

Phase transition and high pressure behavior of Zirconium and Niobium carbides

Research Article

Archana Singh¹, Mahendra Aynyas^{1*}, Sankar P. Sanyal²

¹ Department of Physics, Sadhu Vaswani College, Sant Hirdaram Nagar, Bhopal 462 020, India

² Department of Physics, Barkatullah University, Bhopal 462 026, India

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Abstract:

We have predicted the phase transition pressure (P_T) and high pressure behavior of Zirconium and Niobium carbide (ZrC, NbC). The high pressure structural phase transitions in ZrC and NbC has been studied by using a two body inter-ionic potential model, which includes the Coulomb screening effect, due to the semi-metallic nature of these compounds. These transition metal carbides have been found to undergo NaCl ($B1$) to CsCl ($B2$)-type structural phase transition, at high pressure like other binary systems. We predict such structural transformation in ZrC and NbC at a pressure of 98GPa and 85GPa respectively. We have also predicted second order elastic constant and bulk modulus. The present theoretical work has been compared with the corresponding experimental data and prediction of LAPW and GGA and LDA theories.

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Keywords:

phase transition • high pressure • elastic constant • transition metal carbides

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1. Introduction

The early transition metal monocarbides and nitrides (TMCs; TM = Ti, V, Nb, Zr, Hf and Ta) have been studied intensively in the past years. Several of the carbides and nitrides show number of unusual combinations in their physical properties [1, 2]. The carbides of transition metal have extremely high melting points and therefore referred to as refractory carbides. The carbides of transition metal of groups IV and V group have very high hardness and relatively high superconducting transition temperature. These properties make them attractive for

both theoretical investigations and technological applications [3–9]. Many of their desirable characteristics are critically influenced by the presence of vacancies, which occur on the non-metal sublattice. Experimental evidence shows that, in rock salt ($B1$) phase modification of these compounds, up to 30% of the lattice site may be vacant (i.e. up to 60% of the nonmetal sublattice). Thus presence of vacancies in refractory metal carbides and nitrides seem to be intrinsic properties of these compounds [4–9]. Transition metal carbides and nitrides are chemically stable and exhibit high corrosion resistance. Due to these technologically important properties of these transition metal carbides, they are widely used in dispersion hardening particles in high-speed steel for cutting tools. On the other hand, they are good metals and many of them are superconductors with very high transition temperature. An

*E-mail: aynyas@rediffmail.com

interesting property that is associated with covalent bonding is found in the set of a system, that shows a crystal structure normally associated with ionic bonding (NaCl). Of particular interest is the study of electronic structures of these compounds and to obtain information about the origin of their properties, such as hardness, large bulk modulus and stability. The chemical composition of covalent, ionic and metallic components in these compounds makes it difficult to construct a simple interpretation of their electronic structure. In the past, various theories have emphasized strong metal-metal bonds and the interstitial role of the C atoms. These theories are used to explain, high melting points and deviations from stoichiometry in these materials. Other theories have stressed the importance of strong metal Carbon bonds to account for the extreme hardness found in transition metal carbides. These properties make them technologically important in various fields and are also interesting for fundamental studies.

On the theoretical site, many *ab initio* electronic structure calculations on 3d, 4d and 5d TMCs of the NaCl structure have been carried out [10, 11]. The cohesive properties of series of these materials types was discussed by Haglund *et al.* [12] by using linear muffin tin orbital method (LMTO), while band structure and bonding mechanism and chemical bonding was studied by Zhukov *et al.* [13] for a number of refractory-metal carbides by using again LMTO method within atomic sphere approximation.

In this paper, we have studied pressure induced structural phase transition in carbide's of transition metalnamely ZrC and NbC by using a two body inter-ionic potential model. This model includes d-electron coulomb screening effect between the ions, through modified ionic charge parameter due to semimetallic properties of these two compounds. We examined the first suitable phase transformation in these TMC and used this potential to calculate phase transition pressure and elastic constants. Our main objective however, remained for a qualitative prediction of correct phase transition pressure for this system to encourage further experimental efforts, which remain strongly beyond the capabilities of *ab initio*. We have also predicted second order elastic constants and bulk modulus for TMC.

2. Methodology

The interatomic potential for TMCs compounds in the rigid ion model (RIM) is expressed as [14].

$$U(r) = \sum_{ij} \frac{Z_m^2 e^2}{r_{ij}} + \sum_{ij} \frac{b \beta_{ij} \exp[(r_i + r_j - r_{ij})]}{\rho_{ij}} + \sum_{ij} C_{ij} r_{ij}^{-6} + \sum_{ij} D_{ij} r_{ij}^{-8}. \quad (1)$$

Table 1. Input crystal properties and generated model parameters for transition metal carbides.

