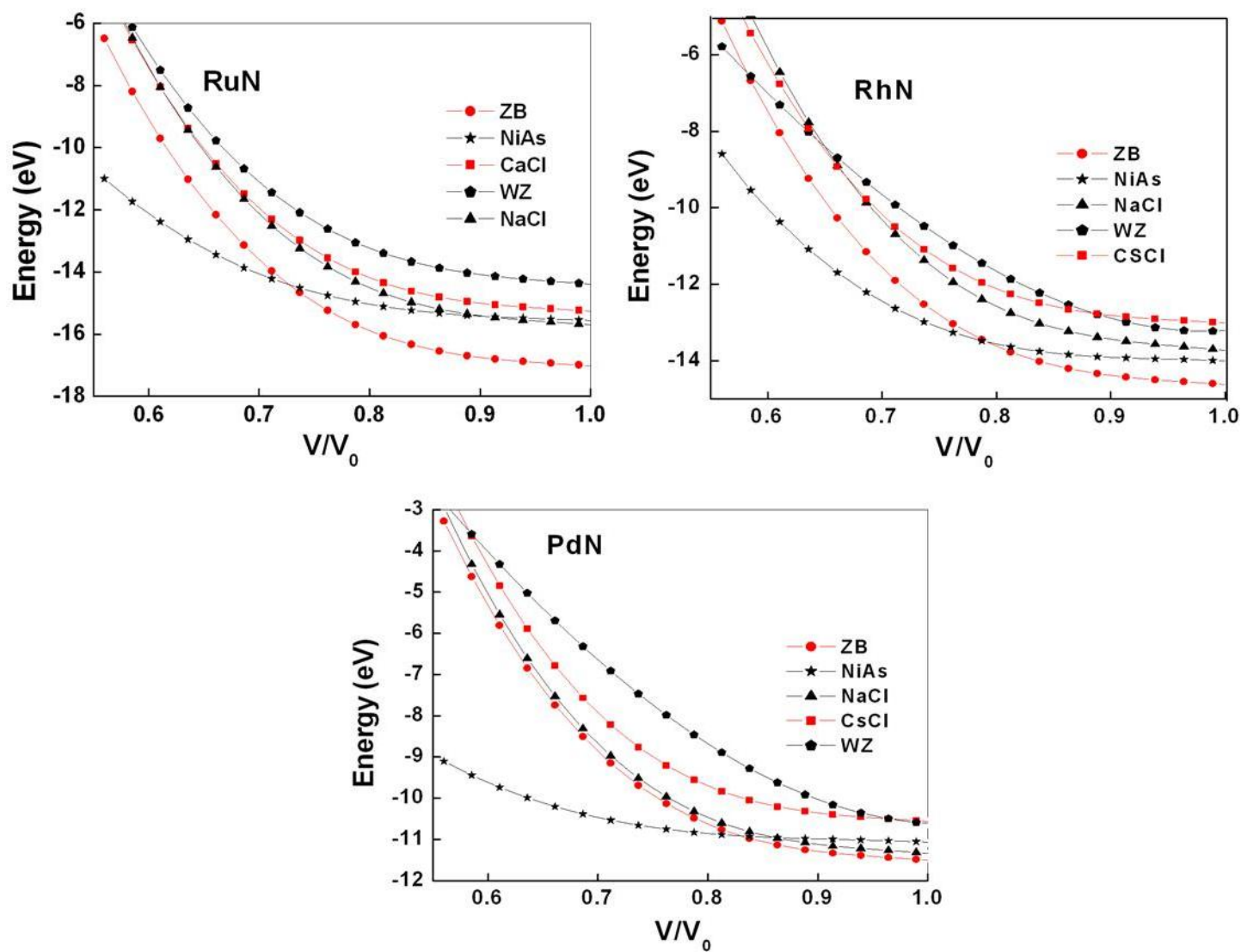


Fig.2(b)

