First Principles Study of Structural Stability and Electronic Structure of 4d Transition Metal Carbides TMC$_2$ (TM= Ru, Rh, Pd)

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Abstract: *Structural stability of 4d – transition metal dicarbides (TMC$_2$) is analysed among the different phases, tetragonal (P4/mbm), fluorite (Fm3m), orthorhombic (Pnnm), pyrite (Pa-3), and hexagonal (P6/mmm) using first principles calculations. The most stable structure for these carbides is found to be hexagonal structure. The calculated formation enthalpy values show that these carbides can be easily synthesized at normal pressure. A structural phase transition is predicted under high pressure in these carbides. The electronic structure reveals that these carbides are metallic under ambient condition. The elastic constant calculations indicate that all these carbides are mechanically stable and ultra incompressible characterized by large bulk moduli.*

Keywords: *Electronic structure; First principles study; mechanical property; Phase transition.*

I. Introduction

Designing ultrahard materials is of always great scientific interest due to its variety of industrial applications from cutting and polishing tools to wear-resistant coatings. Diamond remains the hardest known material, despite years of synthetic and theoretical efforts to improve upon it. However, even diamond has limitations. It is not effective for cutting ferrous metals, including steel, because of a chemical reaction that produces iron carbide. The introduction of light and covalent-bond- forming elements into the transition metal (TM) lattices is expected to have profound influences on their structural, mechanical, and electronic properties [1–3]. The experimental and theoretical investigations on TMC$_2$ are very limited. This motivated to study the structural stability, mechanical property and electronic structure for these exciting compounds. In the present paper the structural, electronic and mechanical properties of TMC$_2$ (TM = Ru, R, Pd) in tetragonal (P4/mbm), fluorite (Fm3m), orthorhombic (Pnnm), pyrite (Pa-3) and hexagonal (P6/mmm) is analyzed using first principles calculations under normal pressure.

II. Theoretical Framework

The total energy calculations are performed in the frame work of density functional theory using the generalized gradient approximation (GGA) as implemented in the VASP code [4]. 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. Brillouin zone integration is performed with a Gaussian broadening of 0.1 eV during all relaxations. The cutoff energy for plane waves in our calculation is 500 eV. The valence electron configurations are $4d^7 5s^1$ for Ru, $4d^8 5s^1$ for Rh, $4d^{10}$ for Pd and C $2s^2 2p^2$ atoms. Brillouin-zone integrations are performed on the Monkhorst-Pack K-point mesh with a grid size of 12x12x12 for structural optimization and total energy calculation.

III. Results And Discussions

Structural properties

The total energy of RuC$_2$, RhC$_2$ and PdC$_2$ is calculated for various phases considered as a function of reduced volume and their plots are given in Fig. 1. It is observed that hexagonal phase is the lowest energy phase for these carbides. When the volume is reduced, a structural phase transition occurs from hexagonal to pyrite in RuC$_2$, hexagonal to orthorhombic in RhC$_2$ and PdC$_2$. On further reducing the volume, RuC$_2$ undergoes a phase transition from pyrite to orthorhombic phase. To determine the transition pressure, the enthalpy values are plotted against pressure in Fig. 2. The transition from hexagonal to pyrite phase is predicted at a pressure of 11 GPa in RuC$_2$. On further increasing the pressure to 24 GPa, pyrite to orthorhombic phase transition is

predicted. Similarly in RhC_2 and PdC_2, pressure induced phase transition from hexagonal to orthorhombic phase is predicted at 392 GPa and 88 GPa respectively.

The calculated ground state properties like lattice constants a, b and c (Å), cell volume V_0 (Å^3), cohesive energy E_{coh} (eV), valence electron density ρ (electrons/Å^3) and formation enthalpy ΔH (eV) are listed in Table 1.
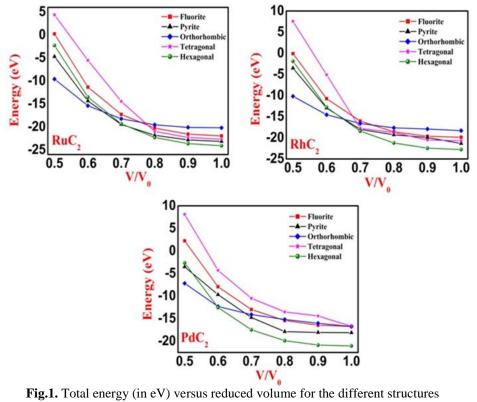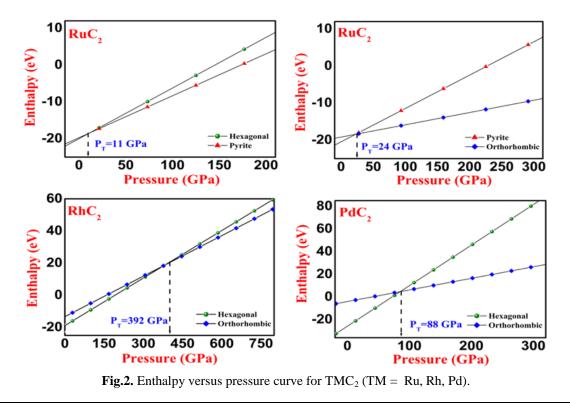

Fig.1. Total energy (in eV) versus reduced volume for the different structures of TMC_2 (TM = Ru, Rh, Pd).

Fig.2. Enthalpy versus pressure curve for TMC_2 (TM = Ru, Rh, Pd).