Solids	Input Parameters			Output parameters	
	r_0 [Å]	B_T [GPa]	Z_m^2	$b(10^{-19})$ [J]	ρ [Å]
ZrC	2.349 [17]	2.65 [18]	2.72	2.978	0.202
NbC	2.235 [17]	3.02 [17]	3.06	1.170	0.206

Where $Z_m e$ is the modified ionic charge parameter, due to screening effect of 3d electrons of transition metal ions. In Eq. (1), the first term is the long-range coulomb potential, the second term represents a short-range repulsive force and the third and fourth terms are the van der Waals interaction energies, respectively. r_{ij} is the nearest neighbours separation between ions; r_i and r_j are ionic radii. Such an interionic potential has been found extremely useful in studying the structural and high-pressure properties of several rare-earth pnictides [15]. The short-range parameters b and ρ have been determined self-consistently from bulk modulus (B_T) and equilibrium condition

$$\left. \frac{dU_{ij}(r)}{dr} \right|_{r=r_0} = 0. \quad (2)$$

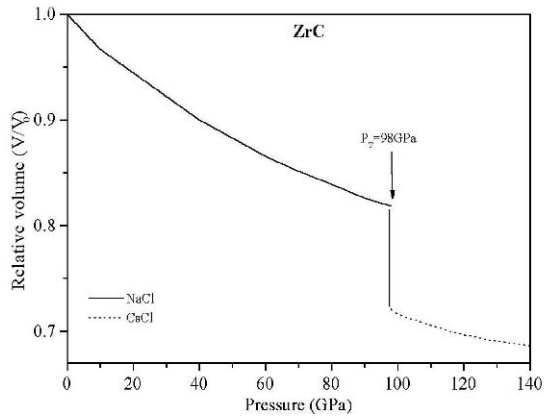
Here r_0 is the equilibrium lattice constant. Thermodynamically, a phase transition is said to occur when the change in the structural details of the phase are caused by a variation of the free energy. These compounds transform from their initial NaCl (B1) to CsCl (B2) structure under pressure. The stability of a particular structure is decided by the minimum of the Gibbs free energy, given by

$$G = U + PV - TS. \quad (3)$$

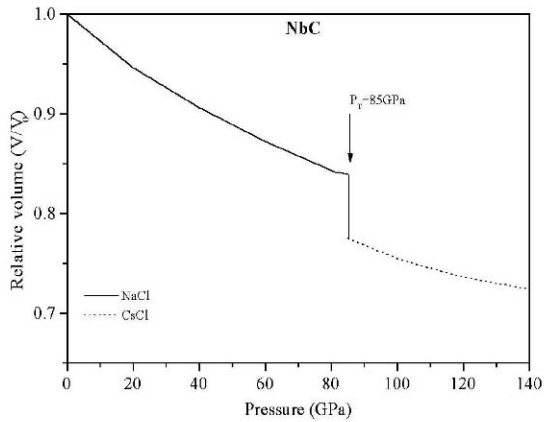
Where U is the internal energy (Eq. 3), which at 0K corresponds to the cohesive energy, S is the vibrational entropy at absolute T at pressure P and volume V . Gibbs

Table 2. Cohesive energies and phase properties of transition metal carbides.

Solids		Equilibrium lattice constant [Å]		Cohesive energy [KJ]/mole		Phase transition pressure	Relative volume collapse
		$R_1(B_1)$	$R_2(B_2)$	$U_1(B_1)$	$U_2(B_2)$	P_T [GPa]	
ZrC	Present	2.350	2.450	-2072.98	-1918.43	98	9%
	Expt	2.349 [17]					
NbC	Present	2.296	2.400	-3101.52	-3005.43	85	6.8%
	Expt	2.235 [17]					



(a)



(b)

Figure 1. Fig. (a) and Fig. (b) variation of relative volume with pressure for ZrC and NbC respectively.**Table 3.** Calculated values of second order elastic constants in [Mbar].

