First principles study of Structural, Electronic, Superconducting and Mechanical properties of Titanium Carbide

M. Kavitha[a], R.Rajeswarapalanichamy[a*] and K. Iyakutti[c]

Abstract: The structural, electronic, superconducting and mechanical properties of TiC are investigated using density functional theory calculations with the generalized gradient (GGA) approximation. The lattice constants, cohesive energy, bulk modulus, band structure and the density of states are obtained. The calculated lattice parameters are in good agreement with the available results. The electronic structure reveals that titanium carbide exhibit metallic behavior at ambient condition. A pressure-induced structural phase transition from NaCl to CsCl phase is observed in TiC. The computed elastic constants indicate that these carbides are mechanically stable at ambient pressure.

Keywords— Ab-initio calculations, Electronic structure, Structural phase transition, Elastic properties.

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1 INTRODUCTION

Transition metal carbides have recently attracted much attention due to their extraordinary mechanical and physical properties,e.g., high melting point, high hardness, high wear and-corrosion resistance, high specific strength, and high conductivity.Many theoretical works have been devoted to the investigation of their properties in connection with electronic structure and bonding characteristics[1].Titanium carbide in the rock salt structure (NaCl phase) exhibits unique features that are of interest for experimental and theoretical investigations[2]. The outstanding physical properties such as elastic properties of TMC (TM=Ti, Zr, Hf and Ta) are associated with their electronic properties, e.g., the simultaneous contributions of strong covalent metal-nonmetal bonding, less important ionic bonding and not negligible metallic bonding [3–5]. So, Das et al. [3] studied the electronic and elastic properties of carbides of the transition metals Ti, V and Zr. In recent years, Bağcı et al. [6] have calculated the structural and elastic properties as well as the phonon spectrum of bulk TiC, but the electronic properties are not reported. First principles calculation have been performed for the lattice constant of TMC by Haas et al. [7], but the relation between elastic and electronic properties are not studied. The electronic properties including the bonding nature of bulk TiC are investigated from first-principles calculations by Fang et al. [8].

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[a]*Department of Physics, N.M.S.S.V.N college, Madurai, Tamilnadu-625019, India*

[b]*Department of Physics & Nanotechnology, SRM University, Chennai, Tamilnadu-603203. India.*

Corresponding author E-mail: rrpalanichamy@gmail.com

To the best of our knowledge, the structural phase transition under high pressure, elastic proerties of CsCl phase and superconductivity of TiC are not yet reported. In the present paper, Structural, electronic superconducting and elastic properties of TiC are investigated using VASP code.

2 COMPUTATIONAL DETAILS

The total energy calculations are performed in the frame work of density functional theory using the generalized gradient approximation (GGA-PBE) as implemented in the VASP code [9]. 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 $Å^{-1}$ and the Brillouin zone integration is performed with a Gaussian broadening of 0.1 eV. The cutoff energy for plane waves in our calculation is 400eV. The valence electronic configurations are Ti $3d^2$ $4s^2$ and C $2s^2$ $2p^4$ atoms. Brillouin zone integrations are performed on the Monkhorst-Pack K-point mesh with a grid size of 12x12x12 for TiC for structural optimization and the total energy calculation.

3 RESULTS AND DISCUSSION

3.1 Structural Properties

The structural stability of TiC is analyzed by calculating the total energy using VASP code based on density functional theory. The calculated ground state properties like lattice constants a (Å), cell volume V_0 ($Å^3$), valence electron density ρ(electrons/ $Å^3$), cohesive energy (eV), bulk modulus B_0 (GPa) and its derivative B_0' for TiC for various considered phases are listed in Table 1 and is compared with the experimental and other available theoretical data [10-14]. From Table 1, it is found that the calculated equilibrium lattice constant and bulk modulus are in good agreement with the experimental and other available theoretical results. It is also observed that, for TiC, NaCl phase owing to its highest cohesive energy, it is the most stable one. The total energy vs reduced volume plot for

TiC is

	NaCl	CsCl
a	4.34	2.708
	4.332 [10]	2.5921[14]
	4.343[11]	
	4.250 [12]	
	4.328[12]	
	4.271 [13]	
V_0	20.44	19.86
VED	0.4892	0.5035
E_{coh}	7.665	5.104
B_0	305	231
	252.25[10]	253[14]
	241.60[11]	
	272.6[12]	
B_0'	4.31	4.46

given in Fig.1. From Fig.1, it is noted that TiC is stable in NaCl phase. On further reducing the volume, a structural phase transition occurs from NaCl→CsCl in TiC.

