Journal of Pure Applied and Industrial Physics, *Vol.6(12), 212-220, December 2016* *ISSN 0976-5727 (Print)*
(An International Research Journal), *www.physics-journal.org* *ISSN 2319-8133 (Online*

Elastic Properties of Rock-salt Structured Transition Metal Carbides

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(Received on: December 11, 2016)

ABSTRACT

In the present paper, author have performed the semi-empirical formula for static stiffness constants (C_{11}, C_{12}, C_{44}) of rock-salt (RS) structured transition metal carbides (TiC, ZrC, HfC, TaC, VC, NbC) in terms of their valence electron plasmon energy. We have applied the proposed empirical model to investigate the static stiffness constants on the transition metal carbides (TMC's). The estimated values of static stiffness constants are in excellent agreement with the values cited in the experimental and theoretical literature. Using these parameters, elastic properties such as bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson ratio (σ) for TMC's have been investigated. The present calculated results are in excellent agreement with available experimental data and previous calculations based on phenomenological methods. A comparison of the calculated static and elastic properties with the available experimental and theoretical estimations leads us the applicability of the method applied. This work highlights the significance of the relationship between static stiffness constants and plasmon energy ($\hbar\omega_p$).

PACS No.: 71.20.Be, 62.20.Dc, 45.10.Ab, 71.15.Mb, 74.70.Ad

Keywords: Transition Metal Compounds, Static and elastic properties.

1. INTRODUCTION

In the recent past, increasing much attention has been given towards the systemic study of various elastic, mechanical, structural, electronic and thermodynamic properties of transition metal carbides due to their scientific and technological importance[1-5]. This is because of their outstanding physical and chemical properties such as extreme stiffness were resistance,

corrosion resistance, high melting point and thermal conductivity. Such outstanding characteristics allow for their wide use in cutting tools and wear resistance part of various mechanisms operating at high temperatures and pressures. So Das *et al*.[6] studies the electronic and elastic properties of a series of rock-salt structured TMC's. Sharma and Verma[7] have derived the expression for the second order elastic constants for ZB structured solids by using three body crystal potential models. Dan *et al*.[8] has perform a systemic *ab-initio* study of the electronic and atomic structure of semi-coherent interfaces between bcc Fe and NaCl MX (M= Sc, Ti, V, Cr, Zr, Nb, Hf, Ta; X= C or N). In recent year, Gilman[9] derived expressions for elastic moduli of metals based on simplified quantum-mechanical consideration. The derived expressions also suffer from notable deficiencies, as they ignore the effects induced by ionicity of the bonds and exchange-correlation interactions amongst others. Srivastava and Diwan[10] have investigated the elastic and thermodynamic properties of transition metal carbides using the three body force potential model and density functional theory (DFT) based on *ab-initio* calculation successfully; but the electronic properties are not considered. Hass *et al*.,[11] has applied the functional within the GGA approximation to the calculation of TMC, but the relation of elastic and electronic properties are not involves. Martin[12] has presented a simple phenomenological theory for elastic constants of sphalerite structure crystals in term of bond-stretching and bond-bending force constant first used by Keating[13].

Recently, Experimental and theoretical method for calculation of structural, electronic, thermo-physical and elastic properties of early transition metal carbides (TMC) and nitrides [TMN] are well established[8,14-19]. Several researchers[20,21] have been investigated the electronic, structural, stability and mechanical properties of these materials using First-principles approach based on density functional theory (DFT) and plane wave pseudo-potential method. Due to difficulties associated with experimental process and their cost, as well as difficulties in obtaining accurate values of bulk modulus and lattice parameter, researchers turned to calculating these parameters through theoretical methods involving a series of approximations, such a method has always been complicated[22]. In the past few years, number of theoretical calculations based on empirical relationships has become an essential part of material research. Empirical formulae have mostly been found to be simple, easy to use and give better results for the physical parameters. Empirical relationships have become widely recognized as the method of choice for computational solid-state studies. In the previous research, author[23-27] has developed empirical relationships for structural, electronic and mechanical properties of zinc blende, wurzite and rock-salt structured binary solids with the help of plasma oscillation theory of solids. This is due to fact that the plasmon energy depends on the number of valence electrons, which changes when a metal forms a compound. In many cases empirical relationships do not give highly accurate results for each specific material, but they can still be very useful. In this paper, empirical relationship is presented for static and elastic properties of rock-salt structured transition metal carbides.