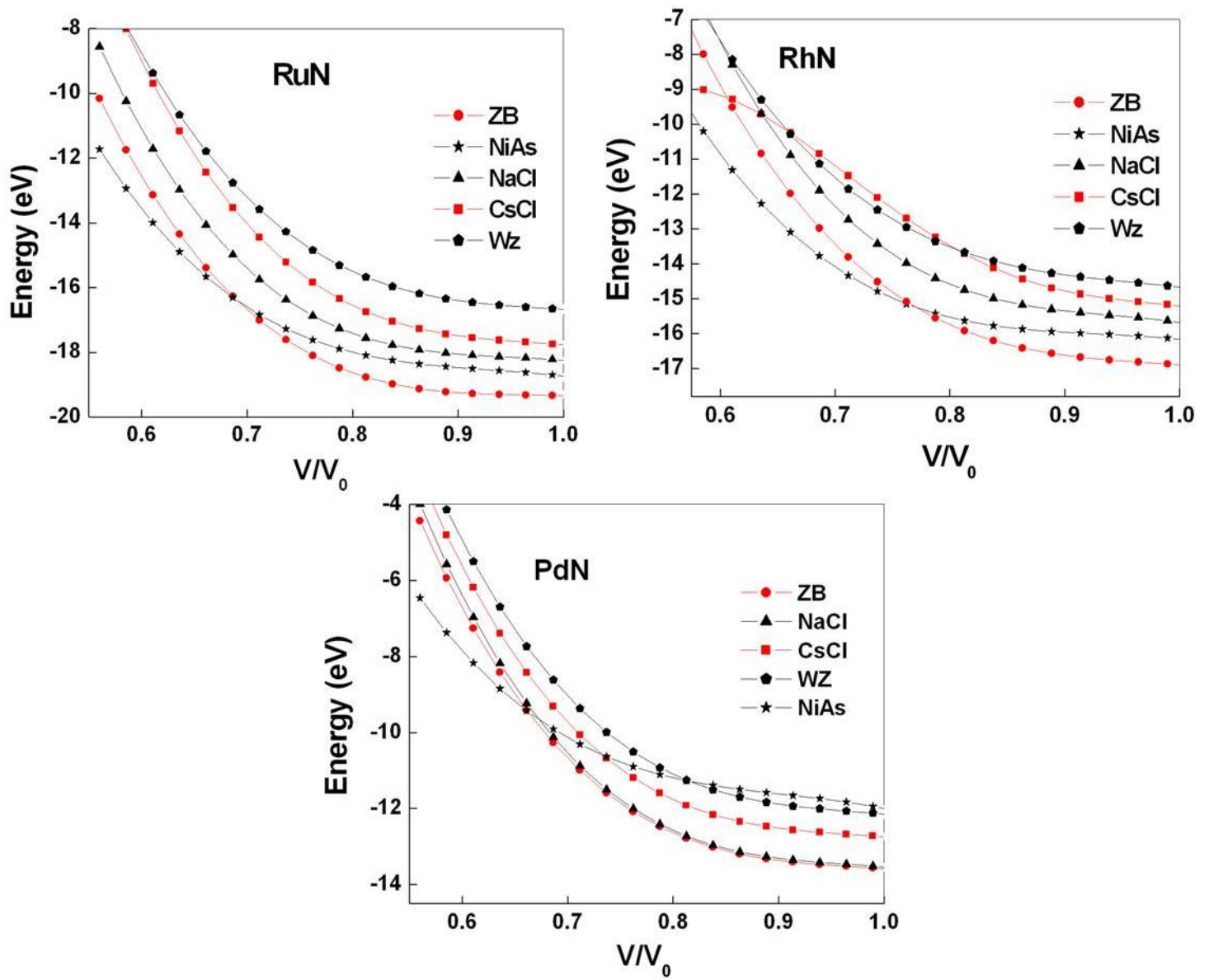


Fig.3

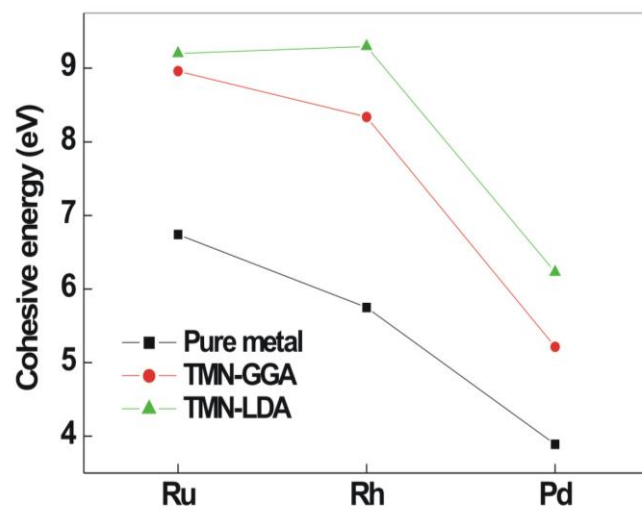


Fig.4

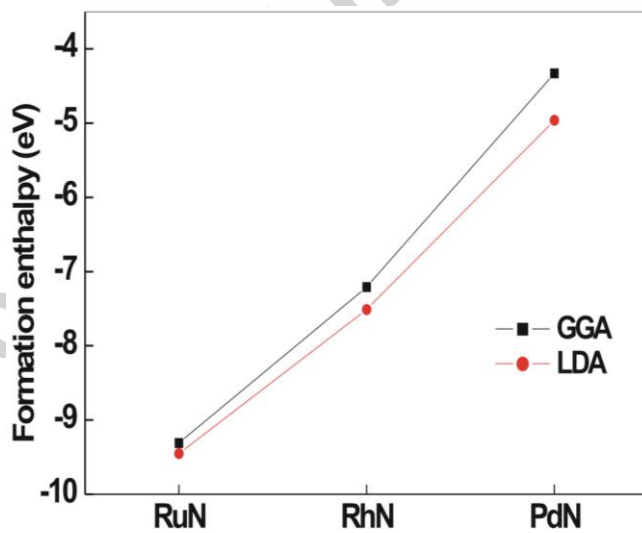


Fig.5(a)

