First principles study of structural, electronic and mechanical properties of transition metal hydrides (TMH, TM=Mo,Tc, Ru)

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Abstract: The structural, electronic and mechanical properties of transition metal hydrides (TMH, TM=Mo, Tc, Ru) are investigated by means of first principles calculation based on density functional theory with generalized gradient approximation. Among the five crystallographic structures that have been investigated, the cubic phase is found to be more stable than the hexagonal ones. A structural phase transition from ZB to WC in MoH, NaCl to NiAs in TcH and NaCl to ZB to NiAs in RuH is also predicted under high pressure. The calculated elastic constants indicate that all the three hydrides are mechanically stable at ambient pressure.
Key words: ab-initio method; structural phase transition; electronic properties; elastic property

1 Introduction

During the past years, the interaction between transition metals and H_2 has raised great interest among the researchers, as transition metals are not only regarded as promising potential materials for H_2 storage [1], but also used as structural materials in nuclear reactors due to their low neutron absorption cross section, high mechanical strength and excellent corrosion resistance at elevated temperatures [2]. Accurate first principles methods can complement and help to interpret high pressure experiments, which can provide a detailed description of the structural and bonding changes that a material undergoes under extreme conditions. The behavior of H_2 at high pressure is important due to a number of fundamental condensed matter and planetary science [3]. FUKAI and MIZUTANI [4] observed phase transformation experimentally in MoH system, by gradually increasing pressure of up to 5 GPa and temperature up to 500 °C using in situ resistometry technique. Later on, ANTONOV et al [5] investigated the phase transformation in MoH up to 1000 °C using the same technique.

Recently, the structural stability of MgH_2 was investigated using the DFT technique as implemented in VASP code [6]. No attempts have been made to predict the structural phase transition in MoH, TcH and RuH under high compression. Also the mechanical stability of these hydrides has not been reported yet. The technological applications of these materials and success of ab-initio methods motivated us to analyze the electronic and structural changes in MoH, TcH and RuH. Apart from the structural phase transition, the present work also includes the discussion on the computation of ground state and mechanical properties of MoH, TcH and RuH.

2 Computational details

The present computation of structural stability and phase transition in MoH, TcH and RuH have been carried out using the DFT-based VASP code [7−9], which is appropriate for electronic structure calculations and ab initio molecular dynamics simulations of molecules and solids. Within the framework of DFT [10−12], the first-principles pseudopotential approach has been used to analyze the stability of the ZB (B4) (space group: $Fm\overline{4}m$), WC (Bh) (space group: $P6\text{-}m2$), NaCl (B1) (space group: $Fm3m$), NiAs (B8) (space group: $P6_3/mmc$) and CsCl (B2) (space group: $Pm3m$) type phases of TcH, MoH and RuH. The unit cells for all five different phases are shown in Fig. 1. The effects of exchange–correlation interactions are handled by the generalized gradient
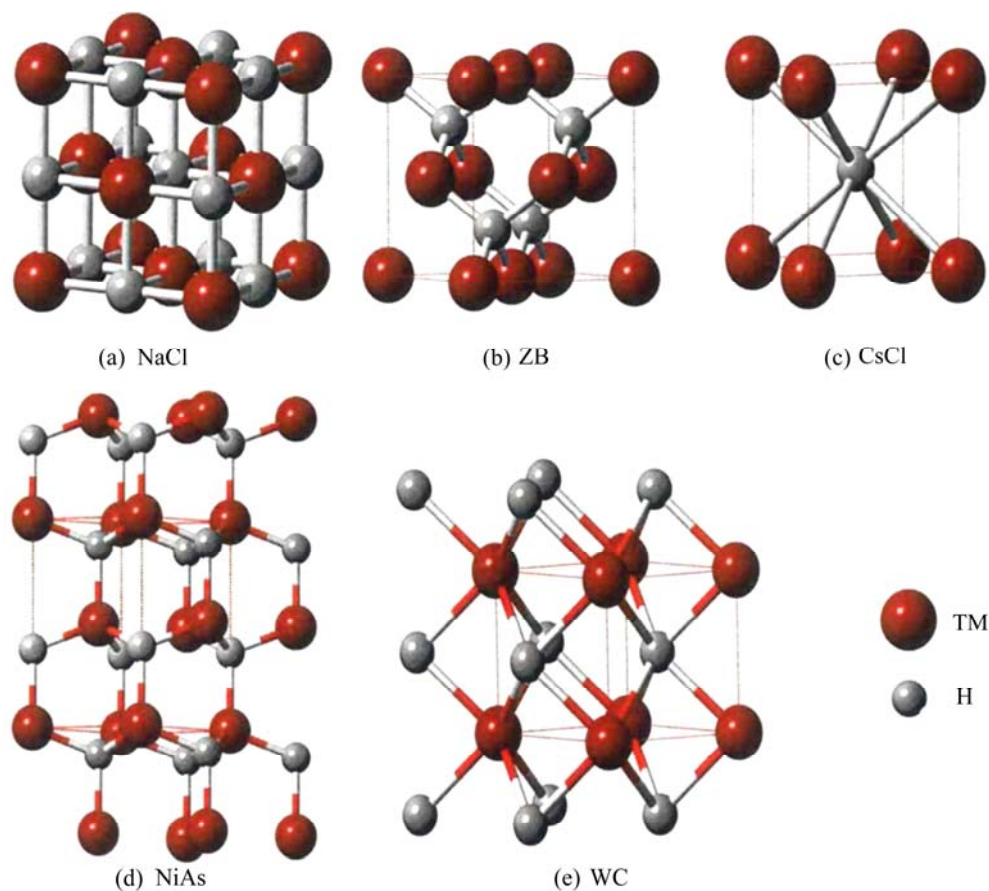
Fig. 1 Unit cell for five different phases of TMH (TM=Mo,Tc,Ru)

