Structural Study of Transition Metal Carbides

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In this research paper we have discovered the structural phase transition and elastic properties of transition metal carbides (TaC and HfC). Phase transition pressures are associated with a sudden collapse in volume showing the incidence of first order phase transition. At ambient condition the present compounds exhibit rock salt (NaCl) structure, they transform into cesium chloride (CsCl) structure under high pressure. The phase transition pressures and associated volume collapses obtained from present potential model show a generally good agreement with the available literature. The elastic constants and bulk modulus are also reported for the present compounds.

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1. Introduction

The carbides of the transition metals in groups IV–VI have extremely high melting points. In addition to their stability at high temperatures, these compounds are extremely hard finding industrial use in cutting tools and wear-resistant parts. Their hardness is retained to very high temperatures, and they have low chemical reactivity. Approximate preparation of the transition metal carbides is simple, but ensuring a given stoichiometry and purity against oxygen contamination is notably difficult. Group IV carbides are difficult to purify without melting. Slow diffusion of carbon in all of the refractory carbides results in stoichiometry gradients which are difficult to detect in bulk materials but which may compromise the material strength, hardness, and high-temperature behaviour. The tantalum carbide system is relatively easy to free of oxygen impurities, but due to the slow rate of carbon diffusion it tends to have inhomogeneities in its bulk composition. These interesting properties of the transition metal carbides have attracted attention of both theoretical and experimental workers [1–11]. At ambient temperature and pressure these transition metal carbides exhibit sixfold coordinated NaCl (B_1) structure. However under pressure they show a first order structural phase transition from NaCl (B_1) to CsCl (B_2) structure.

The electronic band structure and X-ray photoelectron spectra of TaC and HfC has been performed by Ihara et al. [7]. The trends in elasticity and electronic structure of transition metal nitrides and carbides have been studied by Wu et al. [8]. Recently high pressure phase transition of carbides of Ta and Hf has been studied using the first principle calculations by Shrivastava et al. [9]. The computations have been performed using ground state total energy calculation approach of the system. The first principle calculations on the electronic structure of TiC_xN_{1-x}, $Zr_xNb_{1-x}C$, and HfC_xN_{1-x} alloys have been performed by Zaoui et al. [10]. High pressure behaviour and structural properties of HfC and TaC have been predicted by Singh et al. [11] using an interionic potential theory. This interionic potential theory is not able to explain the Cauchy discrepancy in second order elastic constants.

Looking at the fact that these compounds are less explored, we applied our three-body interaction potential (TBIP) model to these compounds to study high pressure phase transition and other properties. The need of inclusion of three-body interaction forces was emphasized by many workers for the enhancement of results [12–14]. Earlier calculations for B_1–B_2 transitions were based on two-body potential mainly. They concluded that possible reasons for disagreements include the failure of the two-body potential model. These studies were based on two-body potentials and could not explain the Cauchy violations ($C_{12} \neq C_{44}$). They remarked that results could be improved by including the effect of non-rigidity of ions in the model.

It is seen from the current literature that TBIP model used and developed by Singh and co-workers [15–18] has been found to be remarkably successful in giving the unified description of structural and elastic properties of ionic and semiconducting crystals [16–18]. In this TBIP model, the three-body interactions owe their origin to the quantum mechanical foundation and also to the phenomenological approach [19, 20] in terms of the transfer

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(or exchange) of charge between the overlapping electron shells of the adjacent ions in solids. The present approach has been extended to include the Hafemeister–Flygare (HF) type [21] overlap repulsion operative up to the second neighbour ions. Also, Tosi and co-workers [22] have demonstrated the significance of van der Waals (vdW) attraction due to the dipole–dipole (d–d) and dipole–quadruple (d–q) interactions to describe the cohesion in ionic solids and they are generally ignored in the first principle calculations.

The purpose of this work is to investigate the structural and elastic properties of TaC and HfC. The rest of this paper is prepared as follows: the method of calculation is given in Sect. 2; the results and conclusion are presented and discussed in Sect. 3.

2. Potential model and method of calculation

Application of pressure directly results in compression leading to the increased charge transfer (or three-body interaction effect [15]) due to the deformation of the overlapping electron shell of the adjacent ions (or non-rigidity of ions) in solids.