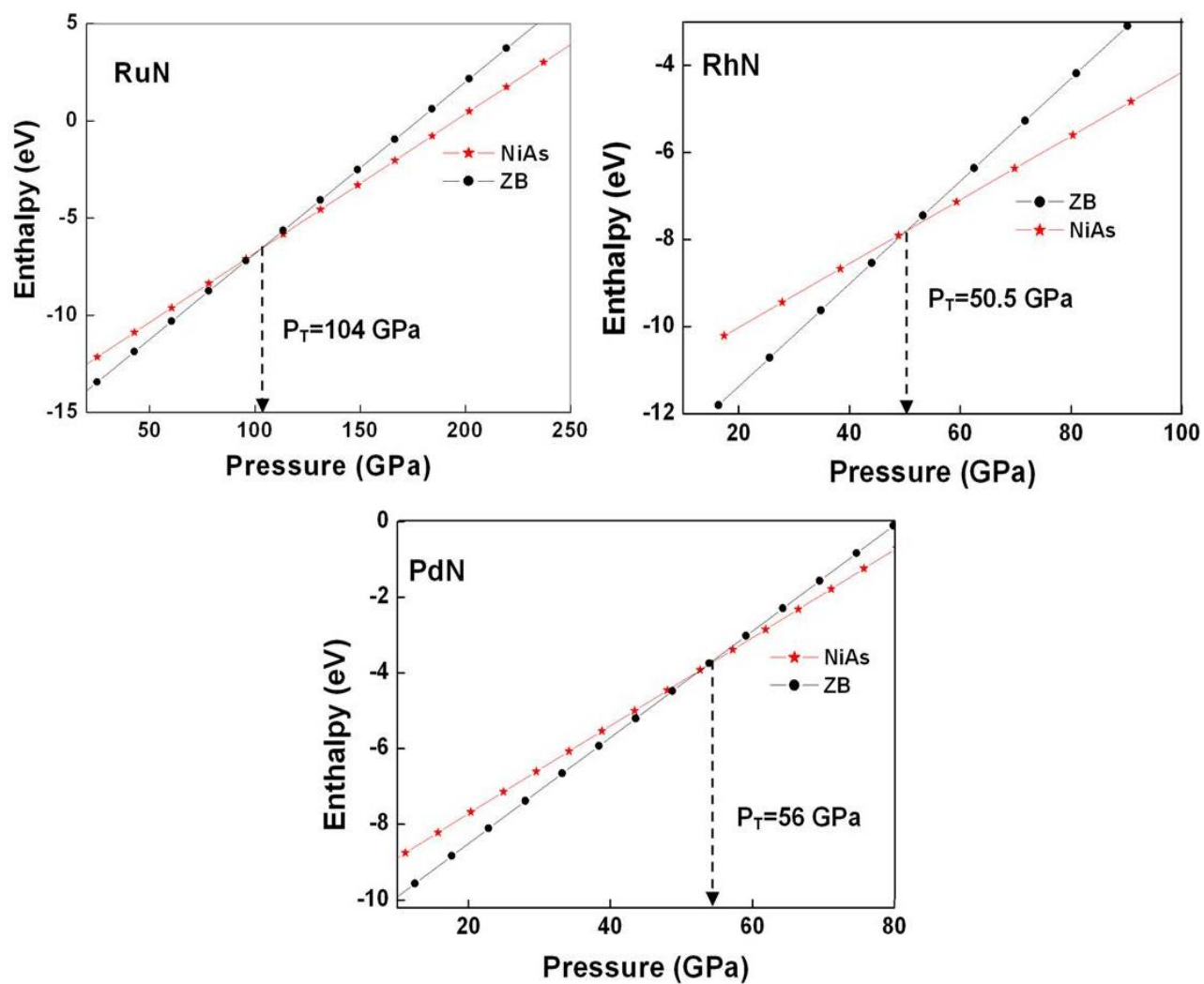


Fig.5(b)