approximation (GGA). In the present computation, the hydrides are assumed to be without any defect and the stoichiometric composition for all the hydrides is taken as 1:1 ratio of metal atom and hydrogen atom. The electronic wave functions are expanded in a plane wave basis set with an energy cut-off of 450, 500 and 600 eV for MoH, TcH and RuH respectively. The total energy is calculated by integration over a monkhorst-pack mesh [13] of k-point in the Brillouin zone by the linear tetrahedron method including Blochl corrections [8] on the relaxed structures with a smearing width of 0.1 eV. After convergence test, 12×12×12 k-point mesh is chosen to make sure the total energy difference less than 1 meV per primitive cell. The electronic configurations of Mo, Tc, Ru and H atoms are [Kr] $4d^55s^1$ (Z=42), [Kr] $4d^55s^2$ (Z=43), [Kr] $4d^75s^1$ (Z=44), and $1s^1$ (Z=1) respectively. The valence electronic configurations chosen in our calculation are $4d^55s^1$ for Mo, $4d^55s^2$ for Tc, $4d^75s^1$ for Ru and $1s^1$ for H atoms.

3 Results and discussion

3.1 Structural stability and ground state properties

The stability of TMH (TM=Mo, Tc, Ru) is analyzed by calculating the total energy using VASP code based

on density functional theory. The computed total energy for all the considered phase of the TMH is listed in Table 1. From Table 1, it is found that both TcH and RuH are energetically stable in the rocksalt (NaCl) structure whereas MoH is energetically stable in the zincblende (ZB) structure. The stability of a solid is determined with the help of its formation energy. The formation energy of a specific compound is defined as the difference between the total energy of the compound and of its constitutive elements. The composition reaction of TMH is as follows:

$$TM + \frac{1}{2}H_2 \rightarrow TMH \tag{1}$$

This yields the following expression for the formation energy

$$E_f(TMH) = E(TMH) - (E_{TM} + 1/2E_{H_2}) \tag{2}$$

In order to calculate the formation energy, E_f, the total energy of TMH, TM and H_2 dimer should be calculated. The formation energies for the transition metals hydrides in five different phases (TMHs) are shown in Fig. 2. From Fig. 2, it is observed that both TcH and RuH are more stable in the NaCl structure whereas MoH is more stable in the ZB structure. The calculated