The aim of this work is to investigate the static and elastic properties of rock-salt structured transition metal carbides using the plasma oscillation theory of solids. In this article the present investigations are organized as follows: the theoretical concept is given in Section

2 and we present the discussion and simulation results for static and elastic properties of rock-salt structured transition metal carbides in this section also. Finally, conclusion is inferred in the last section-3.

2. THEORY, RESULTS AND DISCUSSION

Static stiffness constants are related to the hardness of the materials, and provide valuable information to understand the variety of the materials. There have been a number of reports in the past of empirical relation describing the elastic and mechanical properties. The elastic stiffness tensor is related to the stress tensor and the strain tensor by Hook's law. The elastic constants re calculated as the second derivatives of the internal energy with respect to strain tensor. The elastic stiffness tensor C_{ijkl} can be expressed as[28, 29].

$$C_{ijkl} = \left(\frac{\partial \sigma_{ij}(x)}{\partial e_{kl}} \right)_X \tag{1}$$

Where e_{kl}, σ_{ij}, X and x are Eulerian strain tensors, applied stress, the coordinates before and fter deformation, respectively. When the atoms are combining with incomplete valence shells then the chemical bonds are formed. The valence electrons refer to the electrons that take a part in chemical bonding. These electrons reside in the outer-most electron shell of the atom. The effective no. of valence electrons is related to the plasmon energy as[30].

$$N_e = \frac{m}{4\pi e^2} \left(\hbar \omega_p \right)^2 \tag{2}$$

Where e- electronic charge, m-mass of an electron and the Plasmon energy is explained as-

$$\hbar \omega_p = 28.8 \sqrt{Z\sigma / W} \tag{3}$$

Where Z-the effective no. of electron taking part in plasma oscillation, σ is the density and W-the molecular weight of compounds. This relation is valid for free electrons but also applicable for zinc-blende and rock-salt structured semiconductors, up to a first approximation.

In our previous research[23-27], we proposed simple expression for optical electronic, mechanical and structural properties of Zinc-blende, rock-salt and chalcopyrite structured semiconductors using plasma oscillation theory of solids We are view of this point, to verify the plasma oscillation theory of solids; we have plotted the linear-fitted curve for static stiffness constants (C_{11}, C_{12} & C_{44}) against plasmon energy for TMC's and are shown in Figs.-(1)-(3). We observe that in the plot of C_{11}, C_{12} & C_{44} and Plasmon energy normalization, the TMC's lies on straight line. This effect induced by free electron density of the compounds in 3d-, 4d- and 5d-transitan metal carbides. From Figs. (1)-(3), it is clear that the static stiffness constants (C_{ij}) assume as increasing linear trend with increasing $\hbar\omega_p$ (in eV). The static stiffness constants are expected to exhibit the following linear-fit C_{ij} - $\hbar\omega_p$ equation for rock-salt structured transition metal carbides as follows-

$$C_{ij} = D(\hbar \omega_p) + S \qquad (i=1, 4 \text{ and } j=1, 2, 4) \tag{4}$$

Where D and S are empirical constants that are listed in Table-1 along with the values of the square of correlation coefficient i.e. R^2, which can be used to judge the effectiveness of the correlation, are also incorporated in this Table. Using Eq. (4), the obtained values of static stiffness constants (C_{11}, C_{12} & C_{44}) are displayed in Table-2 and are compared with experimental data and theoretical values cited by several workers. It can be seen that the calculated values agree well with the available experimental data and other such theoretical findings[8, 10, 20, 21]. The elastic stability criteria for cubic crystal at ambient conditions are $C_{11}>0$, $C_{44}>0$, $(C_{11}-C_{12})>0$ & $(C_{11}+2C_{12})>0$. The present static stiffness constants in Table 2 satisfy these stability criterions, indicating that they are mechanically stable[31].