These effects have been incorporated in the Gibbs free energy ($G = U + PV - TS$) as a function of pressure and three-body interactions (TBI) [15], which are the most dominant among the many-body interactions. Here, U is the internal energy of the system equivalent to the lattice energy at temperature near zero and S is the entropy. At temperature $T = 0$ K and pressure (P) the Gibbs free energies for rock salt (B_1, real) and CsCl (B_2, hypothetical) structures are given by

$$G_{B1}(r) = U_{B1}(r) + PV_{B1}(r), \qquad (1)$$

$$G_{B2}(r') = U_{B2}(r') + PV_{B2}(r'), \qquad (2)$$

with V_{B1} ($= 2.00r^3$) and V_{B2} ($= 1.54r'^3$) as unit cell volumes for B_1 and B_2 phases, respectively. The first terms in (1) and (2) are lattice energies for B_1 and B_2 structures and they are expressed as:

$$U_{B_1}(r) = \frac{-\alpha_m z^2 e^2}{r} - \frac{12\alpha_m z e^2 f(r)}{r} - \left(\frac{C}{r^6} + \frac{D}{r^8}\right)$$
$$+ 6b\beta_{ij} \exp((r_i + r_j - r)/\rho)$$
$$+ 6b\beta_{ii} \exp((2r_i - 1.414r)/\rho)$$
$$+ 6b\beta_{jj} \exp((2r_j - 1.414r)/\rho), \qquad (3)$$

$$U_{B2}(r') = \frac{-\alpha'_m z^2 e^2}{r'} - \frac{16\alpha'_m z e^2 f(r')}{r'} - \left(\frac{C'}{r'^6} + \frac{D'}{r'^8}\right)$$
$$+ 8b\beta_{ij} \exp((r_i + r_j - r')/\rho)$$
$$+ 3b\beta_{ii} \exp((2r_i - 1.154r')/\rho)$$
$$+ 3b\beta_{jj} \exp((2r_j - 1.154r')/\rho), \qquad (4)$$

with α_m and α'_m as the Madelung constants for NaCl and CsCl structure, respectively. C (C') and D (D') are

the overall van der Waals coefficients of B_1 (B_2) phases, β_{ij} ($i, j = 1, 2$) are the Pauling coefficients. Ze is the ionic charge and b (ρ) are the hardness (range) parameters, r (r') are the nearest neighbour separations for NaCl (CsCl) structure, $f(r)$ is the three-body force parameter.

These lattice energies consist of long range Coulomb energy (first term), three-body interactions corresponding to the nearest neighbour separation r (r') (second term), vdW interaction (third term), energy due to the overlap repulsion represented by HF type potential and extended up to the second neighbour ions (remaining terms).

3. Results and discussion

The Gibbs free energies contain three model parameters [$b, \rho, f(r)$]. The values of these parameters have been evaluated using the first and second order space derivatives of the cohesive energy (U) expressed as

$$\left(\frac{dU}{dr}\right)_{r=r_0} = 0, \qquad (5)$$

$$\left(\frac{d^2U}{dr^2}\right)_{r=r_0} = 9kr_0 B_T, \qquad (6)$$

and following method adopted earlier [23–25]. Using these model parameters and the minimization technique, phase transition pressures of transition metal carbides have been computed. The input data of the crystal and calculated model parameters are listed in Table I. The B_1 (NaCl) structure is most stable in these compounds and at high pressure they transform to body centre B_2 (CsCl) structure. As the stable phase is associated with minimum free energy of the crystal, we have followed the technique of minimization of the Gibbs free energies of real and hypothetical phases. We have minimized $G_{B1}(r)$ and $G_{B2}(r')$ given by Eqs. (3) and (4) at different pressures in order to obtain the interionic separations r and r' corresponding to B_1 and B_2 phases associated with minimum energies.

TABLE I

Input parameters and generated model parameters for transition metal carbides.

Solid	Input parameters		Model parameters		
	r_0 [Å]	B [GPa]	b [10^{-12} erg]	ρ [Å]	$f(r)$
TaC	2.235[a]	324[a]	2.14623	0.346	-0.13052
HfC	2.325[a]	238[a]	1.37913	0.319	-0.14837

[a] Ref. [1]