Table 1 Total energy of MoH, TcH and RuH

Meatl hydride	Structure	Total energy/(eV·atom^{-1})
MoH	NaCl	−14.0974
	CsCl	−13.6241
	ZB	−14.2108
	WC	−13.4164
	NiAs	−12.3932
TcH	NaCl	−14.5049
	CsCl	−14.4241
	ZB	−13.9732
	WC	−13.1446
	NiAs	−12.4343
RuH	NaCl	−13.6857
	CsCl	−13.0835
	ZB	−13.0359
	WC	−11.7074
	NiAs	−11.8590
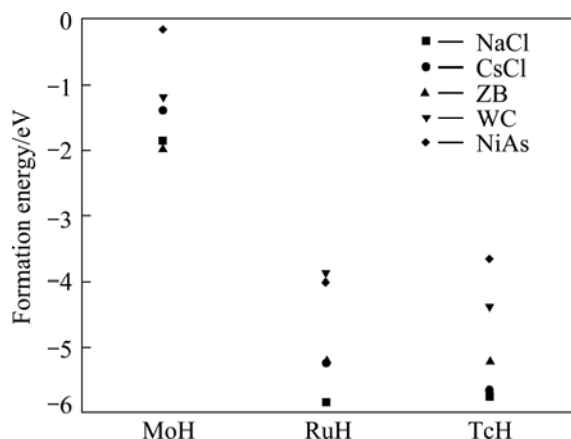
Fig. 2 Formation energy of TMH

ground state properties like lattice constant a_0 (Å), cell volume V_0(Å^3), valence electron density ρ (electron/Å^3), bond length (d) of TM—H (Å), bulk modulus B_0 (GPa) and its derivative B'_0 for the most stable phase of the TMH are listed in Table 2. Valence electron density (VED) is defined as the total number of valence electrons divided by volume per unit cell and is an important factor for analyzing the super hard materials.

Table 2 Calculated ground state properties of MoH, TcH and RuH for five different structures

Parameter	a_0/ Å	V_0/ Å^3	ρ/ (electron·Å^{-3})	B_0/ GPa	B_0'	d/Å
MoH	4.289	19.72	0.3042	196	3.6	1.96
TcH	4.066	16.81	0.4164	217	3.8	1.813
RuH	3.9732	15.68	0.5102	256	4.1	1.71

3.2 Electronic structure

In order to understand the electronic structure of MoH, TcH and RuH, the electronic band structure and density of states (DOS) have been calculated. Figure 3(a) shows the combined band structure and density of states of MoH (ZB), TcH (NaCl) and RuH (NaCl) in their most structure at ambient pressure. The partial density of states (PDOS) for MoH, TcH and RuH is shown in Fig. 3(b). From Fig. 3(a), it is observed that all these hydrides exhibit metallic character and their valence bands split into two parts. The lower part of the valence band is dominated by the ns state electrons of the TM (Mo,Tc,Ru) atoms and slightly influenced by 1s state of the hydrogen atom, while the upper one is a result of strong hybridization from the d state electrons of TM (Mo,Tc,Ru) atoms and the 1s state of H atom. In the density of states of MoH, TcH and RuH (Fig. 3), there is a deep valley called pseudo gap near the Fermi level, which results from the strong hybridization between the transition metal d states and 1s state of H atom. The presence of pseudogap indicates significant covalent bonding between TM and H atoms in the cubic structure.

To further explore the bonding nature, the charge density distribution of MoH, TcH and RuH in the cubic structure is shown in Fig. 4. It is observed that the charge density around H atoms exhibits a strong directional distribution of TM atoms, indicating that the bonding between TM (Mo, Tc, Ru) and H atoms is covalent in nature. The charge density distribution between TM and H atoms in the cubic structure is much denser than those in other structures. Thus the results demonstrate that the bonding in these hydrides is a mixture of metallic, covalent and ionic in attribution.

3.3 Structural phase transition under pressure

At normal pressure MoH is highly stable in zinc blende structure whereas TcH and RuH are stable in the rocksalt structure. The total energy calculations are performed for five different phases of MoH, TcH and RuH, corresponding to the reduced volume of V/Vo=1.0−0.5 and the results are shown in Fig. 5. It is observed that at high pressure, the hexagonal structure becomes more stable in energy than the cubic structure for MoH and TcH. But for RuH, ZB structure is the meta stable phase and hexagonal NiAs is the stable phase at high pressure. Thus it can be concluded that at high pressure all the three hydrides are more stable in the hexagonal phase.