In order to have a further check the validity of the present model for static stiffness constants (C_{11}, C_{12} & C_{44}), we have derived the elastic properties such as bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson's ratio (σ) for TMC's from these data. The static stiffness constants (C_{11}, C_{12} & C_{44}) determine the response of the crystal to external forces, as characterized by elastic moduli and obviously play an important role in determining the strength and stability of materials. The relationship between elastic moduli and static stiffness constants for cubic crystal transition metal carbides[32] are defined as follows-

$$B = (C_{11} + 2C_{12})/3 \tag{5}$$

The upper (G_v) and lower (G_R) bounds of the shear modulus for TMC are given as follows-

$$G_V = (C_{11} - C_{12} + 3C_{44})/5 \tag{6}$$

and $$G_R = 5(C_{11} - C_{12})C_{44}/[4C_{44} + 3(C_{11} - C_{12})] \tag{7}$$

On the basis of Voigt-Reuss-Hill approximation[32-34], the Hill values of bulk- moduli and shear moduli are defined as-

$$B_H = (B_R + B_V)/2 \tag{8}$$

$$G_H = (G_R + G_V)/2 \tag{9}$$

Especially for cubic crystals $B_V = B_H = B_R$, Young's modulus (E) and Poisson ratio (σ), Zener anisotropy factor A, Lame's coefficient (λ) and Kleinman parameter (ξ) are thus computed from the following relations as-

$$E = 9BG/(3B + G) \tag{10}$$

$$\sigma = (3B - E)/6B \tag{11}$$

Using above relations (7-13), the elastic properties such as bulk modulus (B), Young's modulus (E), shear modulus (G) and Poisson ratio (σ) can be determined from the elastic constants, i.e., C_{11}, C_{12} and C_{44}, using the following explicit expressions[32-34] and are presented in the Table-2 along with the available experimental data and theoretical values cited by

previous researchers[8,10,20,21]. The agreement of the results with experiments and other theoretical investigation is excellent, which can be seen in Table-2. It is also clear from table-2 that the mechanical stability conditions in the cubic structures i.e. $C_{11}-C_{12}>0$, $C_{44}>0$, $(C_{11}+2C_{12})>0$, $C_{12}<B<C_{11}$, are well satisfied. Our results are compared to other theoretical works and a good agreement has been obtained between them.

Shear modulus (*G*) and Bulk modulus (*B*) are very important parameters to characterize the mechanical behavior of the material. The bulk modulus (B) is the measure of the resistance to fracture, while the shear modulus, G, is the measure of the resistance to plastic deformation. Calculated values of *B* and *G* are tabulated in Table 2. Ductile/brittle character of the material can be predicted using *B/G* ratio proposed by Pugh[35]. If *B/G* ratio is greater than 1.75, material shows ductile behavior otherwise brittle nature. The ratio of *B/G* for TiC, ZrC, HfC, TaC, VC, NbC is less than 1.75 (see Table 2) which indicates ductile nature of all these compounds. For justification between the brittle and ductile nature of these materials with the help of Poisson's ratio, the concept of the critical value was given by Frantsevich[36], which is equal to 0.330. For ductile nature of the material, Poisson's ratio is grater then 0.33 and for brittle materials, it is less than 0.33. It is clear from Table-2 that, in the present work, the Poisson's ratio lies between 0.192 and 0.213 and are very close to the critical value, which shows the brittle nature of these rock-salt structured transition metal carbides. Higher values of Young's modulus (*E*), in comparison to the bulk modulus (*B*) (see Table 2), of these materials indicate that the TMC's are stiffer material in cubic structure and hard to be broken. In the present study, the computed values of (*E*) vary from 482.4 to 417.1 in the following trend VC >TaC >TiC >NbC >HfC >ZrC, shows that the VC is more stiffer than ZrC. Poisson's ratio is measure of compressibility. The values of Poisson's ratio for these materials (see Table-2) are between 0.192 and 0.213, which shows that all the materials are compressible. Our calculated values of Poisson's ratio are agreed well with experimental values and other such theoretical findings. In the proposed empirical relationship only plasmon energy is required as input parameter. The applicability of our proposed method turns out to be wide.

