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Elastic Properties of Transition Metal Nitrides and Carbides

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Abstract*— In this paper, we study the elastic properties (i.e. Bulk modulus B) of a series of early transition metal mono-nitrides and carbides crystallize in the NaCl-type face centered cubic (FCC) structure has been investigated using plasma oscillation theory of solids. The same approach has previously been applied to rock-salt structured rare-earth mono-chalcogenides [J. Alloys and Compd. 537 (2012) 250-254]. We have presented an expression relating the bulk modulus B (in GPa) for early transition metal mono-nitrides (TMN) and carbides (TMC) with their plasmon energy $\hbar\omega_p$ (in eV). The bulk moduli of these compounds exhibit a linear relationship when plotted on a log-log scale against plasmon energy. We have applied the modified relation on rock-salt structured (TMN's & TMC's) solids. The trends are discussed and compared with available experimental data and theoretical results reported by earlier researchers.

***Index Terms*—Transition metal nitrides and carbides, Mechanical properties**

I. INTRODUCTION

Bulk modulus is of great interest due to its importance in evaluating the mechanical properties of materials. Nitrides and carbides of early-transition metals crystallize in the rock salt structure and are known as hard refractory materials. Transition metal nitrides and carbides possess unusual combination of physical and chemical properties [1], which make them attractive from both fundamental and technological points of view. In recent years, much attention has been paid to the study of early transition metal nitrides and carbides because of their unique physical properties of high hardness, brittleness, high melting point, good electrical and thermal conductivity and good corrosion resistance, excellent thermal stability, and in several those compounds, a relatively high superconducting transition temperature reaching nearly T=18 K indicates a strong electron-phonon interaction, is observed [2-10]. This unique combination of properties has challenged both theoretical and experimental investigations of nature of the chemical bond in these materials and also made possible a large variety of technological applications in the area of hard coatings for cutting tools, diffusion barriers in microelectronics, and corrosion and abrasion resistant layers on optical and mechanical components [1]. Due to their magnetic, superconducting mechanical and structural properties, they are materials of fundamental importance for magnetic storage devices, superconductors and in semiconductor industry [11, 12]. In spite of their significant importance, some of the mechanical properties of transition metal mono-nitrides and carbides have not yet been fully investigated in current literature. In particular, the transition metal mono-nitrides and carbides have been intensively investigated both experimentally and theoretically because of their potential applications in nanotechnology and micro-electronics industry [13-19]. During last few decades, the transition metal nitrides and carbides have attracted the material scientist due to their importance in nanotechnology. Many attempts have been made to synthesize nano-tubes composed of nitrides due to their important applications in technology. Several authors have presented results of electronic structure calculations for 4d-transition metal nitrides from different viewpoints [20, 21]. Theoretically, the cohesive properties of NaCl-type structure nitrides of the 4d-transition metals have been performed by Gelatt et al. [12] with use of the augmented-spherical-wave method. There emphasis is on the contribution of the various electron states to the bonding properties. Papaconstantopoulos et al. [20] studied the electronic properties of VN, NbN, TaN, CrN, MoN and WN. Guillermet et al. [21] have investigated the electronic, cohesive and thermodynamic properties of 3d- and 4d-transition metal mono-nitrides in NaCl-structure. Stampfl et al. [22] investigated the bulk electronic and physical properties of a series of early transition metal mono-nitride, namely, those formed with 3*d* metals (ScN, TiN, VN), 4*d* metals (YN, ZrN, NbN) and 5*d* metals (LaN, HfN, TaN) in the rock-salt structure using the Density-functional theory LDA, GGA, and screened-exchange LDA FLAPW calculations. They reported, in particular, lattice constants, bulk moduli, heats of formation and cohesive energies as well as bulk band structures and densities of states are reported, and trends discussed. 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 [23-31]. 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 moved 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 [32, 33] has developed empirical relationships for structural,

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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 particular, the simplicity of empirical relationships allows a border class of researchers to investigate useful properties, and often trend become more evident. In this paper, empirical relationship is presented for bulk properties of nitrides and carbides of the early-transition metals. In the modified proposed empirical relationship only plasmon energy is required as input; the computation of the bulk modulus B (in GPa) itself is trivial, and results reveals are comparable to the experimental values. The applicability of our proposed method turns out to be wide. The aim of this work is to investigate the bulk properties of early-transition metal mono-nitrides and carbides compounds using the plasma oscillation theory of solids. In this article the present investigations are organized as follows: Next section-2 gives the computational details. Results are reported, discussed and compared in section-3. Conclusions are inferred in the last section-4.