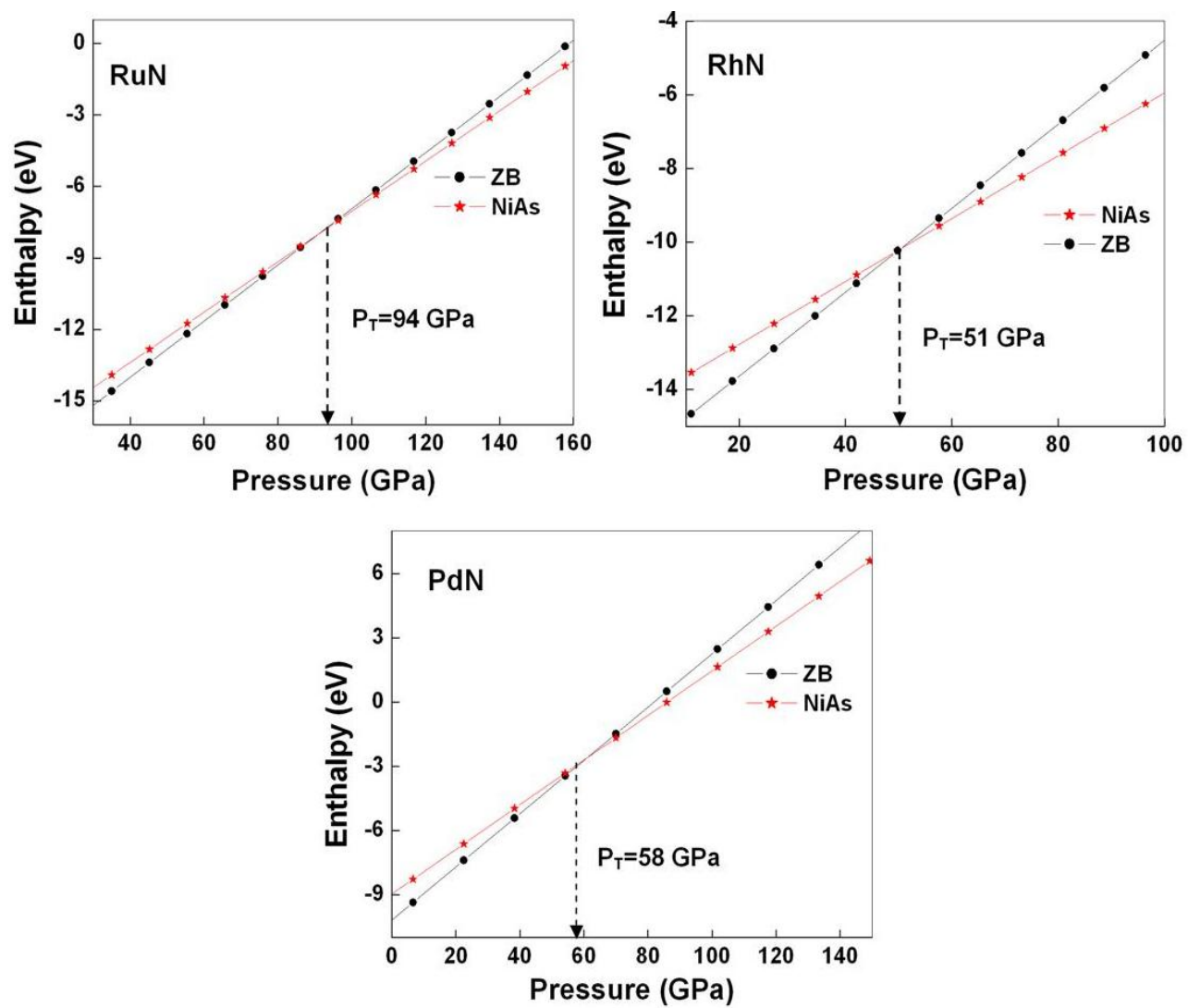


Fig.6

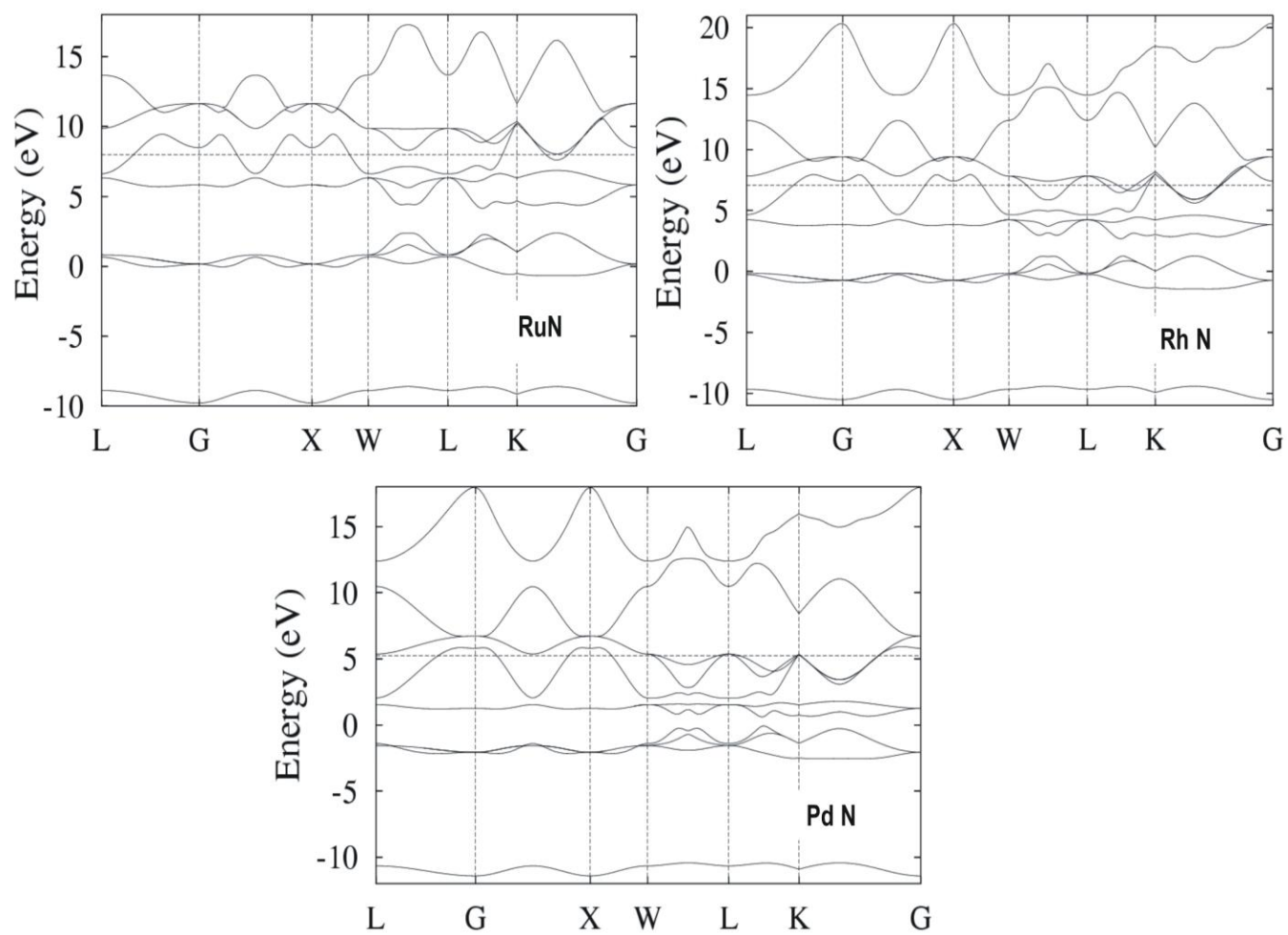