The enthalpy is defined as

$$H(\text{P})=E_{\text{total}}(\text{P})+pV(\text{P}) \tag{3}$$

To analyze the structural phase transition from ZB to WC in MoH, from NaCl to NiAs in TcH and from
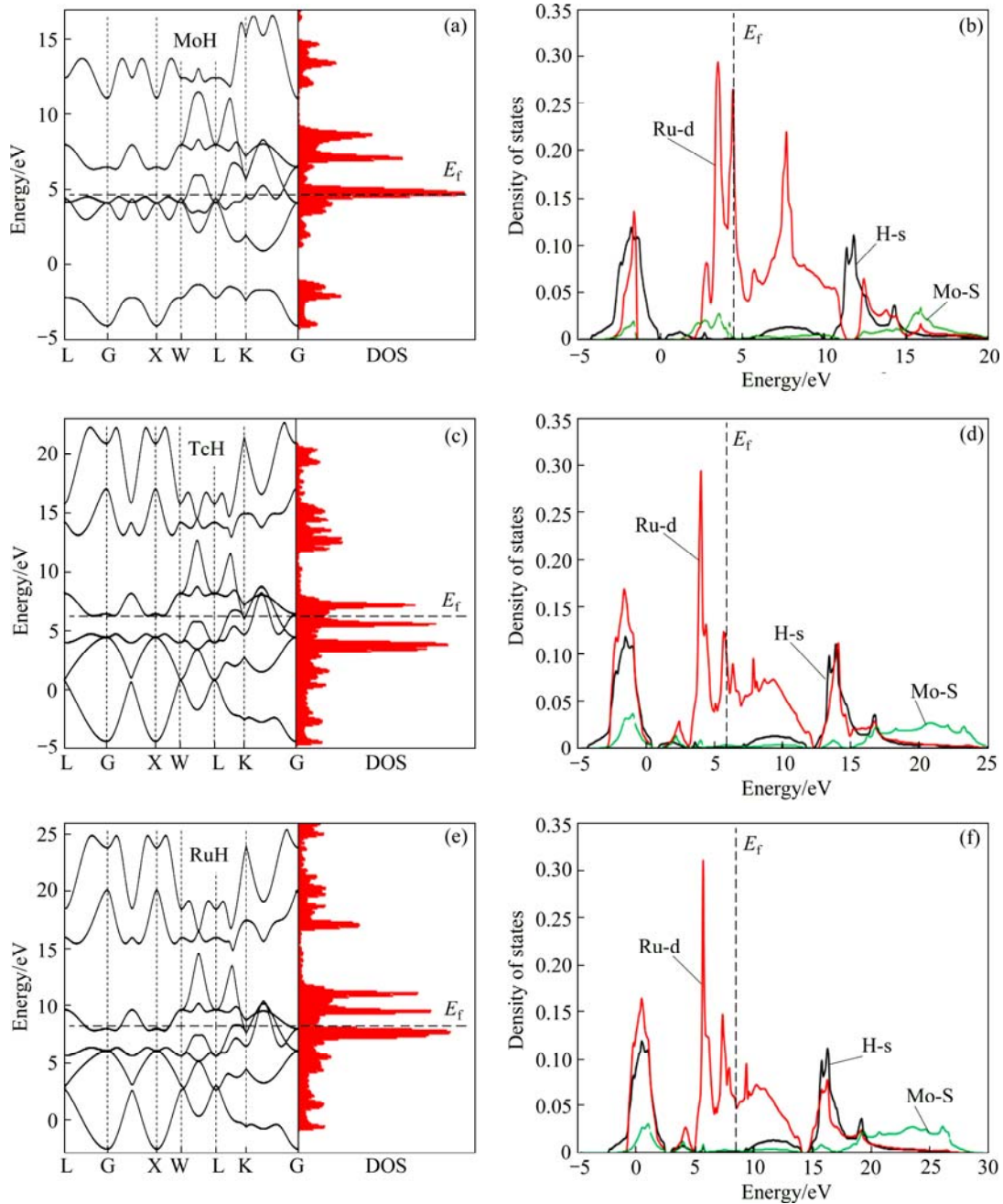
Fig. 3 Electronic band structure (a, c, e) and density and partial density (b, d, f) of states for TMH

NaCl to ZB to NiAs in RuH, enthalpy values are plotted against pressure and are shown in Fig. 6. The transition pressure estimated from Fig. 6 is tabulated in Table 3. From Table 3 it is concluded that all the three hydrides are stable in the hexagonal phase at high pressure. So far, no study on the phase transition has been performed as a function of high pressure for MoH, TcH and RuH.