In order to determine transition pressure, the enthalpy is calculated using the formula
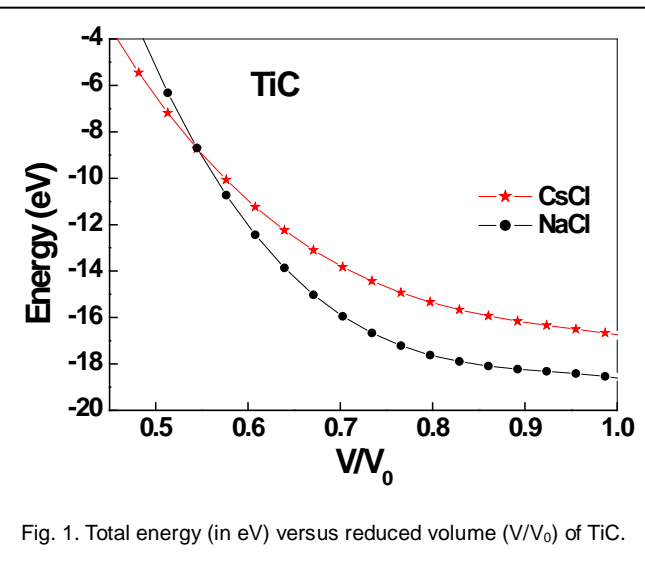
$$H=E+PV$$

Fig. 1. Total energy (in eV) versus reduced volume (V/V₀) of TiC.

The transition pressure (P_T) value is determined from the intersection of enthalpy versus pressure curve and is presented in Fig. 2. For TiC, it is found that the transition pressure for NaCl to CsCl is 228 GPa.
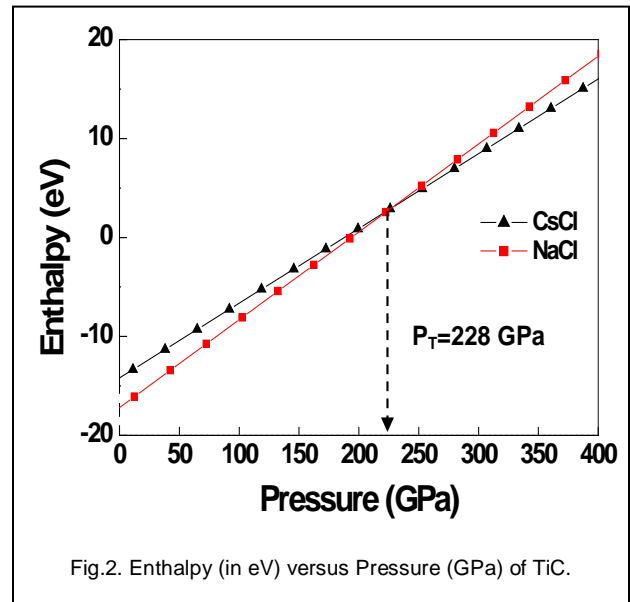

Fig.2. Enthalpy (in eV) versus Pressure (GPa) of TiC.

3.2 Electronic Properties

The normal pressure electronic band structure at the equilibrium lattice constant are depicted in Fig. 3,which are drawn along symmetry directions in the first Brillouin zone for TiC. The Fermi level is indicated by dotted horizontal line. TiC is characterized by an energetically low lying band which is derived from the 2s state of carbon atom. The remaining bands are due to Ti-3d states and Ti-4s states.The empty conduction bands above the Fermi level are due to Ti-3d and C-2p states with little contribution of Ti-p states. There is no energy gap between the conduction band and valence band.Hence at normal pressure TiC exhibit metallic character.
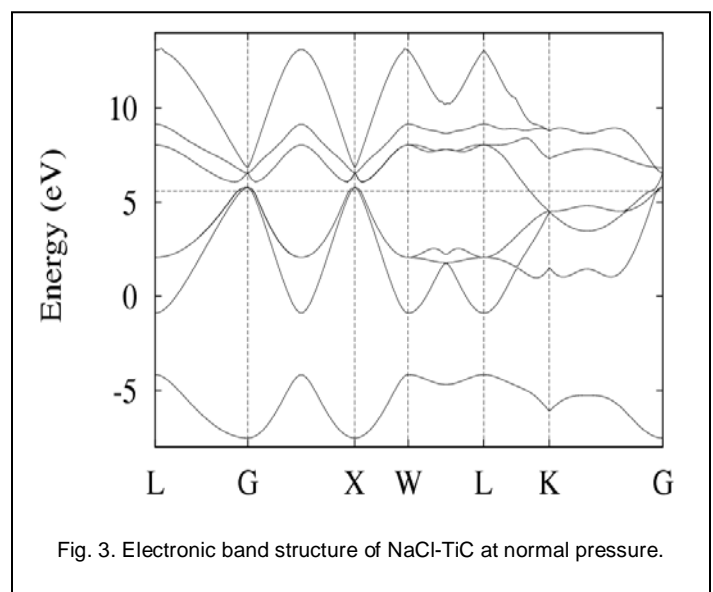

Fig. 3. Electronic band structure of NaCl-TiC at normal pressure.