II. COMPUTATIONAL DETAILS

There have been a number of reports in the past of empirical relations describing the mechanical properties of solids. From the observed relationship between B_0 and V_0, Anderson and Nafe [34] first proposed an empirical relationship –

$$\ln B_0 = -\ln(V_0) + \ln(Z_1^* Z_2^*) + Const. \qquad (1)$$

Where V_0- represents volume per ion pair and $Z_1^* Z_2^*$ - product of the effective valence of the cation and anions. The above empirical equation is derivable from simple concepts of chemical ionic crystal physics. Recently, many theoretical and experimental approaches [30, 31, 35-38] have been reported to determine the values of the lattice constant, bulk modulus and elastic constants for early transition metal carbides, nitrides and solid state compounds. K. Li et al [39] predicted that the bulk modulus directly depends on the product of the electro-negativity (EN) of the atoms. According to them, the bulk modulus of rock-salt structured solid state compounds may be expressed as-

$$B = K_1 (\chi_A \chi_B)^{K_2} \qquad (2)$$

where K_1 and K_2 are constants and χ_A and χ_B are the EN of atoms, respectively. Cohen [40] predicted that the zero pressure isothermal bulk-modulus B in term of nearest-neighboring distance d (in A^0) for rock-salt structured solids may be expressed as-

$$B = \alpha d^{-\beta} \qquad (3)$$

Where α and β are the numerical constants. The relation of bulk moduli and geometrical properties of diamond and zinc-blende solids has been investigated by Cohen [40] Lam [41]. Based on Phillips and Van-Vechten scheme [42] and theoretical analysis of bond geometry of covalent ZB solids, Cohen proposed the following empirical relation as-

$$B = Ad^{-3.5} \qquad (4)$$

Where A- is numerical constant and d- nearest neighbor distance (in A^0) and Bulk modulus B (in GPa). In the previous work [32, 33], author proposed simple expressions for the structural, electronic and mechanical properties of rock-salt and zinc-blende structured binary semiconducting materials in term of plasmon energy. Using this idea to get better agreement between experimental data and theoretical values for the bulk modulus of rock-salt structured early transition metal mono-carbides and nitrides, K. Li and Cohen relations (2) and (3) may be extended to-

$$B = D(\hbar\omega_p)^S \qquad (5)$$

Where D and S are numerical constants and have values 0.518 and 2.0 respectively. In this expression the valence electron plasmon energy is to be determined using the relation (6) in our previous publication [43] and the molecular weight (M) and density (d) has been taken from refs. [1,44]. A detailed study of bulk properties of these materials has been given elsewhere [23-28, 34-41] and will not be presented here.

III. RESULTS AND DISCUSSION

Bulk modulus is an important microscopic property of materials, which reflects the ability of solids to resist compression deformation within the limits of the regime. At the microscopic level, the bulk modulus of an ideal solid depend on the nature of its chemical bonds and it is the strength and compressibility of the bonds that play the role in a solids ability to resist deformation. Essentially, the bulk modulus of the crystals is determined by the resisting ability of chemical bonds to compression. Both experimental and theoretical results suggest that the bulk modulus is a critical single material property to indicate its harness. Any change in the crystallographic environment of an atom is related to core electrons via the valence electrons. The change in wave-function that occurs for the outer electrons usually means a displacement of electric charge in the valence shell so that the interaction between valence, shell and core electrons is changed. This leads to a change in binding energy of the inner electron and to a shift in the position of absorption edge. The plasmon energy of any compound depends on the valence electrons and changes when a metal form a compound. We have calculated the bulk modulus (B in GPa) for early-transition metal mono-nitride and carbide materials using this idea. We have plotted log B versus log($\hbar\omega_p$) of a series of early transition metal mono-nitrides, namely, those formed with 3d-metals (ScN, TiN, VN, CrN, MnN, FeN, CoN, NiN, CuN), 4d-metals (YN, ZrN, NbN, MoN, TeN, RuN, RhN, PdN, AgN) and 5d-metals (LaN, HfN, TaN, WN, ReN, OsN, IrN, PtN, AuN) and carbides (ScC, TiC, VC, CrC,

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FeC, NbC, HfC, TaC, ZrC, YC, WC) in rock-salt structure are presented in figs. 1 & 2. We observed that in the plot of bulk modulus versus plasmon energy, the series of early transition metal compounds lie on the straight line. From these figs. it is quite obvious that the bulk modulus trends in these compounds increases with increasing plasmon energy and falls on the same straight line. The proposed empirical relationship has been applied to investigate the bulk modulus of these materials. The values so obtained are presented in Table 1 & 2 and are compared with the experimental data and theoretical values reported by earlier researchers. We note that the bulk moduli evaluated by our proposed empirical relation are in closed agreement with the experimental data as compared to theoretical values reported by earlier researchers. In the present model, elastic properties of these materials can be investigated by the Plasmon energy as a key parameter alone.