Table 1: Calculated lattice parameters a, b, c (Å), equilibrium volume V_0 (Å^3), cohesive energy E_{coh} (eV), valence electron density ρ (electrons/Å^3) and formation enthalpy ΔH (eV) for TMC_2 (TM = Ru, Rh, Pd).

	Space group	a	b	c	V_0	E_{Coh}	ρ	ΔH
RuC_2	Fm3m	4.925			29.86	17.66	0.5358	-17.66
	Pa-3	3.099			26.78	18.88	0.5975	-18.88
	Pnnm	3.772	4.315	2.099	34.17	15.91	0.4682	-15.91
	P4/mbm	3.776		2.535	33.07	18.41	0.4833	-18.41
	P6/mmm	2.621		4.291	25.53	19.75	0.6267	-19.75
RhC_2	Fm3m	4.977			30.82	11.82	0.5516	-11.82
	Pa-3	3.115			30.2333	13.29	0.5623	-13.29
	Pnnm	3.913	4.476	2.177	8.14	10.25	0.4457	-10.25
	P4/mbm	3.869		2.598	35.58	12.64	0.4778	-12.64
	P6/mmm	2.635		4.313	25.94	14.72	0.6554	-14.72
PdC_2	Fm3m	5.019			31.61	10.87	0.5694	-10.87
	Pa-3	3.184			32.28	12.26	0.5576	-12.26
	Pnnm	4.003	4.579	2.228	40.84	10.89	0.4407	-10.89
	P4/mbm	3.881		2.606	35.91	10.86	0.5012	-10.86
	P6/mmm	2.683		4.392	27.38	15.19	0.6574	-15.19

Electronic properties

The band structure of RuC_2, RhC_2 and PdC_2 are shown in Fig. 3(a-c). It is observed that, all the three carbides in the hexagonal 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 due to the mixture of metal 4d (TM=Ru, Rh, Pd) and C 2p states. The band appears at the bottom of the valence band is due to the 2s state electrons of carbon 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) (TM=Ru, Rh, Pd) and C 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 C 3d states.
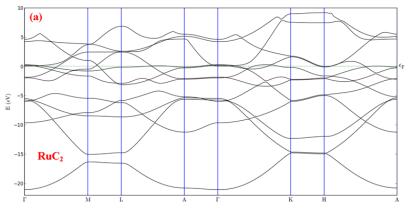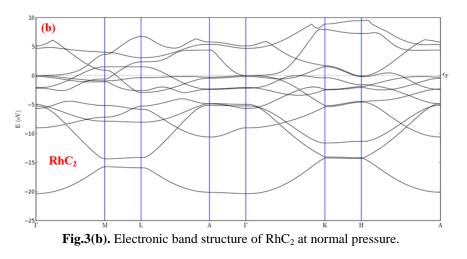

Fig.2(a). Electronic band structure of RuC_2 at normal pressure.

Fig.3(b). Electronic band structure of RhC_2 at normal pressure.

Fig.3(c). Electronic band structure of PdC_2 at normal pressure
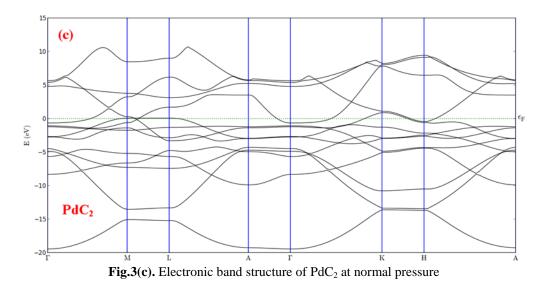
Table 1: Calculated elastic constants C_{11}, C_{33}, C_{44}, C_{12}, C_{13} (GPa), bulk modulus B_0 (GPa), shear modulus G (GPa), Young's modulus (GPa), B/G ratio, Poisson's ratio ν and microhardness parameter H for TMC2 (TM = Ru, Rh, Pd).

	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}	B_0	G	E	B/G	ν	H
RuC_2	510	688	120	163	62	253	223	517	1.13	0.2421	36.81
RhC_2	492	656	113	144	66	243	214	496	1.13	0.2264	35.75
PdC_2	480	503	106	137	51	215	192	444	1.11	0.2220	33.79

Elastic properties

The elastic constants are determined using total energy method [5]. It is noted that, the elasticity tensor has five independent components (C_{11}, C_{33}, C_{44}, C_{12} and C_{13}) for hexagonal crystal. The calculated mechanical properties TMC_2 (TM = Ru, Rh, Pd) for stable hexagonal structure are given in Table 2. The computed young's modulus values indicate that RuC_2 is stiffer among these carbides. The Poisson's ratio measures the degree of directionality of the covalent bonds. The Poisson's ratio of PdC_2 is the lowest, indicating that the Pd - C bonding is more directional in nature. The calculated hardness values predict that RuC_2 is a hard material.

IV. Conclusion

The structural stability, electronic and mechanical properties of 4d transition metal carbides TMC_2 (TM = Ru, Rh, Pd) are investigated. It is found that all these carbides are most stable in hexagonal structure. A pressure induced structural phase transition is observed in all these carbides. The transition from hexagonal to pyrite structure is predicted at a pressure of 11 GPa. On further increasing the pressure to 24 GPa pyrite to orthorhombic transition is predicted. Similarly hexagonal to orthorhombic phase transition is predicted at a pressure of 392 GPa in RhC_2 and 88 GPa in PdC_2. The band structure of 4d transition metal carbides TMC_2 (TM = Ru, Rh, Pd) confirm that they are metals. The computed elastic constants obey the necessary mechanical stability condition suggesting that all the materials are mechanically stable.

Acknowledgements

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