The total and partial density of states (DOS) of TiC at normal pressure is shown in Fig.4 (a-b). The peak due to 2s state electrons of the carbon atom present at the energy range of ~ -5eV. The d state electrons of the Ti atom and the C-2p state electrons contribute to the highest spike just below the Fermi level, indicating that the Ti-d states intensively hybridize with the C-2p states. Above the Fermi level the peaks are due to Ti-p, Ti-3d states and C-2p states. The pseudo gap found near the Fermi level indicates the possibility of superconducting nature of TiC even at normal pressure.The general features of the DOS are similar to the result obtained by Dridi et al [15]
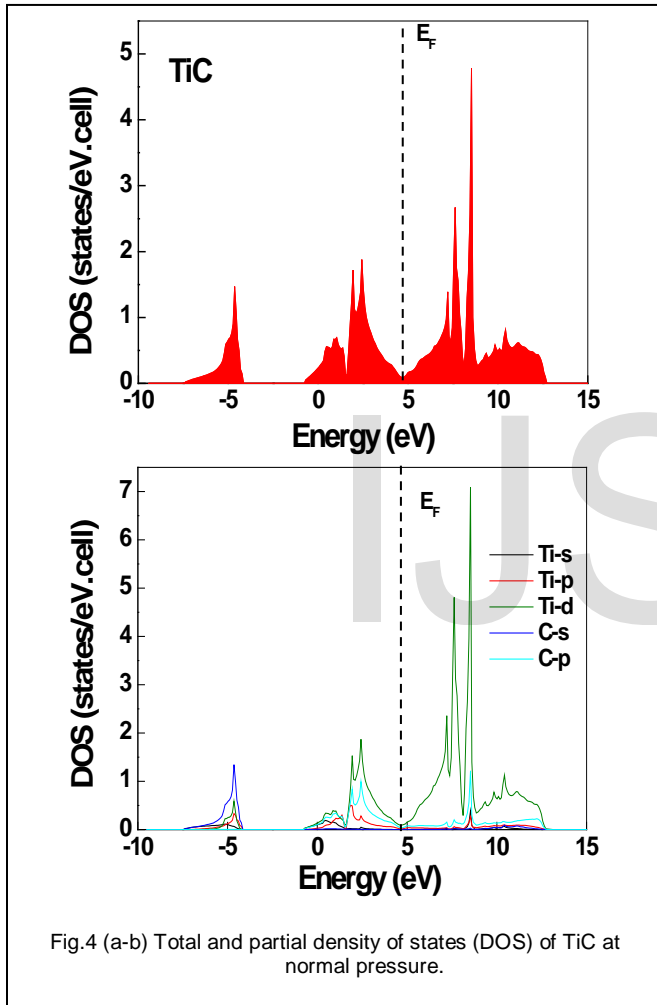

Fig.4 (a-b) Total and partial density of states (DOS) of TiC at normal pressure.

The covalent characteristics between titanium and C atoms can be confirmed by the charge density distribution. The charge density distribution for TiC at normal pressure is shown in Figure 5. The charge density transfer plot clearly display some of the important features of the bonding mechanism in titanium carbide.The plot show the charge transfer from the Ti to C atom leading to electrostatic interactions which constitutes the ionic component of bonding,and also the charge transferred to the interstitial regions between the atoms,constituting the covalent part of the bonding. It is clearly seen that charge strongly accumulates between Ti and C atoms, which means that a strong directional bonding exists between them. Thus, our results demonstrate that the bonding is a mixture of covalent and ionic attribution.
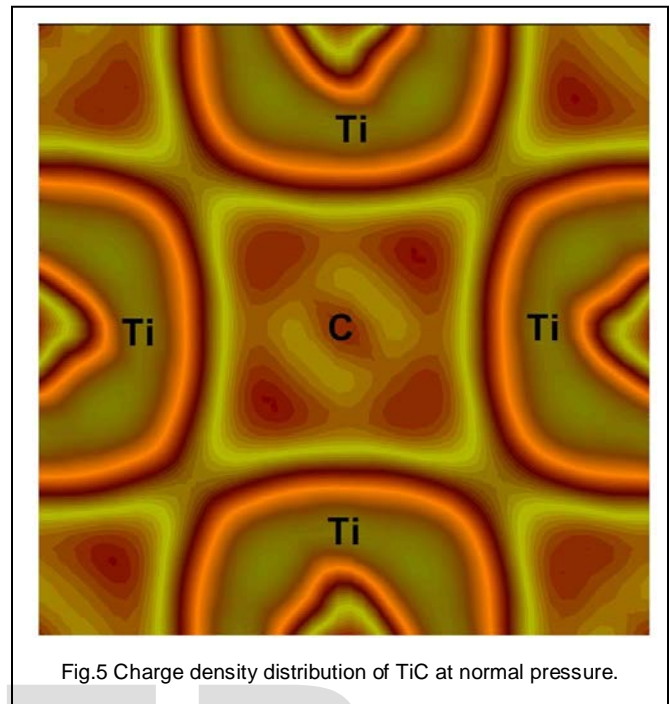