Fig.7

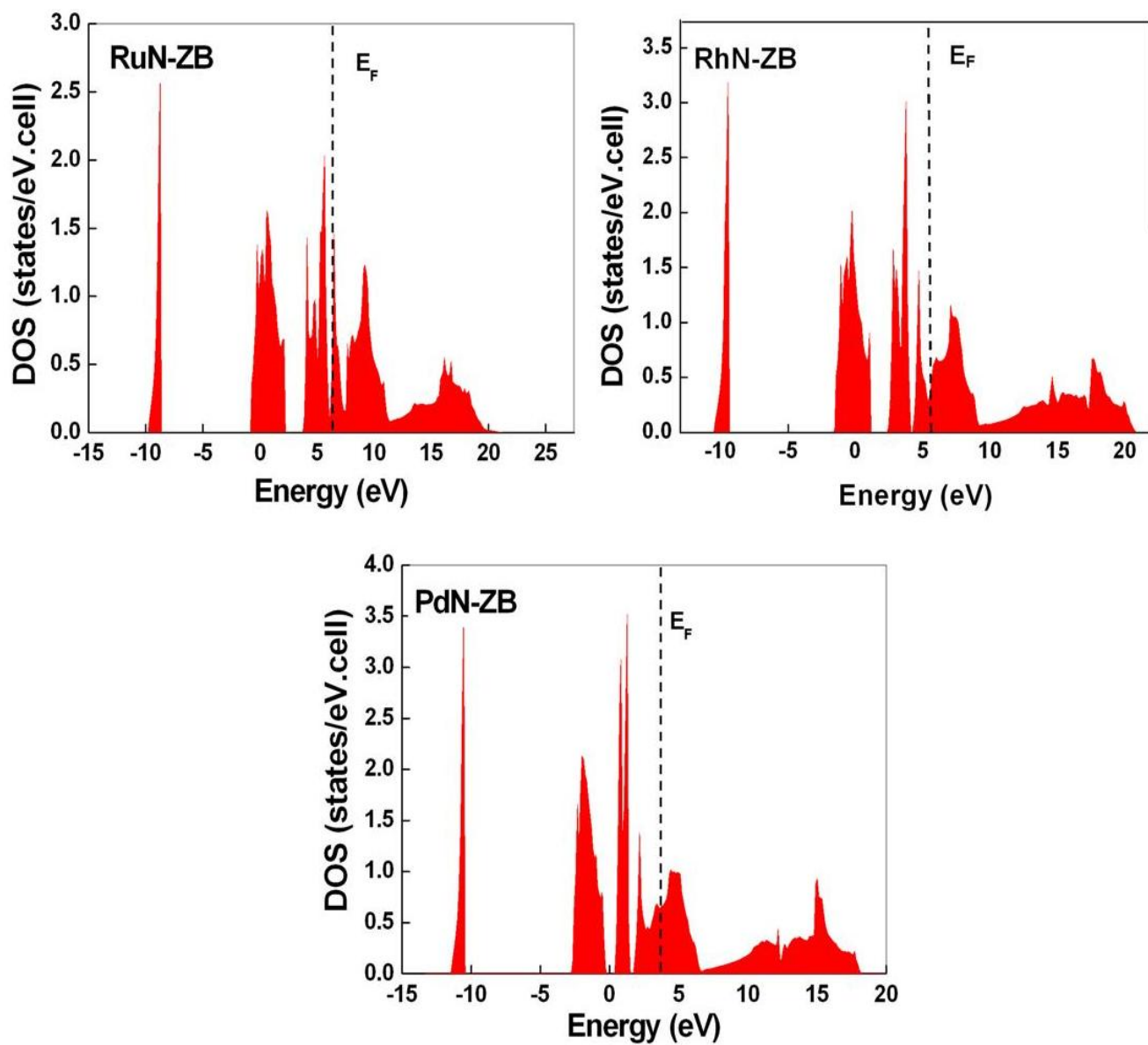


Fig.8