Solids		C_{11}	C_{12}	C_{44}
ZrC	Present	5.488	0.538	0.538
	Expt.	4.70 [19]	1.00 [19]	1.60 [19]
	GGA	5.12 [21]	0.73 [21]	1.21 [21]
	LDA	6.43 [21]	0.95 [21]	1.21 [21]
NbC	Present	6.47	1.089	1.109
	Expt.	6.20 [19]	2.00 [19]	2.00 [19]
	LAPW	6.4 [20]	1.8 [20]	1.4 [20]

free energies, $G_{B1}(r)$ for NaCl ($B1$) and $G_{B2}(r')$ for CsCl ($B2$) phase become equal at phase transition pressure P_T at temperature 0K. In the present study, we have considered $B1$ to $B2$ phase transition only from the point of view of thermodynamical stability. In the present paper, we have calculated the second-order elastic constant (SOE) constants using the following expressions derived from the interionic potential (Eq. 1) [16] as

$$C_{11} = \alpha \left[-5.112Z_m^2 + A_1 + \frac{1}{2}(A_2 + B_2) \right], \quad (4)$$

$$C_{12} = \alpha \left[0.226Z_m^2 - B_1 + \frac{1}{4}(A_2 - 5B_2) \right], \quad (5)$$

$$C_{44} = \alpha \left[2.556Z_m^2 + B_1 + \frac{1}{4}(A_2 + 3B_2) \right]. \quad (6)$$

With $\alpha = e^2/4r_0^4$ and, $A_1 = A_{12}$, $B_1 = B_{12}$, $A_2 = (A_{11} + A_{22})$, and $B_2 = (B_{11} + B_{22})$, are short-range force constant and are expressed as

$$A_{ij} = 2V/e^2 \left[d^2 \Phi(r)/dr^2 \right], \quad (7)$$

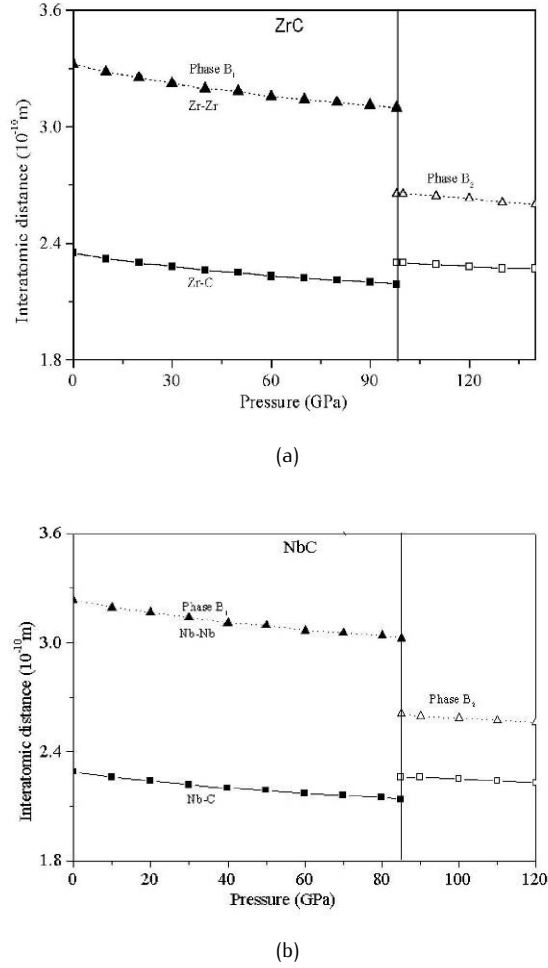


Figure 2. Fig. (a) and Fig. (b) variation of interatomic distance with pressure for ZrC and NbC respectively.

$$B_{ij} = 2V/e^2 \left[1/r_{ij}(d\Phi(r)/dr) \right]. \quad (8)$$

Where $\Phi_{ij}(r)$ is the short-range potential, (last three terms in Eq. 1).

3. Results and discussion

The input crystal properties and model parameters for ZrC and NbC are given in Table 1. In Table 2; we have presented calculated values of cohesive energies and structural properties of these compounds at high pressure, compared with available experimental data.

It is seen from Table 1 that calculated values of model parameters follow a systematic trend of variation, in the series of two transition metal carbides. Since effective