3.4 Elastic properties

The elastic constants of solids provide a link between mechanical and dynamical behaviors of crystals, and give important information concerning the nature of forces operating in solids. In particular, they provide information on stability and stiffness of materials [14]. Thus, it is essential to investigate the elastic constants to understand the mechanical properties of MoH, TcH and RuH. Consider a symmetric 3×3 nonrotating strain tensor ε which has matrix elements ε_{ij} (i, j=1, 2 and 3) defined by

$$\boldsymbol{\varepsilon}_{ij} = \begin{pmatrix} e_1 & \dfrac{e_6}{2} & \dfrac{e_5}{2} \\ \dfrac{e_6}{2} & e_2 & \dfrac{e_4}{2} \\ \dfrac{e_5}{2} & \dfrac{e_6}{2} & e_3 \end{pmatrix} \tag{4}$$
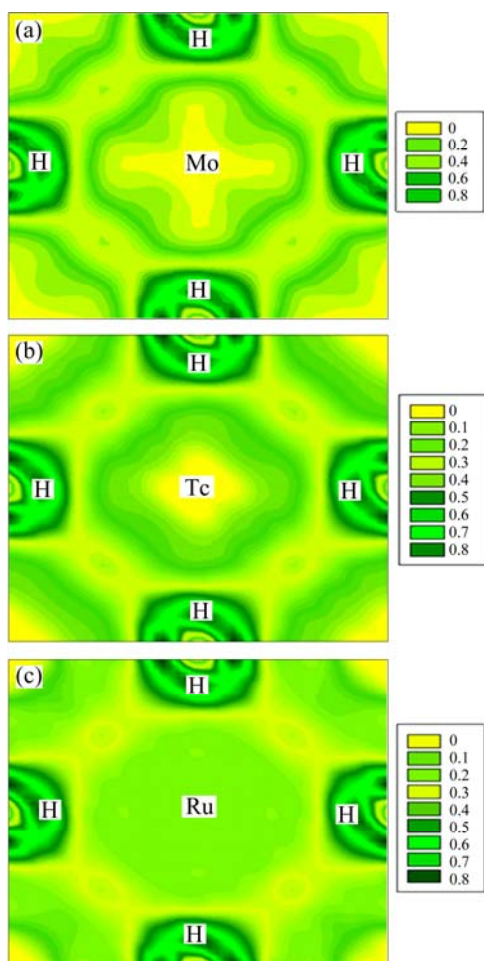
Fig. 4 Charge density distribution of TMHs

Such a strain transforms the three lattice vectors defining the unstrained Bravais lattice {a_K, K=1, 2 and 3) to the strained vectors {a'_K, K=1, 2 and 3} as given by Eq. (5).

$$a'_K = (I + \varepsilon)a_K \tag{5}$$

where I is defined by its elements, and I_{ij} =1 for i=j and 0 for i≠j. Each lattice vector a_k or a'_k is a 3×1 matrix. The change in total energy due to the above strain is

$$\Delta E = \frac{E(\{e_i\}) - E_0}{V_0} = \left(1 - \frac{V}{V_0}\right)p(V_0) + \frac{1}{2}\left(\sum_1^6 \sum_1^6 C_{ij}e_ie_j\right) + O(\{e_i^3\}) \tag{6}$$

where V_0 is the volume of the unstrained lattice, E_0 is the total minimum energy in this unstrained volume of the crystal, $p(V_0)$ is the pressure of the unstrained lattice, and V is the new volume of the lattice due to strain in Eq. (4) where C_{ij}=C_{ji} due to crystal symmetry. This reduces the elastic constants from 36 to 21. Further crystal symmetry reduces the number to 5 (C_{11}, C_{12}, C_{44}, C_{13}, C_{33}) for hexagonal crystals and 3(C_{11}, C_{12}, C_{44}) for cubic crystals. A proper choice of the set of strains (e_i, i=1, 2, $\cdots$, 6)
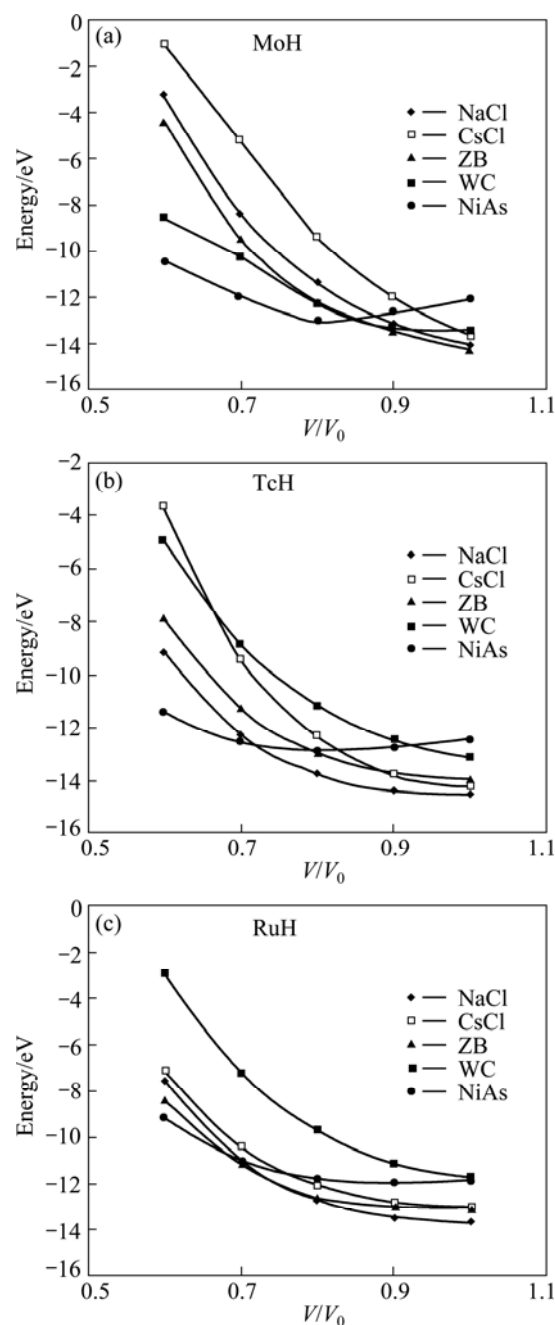