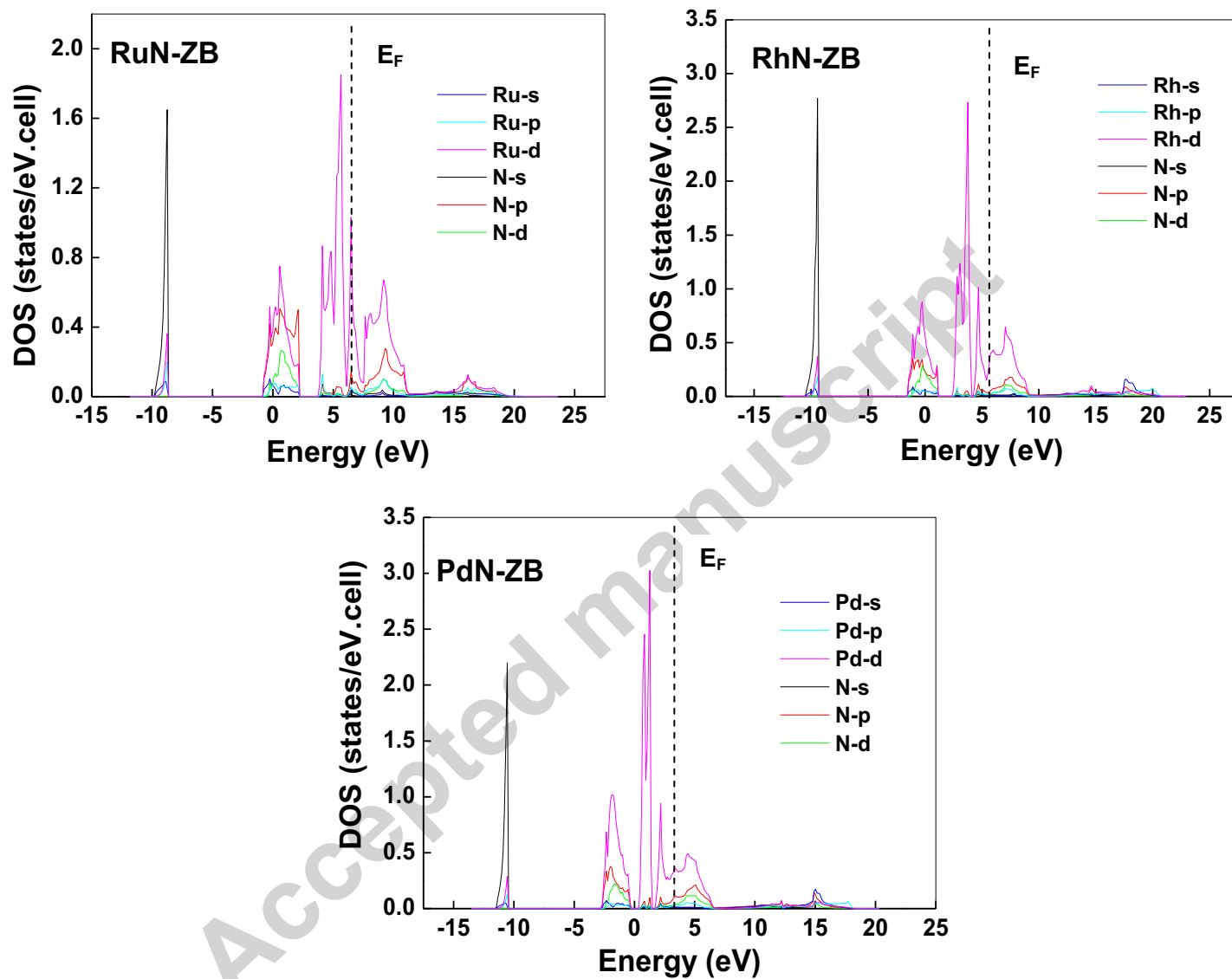


Fig.9

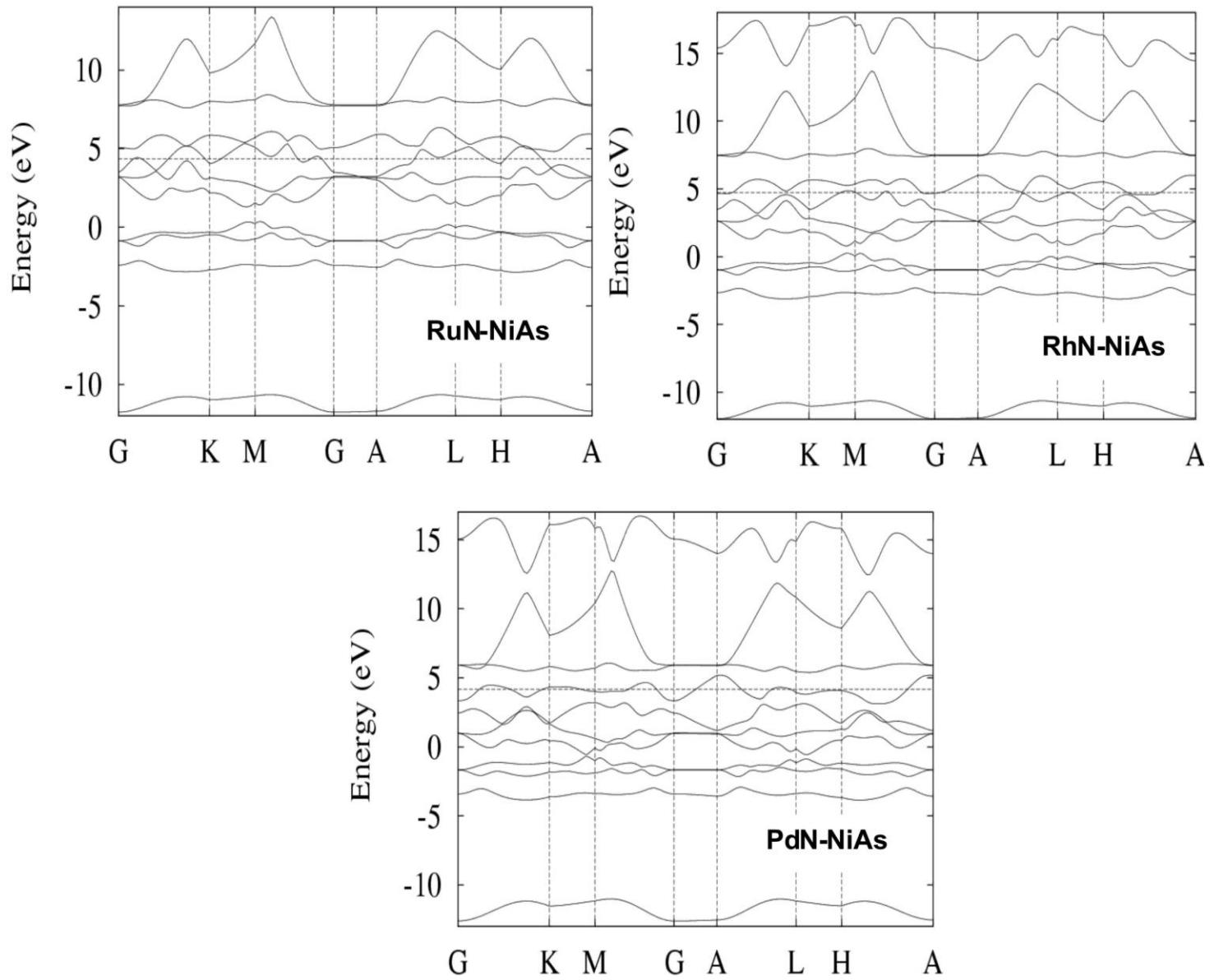