The factor ΔG [$G_{B1}(r) \sim G_{B2}(r')$] plays an important role in stability of structures. The phase transition occurs when ΔG approaches zero ($\Delta G \to 0$). The phase transition pressure (P_t) is the pressure at which ΔG approaches zero. At P_t these compounds undergo a $B_1 - B_2$ transition associated with a sudden collapse in volume. Figure 1 shows our presently computed phase transition pressure for NaCl-type (B_1) to CsCl-type (B_2) structures

in TaC at 93.2 GPa and in HfC at 86.4 GPa, respectively. The present phase transition pressures illustrated by arrows in Figs. 1 and 2 and their values have been listed in Table II and compared with available results. It is interesting to note from Table II and Figs. 1 and 2 that the phase transition pressures (P_t), obtained from our model, are in general in closer agreement with available results [9, 11].
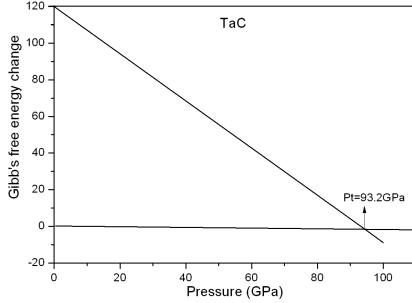

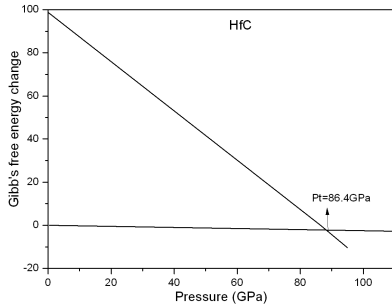Fig. 1. Variation of Gibbs free energy with pressure for TaC.

Fig. 2. Variation of Gibbs free energy with pressure for HfC.

TABLE II

Phase transition and volume change of transition metal carbides.

Solid	Phase transition pressure [GPa]		Volume collapse [%]	
	Present	Others	Present	Others
TaC	93.2	96^a, 641^b	6.73	7.6^a
HfC	86.4	85^a, 485^b	5.14	6.8^a

^{a} Ref. [9], ^{b} Ref. [11]

During the phase transition from NaCl to CsCl, the volume discontinuity in pressure volume phase diagram identifies the occurrence of first order phase transition. The compression curves are plotted in Figs. 3 and 4. The values of the volume collapses $(-\Delta V(P)/V(0))$ are depicted in Table II and compared with corresponding theoretical results [9, 11]. The experimental values of volume collapses are not available for the present compounds.
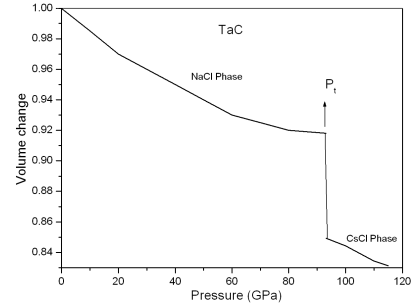

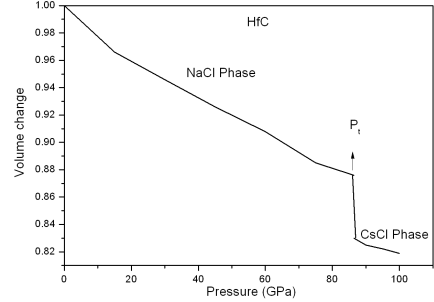Fig. 3. Variation of volume change V_P/V_0 with pressure for TaC.

Fig. 4. Variation of volume change V_P/V_0 with pressure for HfC.

We have calculated the second order elastic constants of the materials under study. Also, we could reproduce the correct sign of the elastic constants $(C_{11}-C_{12})$. The study of second order elastic constants (SOECs) under pressure is important as C_{11} represents elasticity in length and C_{12} and C_{44} are shape related elastic constants. The SOECs and pressure derivatives of transition metal carbides are given in Table III. Our present values of SOECs are close to available theoretical data [11]. The calculated SOECs and their pressure derivatives could not be compared due to lack of experimental data on them but the values of SOECs are of the same order as reported by others [11].

TABLE III

Calculated values of elastic constants (in GPa), bulk modulus (in GPa), pressure derivative and Cauchy discrepancy of transition metal carbides.

Solid	C_{11}	C_{12}	C_{44}	B	dB/dP	δ
TaC						
present	6.29	1.64	1.53	3.19	0.326	-0.14
others	6.94^a	1.27^a	1.27^a	3.18^a	–	–
HfC						
present	4.651	0.790	0.910		0.301	-0.12
others	4.541^a	0.865^a	0.865^a	2.18^a	–	–

^{a} Ref. [11]

4. Conclusions

In view of the overall achievements, it may be concluded that there is generally a good agreement of TBIP model with the available experimental and theoretical values.

Finally, it may be concluded that the present model has successfully predicted the compression curves and phase diagrams giving the phase transition pressures, associated volume collapses and elastic properties correctly for these transition metal carbides.

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