Fig. 5 Total energies as a function of reduced volume

in Eq. (4) leads to a parabolic relationship between $\Delta E/V_0$ ($\Delta E \equiv E - E_0$) and the chosen strain. Such choices for the set e_i and the corresponding form for ΔE are listed in Table 4 for cubic [15] and Table 5 for hexagonal [16] lattices. For each lattice structure of TMH (TM=Mo, Tc, Ru) studied, the lattice was strained by 0, ±1%, and ±2% to obtain the total minimum energies $E(V)$ at these strains. These energies and strains were fitted with the corresponding parabolic equations of $\Delta E/V_0$ as listed in Table 4 and 5 to yield the required second-order elastic constants. While computing these energies all atoms are allowed to relax with the cell shape and volume fixed by the choice of strains e_i.
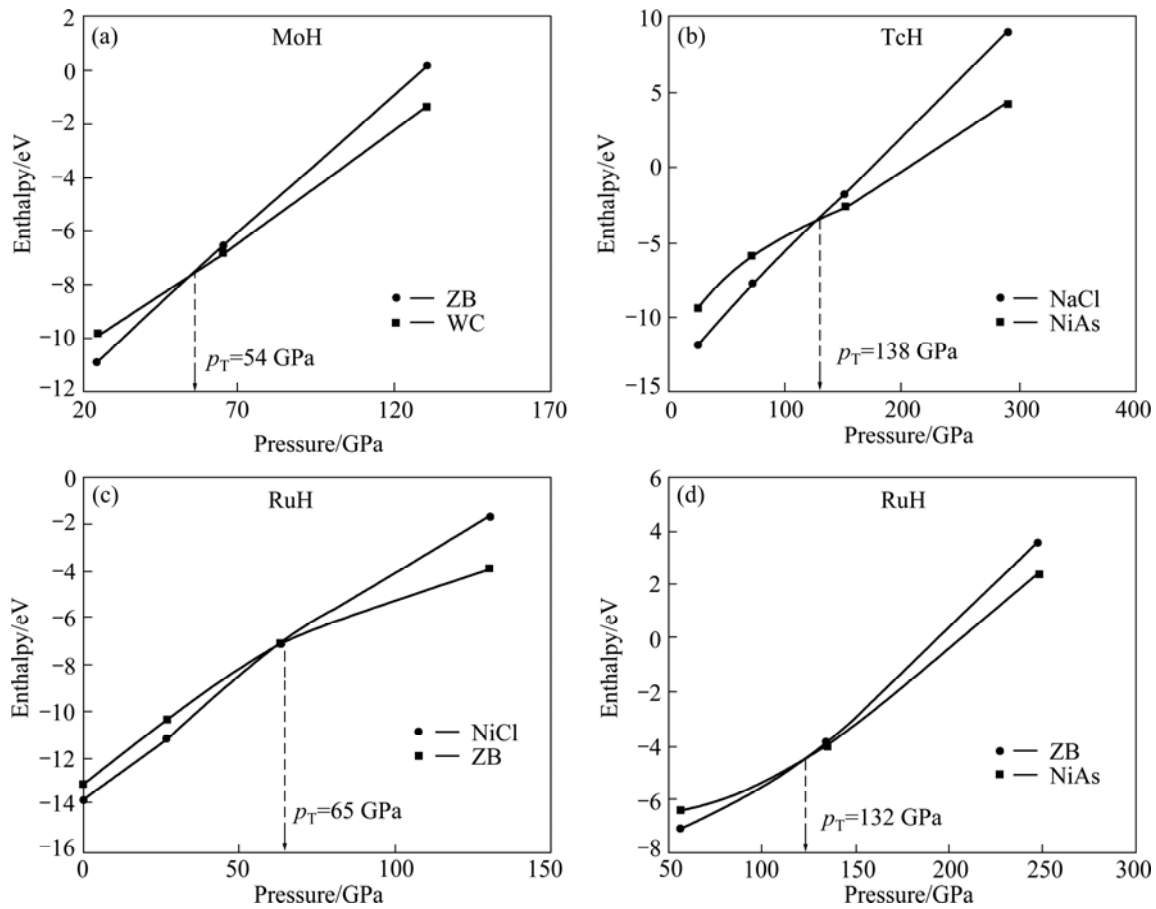
Fig. 6 Enthalpy as function of pressure