Fig.10

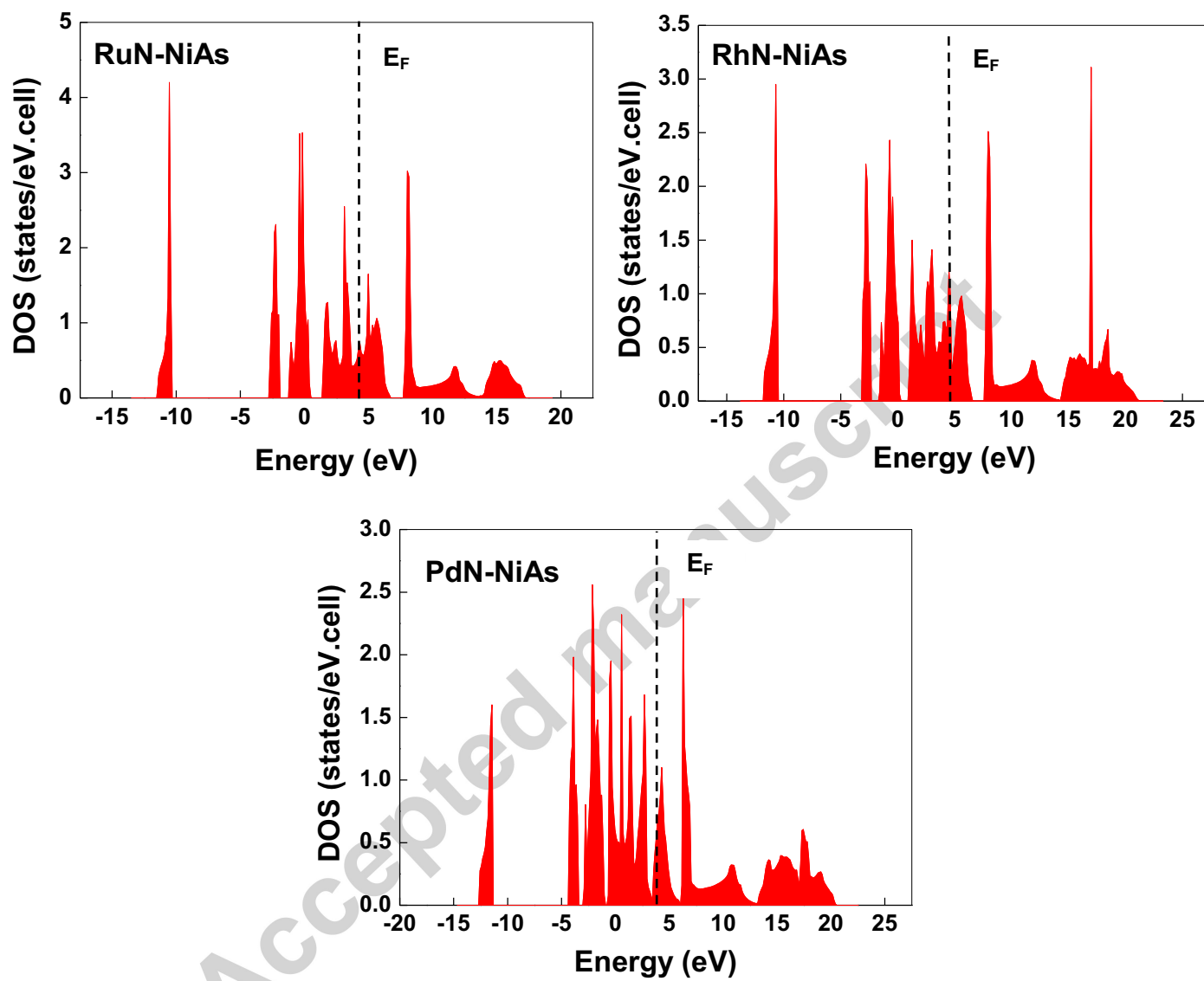


Fig.11

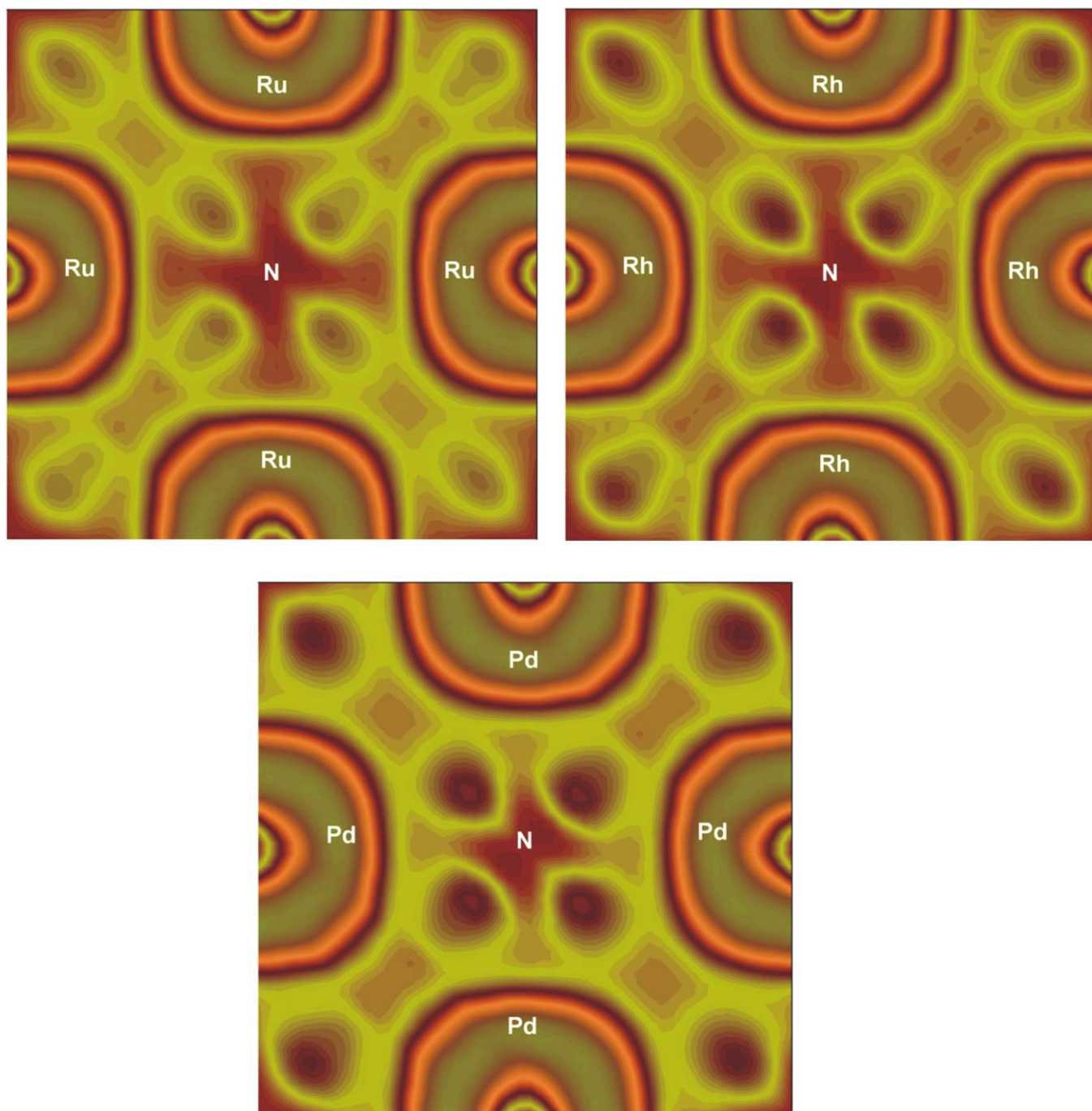