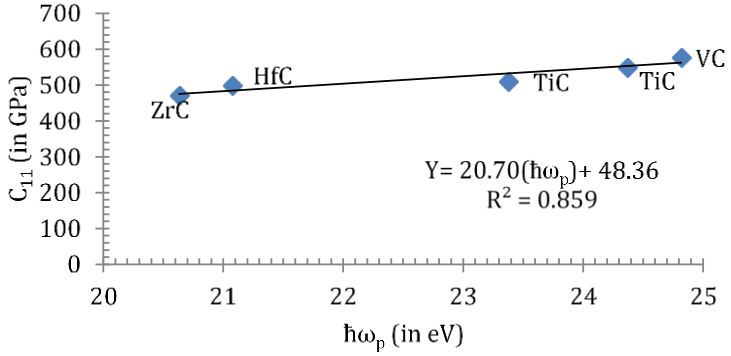

Fig. 1: Plot of Stiffness constant (C_{11}) for transition metal carbides as a function of plasmon energy ($\hbar\omega_p$). This line show linear relationship as determined by linear-fit calculation. In this figure, the experimental values of C_{11} are taken from[8,10,20].

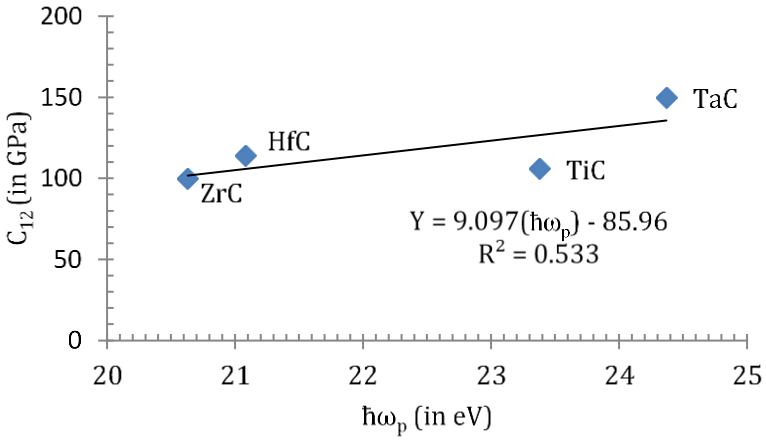

Fig. 2: Plot of Stiffness constant (C_{12}) for transition metal carbides as a function of plasmon energy ($\hbar\omega_p$). This line show linear relationship as determined by linear-fit calculation. In this figure, the experimental values of C_{12} are taken from[8, 10,20].

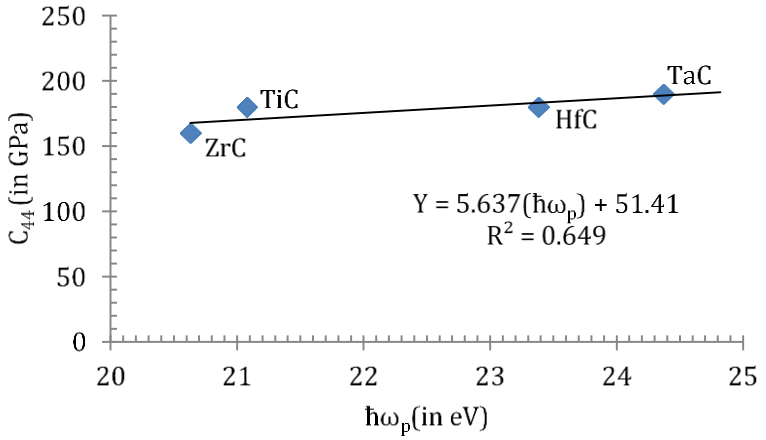

Fig. 3: Plot of Stiffness constant (C_{44}) for transition metal carbides as a function of plasmon energy ($\hbar\omega_p$). This line show linear relationship as determined by linear-fit calculation. In this figure, the experimental values of C_{44} are taken from[8,10,20].

Table-1: In this table, we present the values of the constant D and S for static stiffness constant of TMC's, which are used in relation (4).