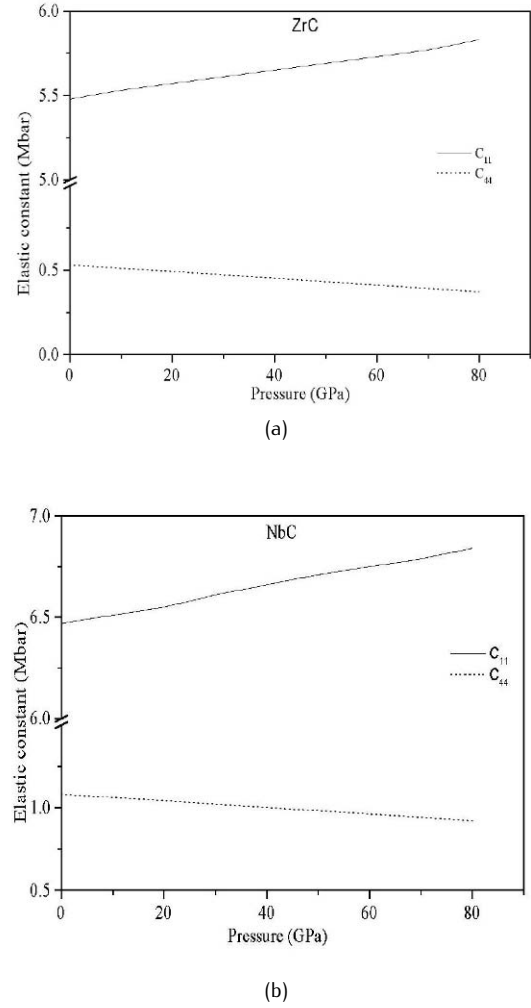


Figure 3. Fig. (a) and Fig. (b) variation of elastic constant with pressure for ZrC and NbC respectively.

charge parameter Z_m^2 has been derived from measured values of bulk modulus (B_T) and values of Z_m^2 in the range 2.72 to 3.0. Therefore it is easy to point out the increase in variation, while values of short-range parameters b and ρ do not much differ with each other. The inter-ionic potential considered here, includes the screening effect of d-electrons of transition metal ions on the Coulomb interaction between ions through modified charge parameter Z_m . In Table 2, lattice constants and cohesive energies in NaCl (B1) and CsCl (B2) phase and phase transition pressure and relative volume collapse (V/V_0) are presented. The values of cohesive energy in NaCl structure show that these compounds are more stable for the NaCl structure than for CsCl structure at ambient pressure. The calculated value of phase transition pressure indicate that these two transition metal compounds, in general transform to

CsCl phase at transition pressures less than 100 GPa. The equation of states i.e., changes in relative volume (V/V_0) with pressure for ZrC and NbC are shown in Fig. 1(a) and Fig. 1(b) respectively. We have predicted a NaCl-type to CsCl-type structural phase transition in two transition metal carbides. The calculated value of phase transition pressure for ZrC was found to be 98 GPa with a relative volume collapse (V/V_0) of 9%, while transition pressure for NbC was calculated to be 85 GPa. The calculated value of volume collapse of 6.5% for NbC was determined. We have no experimental and theoretical data for comparison with our predictions. It is clear from Table 2, transition pressure decreases from ZrC to NbC. It is noteworthy to comment that there is transfer of electrons from s and p like state of carbon atom to Zr(Nb)-d like state of transition metal continuously under high pressure, which may be responsible for the observed reduced structural phase transition pressure. Since, these TMCs are superhard materials; such behavior of high phase transition pressure is of course expected. The calculated value of relative volume change at transition pressure is very small as compared to other ionic solids which also signifies the superhard property.

In order to study the high-pressure elastic behavior of transition metal carbides ZrC and NbC, we have calculated second order elastic constants (SOECs) for NaCl structure and find out variation of elastic constants corresponding to pressures shown in Fig. 3(a) and Fig. 3(b). It can be seen from Fig. 3(a) and Fig. 3(b) that C_{11} increases linearly with pressure increase, but C_{44} linearly decrease as pressure increases, showing the reduction in resistance to shear as phase transition approaches. In Table 3, we have presented calculated values of second order elastic constants and compared these with the available experimental and theoretical results. It is noted from Table 3 that the calculated values of C_{11} are slightly greater than corresponding experimental values for both ZrC and NbC. This is because of serious limitations of the present theoretical approaches it never serves to fit individual elastic constants, but the bulk modulus only. Our calculated values of C_{11} and C_{44} of ZrC are nearly equal to the other results [19–21]. In case of NbC, predicted values of elastic constants are in good agreement with LAPW method. The calculated values of C_{12} and C_{44} show correct orders of magnitude though they are equal to the Cauchy relation.

The interaction between orbitals should also vary, and are dependent on their inter-ionic distance with change in pressure. We have also calculated variation in Zr-Zr, Nb-Nb distance and Zr-C, Nb-C distance with increase in pressure, as shown in Fig. 2(a) and Fig. 2(b). We observed that inter-ionic distances decrease with increasing pressure. At phase transition pressure, Zr-Zr and Nb-Nb

distance suddenly decreases, while Zr-C and Nb-C distance increase and reaches its ambient pressure value. The change in inter-ionic distance may be due to changes in the co-ordination number due to high pressure.

4. Conclusion

We have presented detailed theoretical prediction of structural properties of transition metal carbides namely ZrC and NbC at high pressure and ambient pressure by using a two body potential model. These two compounds of transition metal carbides are predicted to undergo a NaCl-type to CsCl-type structural phase transition at a high pressure lower than 100 GPa. We have also predicted second order elastic constants and compared these with experimental data which appear to be in good agreement.

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