Fig.12

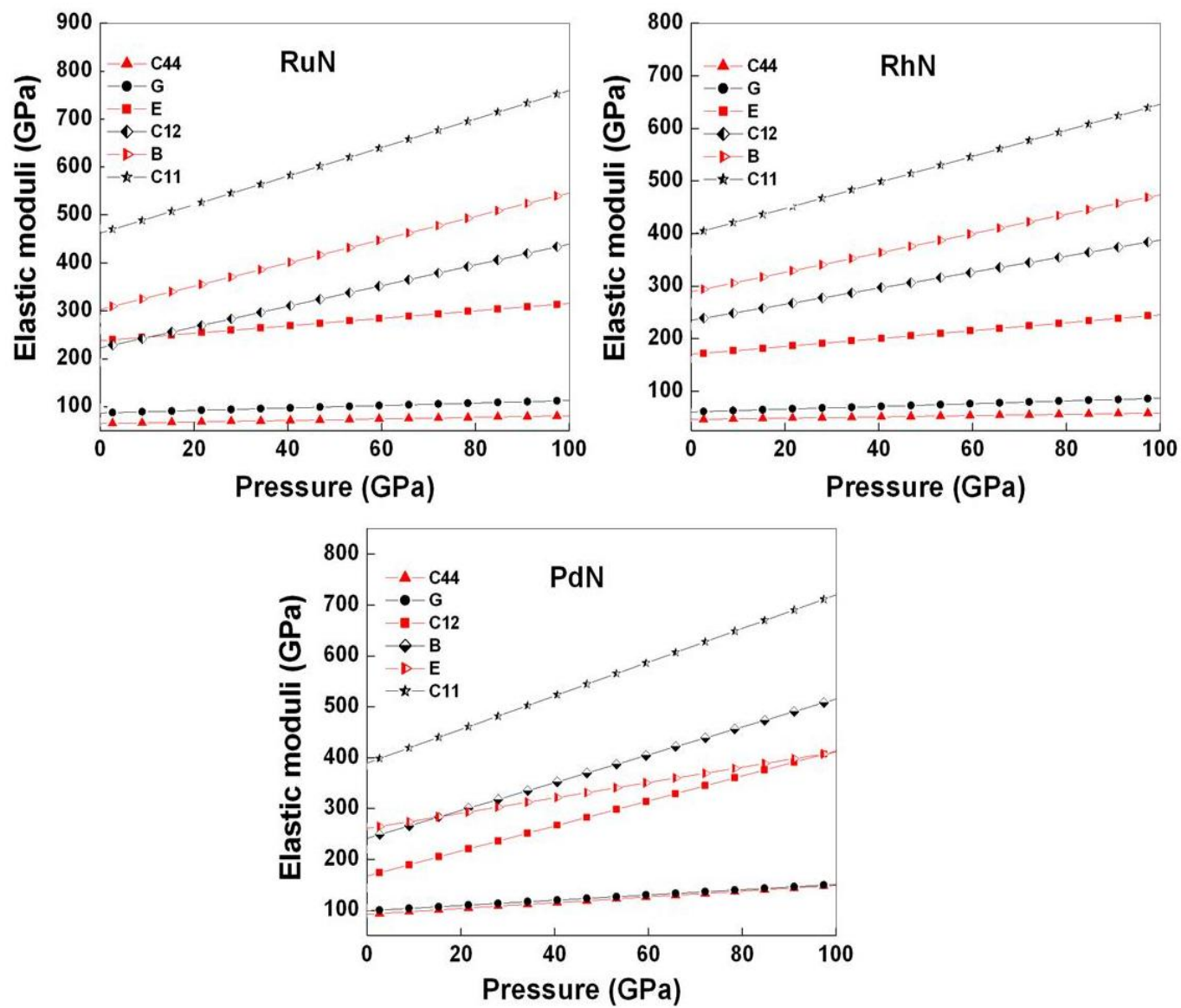


Fig.13