Table 3 Estimated transition pressure p_T

Compound	Phase	Transition pressure p_T/GPa
MoH	ZB → WC	54
TcH	NaCl → NiAs	138
RuH	NaCl → ZB	65
	ZB → NiAs	132

Table 4 Strain combinations in strain tensor by Eq. (4) for calculating elastic constants of cubic structures (rock salt, zinc blende and CsCl)

Strain	Parameter (unlisted e_i=0)	$\Delta E/V_0$
1	$e_1=e_2=\delta$, $e_3=(1+\delta)^{-2}-1$	$3(C_{11}-C_{12})\delta^2$
2	$e_1=e_2=e_3=\delta$	$(3/2)(C_{11}+2C_{12})\delta^2$
3	$e_6=\delta$, $e_3=\delta^2(4-\delta^2)^{-1}$	$(1/2)C_{44}\delta^2$

Table 5 Strain combinations in the strain tensor Eq. (4) for calculating elastic constants of hexagonal structures (wurtzite and NiAs)

Strain	Parameters (unlisted e_i=0)	$\Delta E/V_0$
1	$e_1=\delta$	$(1/2)\,C_{11}\delta^2$
2	$e_3=\delta$	$(1/2)\,C_{33}\delta^2$
3	$e_4=\delta$	$(1/2)C_{44}\delta^2$
4	$e_1=e_2=\delta$	$(C_{11}+C_{12})\delta^2$
5	$e_1=e_3=\delta$	$(1/2)\,(C_{11}+C_{33}+2C_{13})\delta^2$

In this work, the calculated single crystal elastic constants C_{ij}, bulk modulus B_0, elastic modulus E, shear modulus G, Poisson ratio v, B/G ratio of TMH (TM= Mo,Tc,Ru) at ambient pressure for cubic structure and high pressure for hexagonal structure are shown in Table 6.

The bulk modulus B_0 and shear modulus G for cubic and hexagonal crystal are calculated using the Voigt Reuss−Hill (VRH) approximation [17−19].

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

$$B_0 = \frac{C_{11}+2C_{12}}{3} \tag{7}$$

$$B_0 = \frac{2}{9}[C_{11}+C_{12}+2C_{13}+(1/2)C_{33}] \tag{8}$$

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

$$G = \frac{3C_{44}+C_{11}-C_{12}}{5} \tag{9}$$

$$G = \frac{2(C_{11}+C_{33})}{15} - \frac{C_{12}+2C_{13}}{15} + \frac{3[2C_{44}+(1/2)(C_{11}-C_{12})]}{15} \tag{10}$$

Table 6 Calculated elastic constants C_{11}, C_{12}, C_{44}, C_{13}, C_{33}, elastic modulus E, shear modulus G, B/G ratio and Poisson ratio v