C_{ij}	D	S	R^2
C_{11}	20.70	48.36	0.859
C_{12}	9.097	-85.96	0.533
C_{44}	5.637	51.41	0.649

Table-2: In this table, we display the calculated values of Static Stiffness Constants (C_{ij} in GPa) and elastic constants (in GPa), along with theoretical and experimental data.

TMC	$\hbar\omega_p$ (in eV) Eq. (3)	Static Stiffness Constants (in GPa)			Elastic constants (in GPa)			Poisson ratio (σ)	Pugh Ratio (B/G)
		C_{11}	C_{12}	C_{44}	B	G	E		
TiC	23.38	532.3	126.7	183.2	261.9	190.5	460.1	0.207	1.372
Theo.		523.2[a]	121.3[b]	183[b]	257[b]	190.5[b]	466.2[b]	0.210[b]	
		573[b]	122[a]	180[a]	255[b]	190[b]	457[c]	0.204[b]	
Expt.		510[b]	113[b]	180[b]	242[b]	182[b]	437[b]	0.200[c]	
ZrC	20.63	475.4	101.7	167.7	226.2	174.8	417.1	0.192	1.291
Theo.		474[b]	102[c]	162.8[b]	228[c]	176.9[b]	406[a]	0.189[a]	
		513[b]	103.5[a]	170[b]	225[b]	169[c]	428[b]	0.180[c]	
Expt		470[a]	100[c]	160[c]	242[c]	170[c]	407[c]	0.191[c]	
HfC	21.08	484.7	105.8	170.2	232.1	177.4	424.2	0.195	1.306
Theo.		498[c]	107[c]	179[c]	236[a]	176.6[a]	422[b]	0.190[c]	
Expt.		500[c]	114[c]	180[a]	242[c]	185[c]	430[c]	0.180[b]	
TaC	24.37	552.8	135.7	188.7	274.7	196.2	475.4	0.211	1.398
Theo.		547[c]	127[c]	176[c]	293.5[a]	189.6[c]	491.8[a]	0.211[a]	
Expt.		550[c]	150[b]	190[b]	332[c]	202[c]	490[c]	0.240[b]	
VC	24.82	562.1	139.8	191.3	280.5	198.7	482.4	0.213	1.409
Theo.		540[c]	145[c]	175.4[a]	280.5[a]	192[c]	478[c]	0.210[a]	
Expt.		500[c]	290[c]	150[c]	290[a]	209[c]	446[c]	0.19-.32[c]	
NbC	22.40	512.0	117.8	177.6	249.2	184.9	444.8	0.202	1.346
Theo.		557.3[a]	127[d]	163[d]	212[c]	179[c]	483.9[a]	0.226[a]	
Expt.		620[c]	200[c]	160[c]	300[c]	197[c]	514[c]	0.220[c]	

Ref. [21][a], Ref. [20][b], Ref. [10][c], Ref. [8][d]

3. CONCLUSION

The present paper reports an empirical relation for three independent static stiffness constant (C_{ij} GPa) with their valence electron plasmon energy of rock-salt structured transition metal carbides. This can be successfully employed to estimate the static stiffness constant (C_{11}, C_{12} and C_{44} in GPa) from their plasmon energy ($\hbar\omega_p$ in eV). The proposed empirical model (6) has been applied to calculate the stiffness constants of transition metal carbides. Employing the proposed empirical model, we have investigated the elastic properties such as bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson's ratio (σ) for TMC's successfully. The calculated values are cited in Table-2 along with the experimental data and other such theoretical findings. We note that the values of the stiffness constants C_{11}, C_{12} and C_{44} calculated from proposed empirical model are in fairly good agreement with the values reported by earlier researchers[8,10,20,21]. Closer agreement of the results support our assumption

that the set of values of the constants in Eq. (4) remain the same (see Table-1) for a given crystal and they may be regarded as the characteristic of a crystal structure as they remain the same for all compounds belonging to a given crystal structure. These results shows that our current approach is quite reasonable and can lead us a useful guide in calculating and predicting the static and elastic properties of these materials.

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