Fig.5 Charge density distribution of TiC at normal pressure.

3.3 Superconductivity of TiC

The continuous promotion of s electron to d shell in solids is one of the factors which will induce superconductivity. In the TiC, the d – electron number increases as a function of pressures ranging from normal to high pressure. This leads to the improvement of superconducting transition temperature (T_c) value. Therefore, the interaction between the conduction electrons and phonons increases and also electron – phonon coupling constant factor λ_{e-ph} increases. This determines the superconducting nature of a compound. The calculated Tc values depend more sensitively on λ rather than θ_D and μ^*. TiC is found to have superconducting nature at ambient condition. For normal pressure, the superconducting transition temperature is estimated by using the McMillan equation modified by Allen and Dynes [16],

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right]$$

where λ is the electron- phonon coupling constant, μ^* is the electron – electron interaction parameter and $\omega_{\log}$ is the average phonon frequency. The T_c, μ^* and λ values are computed for TiC at normal pressure using the results obtained from the electronic structure calculated using TB-LMTO. The superconducting transition temperature (T_c) is calculated as 2.889 K.

3.4 Elastic Properties

In order to calculate the elastic constants of a structure, a small strain is applied on to the structure and its stress

TABLE 2
CALCULATED ELASTIC CONSTANTS C_{11}, C_{12}, C_{44} (GPA), YOUNG'S MODULUS E (GPA), SHEAR MODULUS G(GPA),
B/G RATIO, ANISOTROPIC FACTOR AND (A) POISSON'S RATIO FOR THE TiC.

	C_{11}	C_{12}	C_{44}	E	G	ν	B/G	A
NaCl	611	152.76	193.58	508.21	207.81	0.199	1.46	0.844
	522[10]	117[10]	186.36[10]			0.17[18]		0.938[10]
	606 [12]	106 [12]	230 [12]			0.19[19]		
	500 [13]	113[13]	175 [13]					
CsCl	437.08	127.80	209.82	441.78	187.74	0.226	1.23	0.741

is determined. The energy of a strained system [17] can be expressed in terms of the elastic constants C_{ij} as:

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

where V_0 is the volume of the unstrained lattice, E_0 is the total minimum energy at 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 tensor. The elasticity tensor has three independent components (C_{11}, C_{12}, C_{44}) for cubic crystals. The calculated elastic constants C_{ij}(GPa), Young's modulus E(GPa), shear modulus G(GPa), and Poisson's ratio (ν) are presented in Table 2. From tabulated values, it is found that the calculated elastic constants are in agreement with the experimental and other available theoretical data [10-13, 18, 19]. For a stable cubic structure, the three independent elastic constants C_{ij} (C_{11}, C_{12}, C_{44}) should satisfy the Born-Huang criteria for the stability of cubic crystals [20]. It is seen that, the calculated elastic constants of TiC satisfy Born-Huang criteria, suggesting that they are mechanically stable. Young's modulus is often used to provide a measure of stiffness of a solid, i.e., larger the value of Young's modulus, stiffer is the material. From the Young's modulus values, it is seen that NaCl-TiC is the stiffest material. The Poisson's ratio of NaCl TiC is the lowest, indicating that the Ti–C bonding is more directional in nature. The calculated values of B/G predict that TiC is brittle in both NaCl and CsCl phase.

4 CONCLUSION

The structural, electronic, superconducting and elastic properties of TiC are investigated. The computed equilibrium lattice parameters and bulk modulus values are consistent with the experimental and other available theoretical results. TiC is found to be stable in the NaCl phase at ambient pressure. A pressure-induced structural phase transition occurs from NaCl→CsCl. The electronic band structure and density of states of TiC confirm their metallic nature. The superconducting transition temperature (T_C) is found to be 2.889 K. The calculated elastic constants obey the necessary mechanical stability conditions suggesting that they are mechanically stable at ambient pressure and TiC is found to be hardest material in NaCl phase.

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