Parameter	MoH		TcH		RuH	
	ZB (0 GPa)	WC (54 GPa)	NaCl (0 GPa)	NiAs (138 GPa)	NaCl (0 GPa)	NiAs (132 GPa)
C_{11}/GPa	412	418	401	423	497	443
C_{12}/GPa	89	115	127	124	136	142
C_{44}/GPa	72	80	106	76	114	83
C_{13}/GPa	−	53	−	55	−	56
C_{33}/GPa	−	364	−	384	−	394
B_0/GPa	196	182	218	189	256	199
E/GPa	273	354	299	355	357	374
G/GPa	108	151	118	150	141	158
v	0.1786	0.2672	0.2405	0.1861	0.2148	0.1861
B/G	1.81	1.20	1.84	1.26	1.81	1.25

The strain energy $1/2C_{ij}e_ie_j$ of a given crystal in Eq. (6) must always be positive for all possible values of the set e_i, otherwise the crystal would be mechanically unstable. For a stable cubic structure, the three independent elastic constants C_{ij} (C_{11}, C_{12}, $C_{44)}$ should satisfy the well known Born−Huang criteria for the stability of cubic crystals [20].

$$C_{44} > 0, C_{11} > | C_{12} |, C_{11} + 2C_{12} > 0 \qquad (11)$$

while for a hexagonal crystal, the five independent elastic constants C_{ij} (C_{11}, C_{12}, C_{33}, C_{13}, C_{44}) should satisfy the well known Born-Huang criteria for stability [20].

$$C_{12} > 0, C_{33} > 0, C_{11} > C_{12}, C_{44} > 0 \qquad (12)$$

$$(C_{11} + C_{12})C_{33} > 2C_{13}^2 \qquad (13)$$

Clearly, the calculated elastic constants for cubic and hexagonal TMHs (TM= Mo, Tc, Ru) satisfy Born−Huang criteria, suggesting that they are mechanically stable.

Elastic modulus (E) is calculated in terms of the computed data using the following relation:

$$E = \frac{9BG}{3B+G} \qquad (14)$$

B_0 and G can measure the resistance of a material to volume and shape change respectively. As listed in Table 6, the results indicate that all the three transition metal hydrides have seemed to more incline to resist with volume change than shape change. Elastic modulus is often used to provide a measure of stiffness of a solid, i.e., the larger the value of elastic modulus, the stiffer the material. The B_0, G and elastic modulus of molybdenum hydride are comparable with those of CrH$_2$ [21]. Among these hydrides cubic RuH is stiffer than MoH or TcH.

Poisson ratio is associated with the volume change during uniaxial deformation, which is expressed by

Eq. (15) for cubic and Eq. (16) for hexagonal crystals:

$$v = \frac{C_{12}}{C_{11} + C_{12}} \qquad (15)$$

$$v = \frac{3B - 2G}{6B + 2G} \qquad (16)$$

During elastic deformation no volume change occurs. If v=0.5, it indicates that the material is incompressible. The low v value means that a large volume change is associated with its deformation. In addition, Poisson ratio provides more information about the characteristics of the bonding forces than any of the other elastic constants. Among the three hydrides, Poisson ratio of cubic MoH is lower than TcH and RuH, indicating that Mo–H bonding is more directional. The ratio of bulk modulus to shear modulus 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 brittle nature. The critical value which separates ductile and brittle materials is about 1.75. From Table 6, it is found that cubic MoH,TcH and RuH are brittle in nature.

4 Conclusions

1) Cubic structure is the most stable structure at ambient pressure.

2) All the calculated elastic constants obey the Born−Huang criteria, suggesting that they are mechanically stable.

3) It is observed that the bonding in cubic MoH, TcH and RuH structure is a mixture of metallic, covalent, and ionic characters.

4) A pressure induced structural phase transition from cubic to hexagonal phase is also predicted in MoH, TcH and RuH. This work can stimulate research on MoH, TcH and RuH.

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过渡金属氢化物 TMH(TM=Mo、TC、RU)的显微组织、电子特性和力学性能的第一性原理研究

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摘　要：通过基于广义梯度近似密度泛函理论的第一性原理研究过渡金属氢化物 TMH(TM =Mo、TC、RU)的显微组织、电子特性和力学性能。在被研究的 5 个晶体结构中，立方结构比六方晶结构更稳定。预测了不同过渡金属氢化物在高压下的相结构转变，如：MoH 中从 ZB 结构到 WC 结构的转变、在 TcH 中从 NaCl 结构到 NiAs 结构的转变以及在 RuH 中从 NaCl 结构到 ZB 结构再到 NiAs 结构的转变。弹性常数的计算表明：三种氢化物的力学性能在环境压力下是稳定的。

关键词：第一原理；结构相变；电子特性；弹性特性

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