IV. CONCLUSIONS

Based on above results obtained using the proposed approach, and the discussion given, it is quite obvious that the parameter i.e. bulk modulus reflects the bulk-properties can be expressed in term of plasmon energy of these materials. This definitely a surprising phenomenon and needs further investigations of the reason. The calculated values are presented in Table 1 & 2. We come to the conclusion that the plasmon energy of any compound is a key parameter for calculating the elastic properties. The bulk modulus is directly depends on the plasmon energy. The bulk modulus of rock-salt structured early-transition metals nitrides and carbides exhibits a linear relationship when plotted on a log-log scale against the plasmon energy. It is also noteworthy that our proposed empirical relationship is simpler, widely applicable, and values obtained are in better agreement with experimental data [22, 23, 36, 48, 49, 53, 54] as compared to the theoretical findings [22-25, 27, 36, 45-54]. We have reasonably successful in calculating this parameter using the valence electron plasma oscillation theory of solids for these materials in rock-salt crystal structure. It is natural to say that this model can easily be extended to rock-salt structured rare-earth mono-pnictides, for which the work is in progress and will be appearing in forthcoming paper. Hence it is possible to predict the order of bulk-properties of metallic alloys from their plasmon energy. The method presented in this work will be helpful to material scientists for finding new materials with desired bulk-modulus among a series of early transition metal mono-nitrides and carbides, namely, those formed with 3d-metals, 4d-metals and 5d-metals in rock-salt structure.

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Dheerendra Singh Yadav has completed his Ph.D in Physics (Condensed Mater Physics and Material Science) from Dr. B R A University, Agra (U.P), India, and Masters Degree in Physics from this University also. He is presently the Ass. Professor at Department of Physics Ch. Charan Singh P G College Heonra (Saifai) Etawah, (U.P.) India. He has 08 years experience as a researcher. His research interests include Optical, Electronic, Elastic properties of Ternary Chalcopyrite semiconductors, binary solids and Rare earth compounds. He has published a number of research papers in international journal of repute and presented papers at national and international conferences.

APPENDIX

Table 1: The calculated values of bulk-modulus of 3d-, 4d-, and 5d-transition metal mono-nitrides

TMN	$\hbar\omega_p$	Bulk modulus [in GPa]		
	[in eV]	$B_{[Calc.]}$	$B_{[Expt.]}$	$B_{[Theo.]}$
ScN	22	250		235[c], 220[e]
TiN	23.97	297	288[c]	304[d], 273[e], 289[g]
VN	25.06	324	268[m]	330[e], 317[a], 338[d], 316[b]
CrN	24.88	320	326[h]	361[d], 340-430[g], 247[e]
MnN	26.81	372		374[p]
FeN	26.95	376		368[p]
CoN	26.95	376		358[p]
NiN	26.43	361		311[p]
YN	19.66	200		204[c], 158[f]
ZrN	22.83	269		264[c], 250[f], 248[e], 282[h]
NbN	24.16	302	287[f]	309[f], 292[h]
MoN	24.83	317	390[n]	331[h], 327[f], 354[d]
TcN	23.72	291		379[h]
RuN	23.7	290		305, 361[h]
RhN	23.15	277		286[h]
PdN	22.76	268		287, 234[h]
AgN	21.71	244		200[h]
LaN	17.36	156		148[c]
HfN	24.5	310	306[f]	314[h], 320[c]
TaN	24.71	316		328[e], 338[c]
WN	22.37	259		299, 354[f]
ReN	23.47	285		396[d], 364
AuN	21.02	228		220[h]
OsN	23.49	285		382[h], 372[d]
IrN	22.84	270		317, 363[h]
PtN	22	250		243, 288[h]

a-[50], b-[51], c-[22], d-[52], e-[27], f-[23], g-[36], h-[25], i-[48], j-[46], k-[47], l-[49], m-[53], n-[54], o-[45] p-[55].

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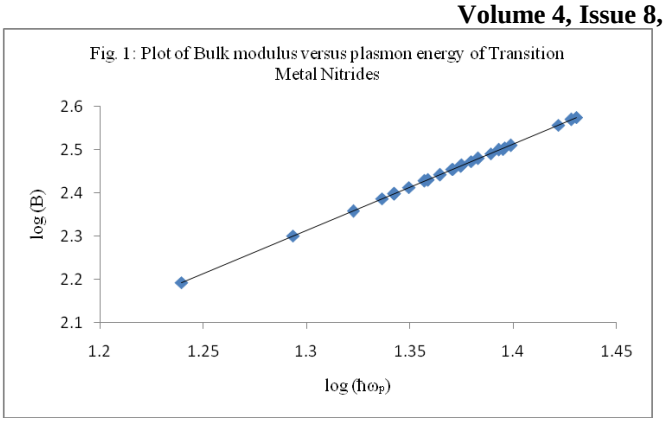

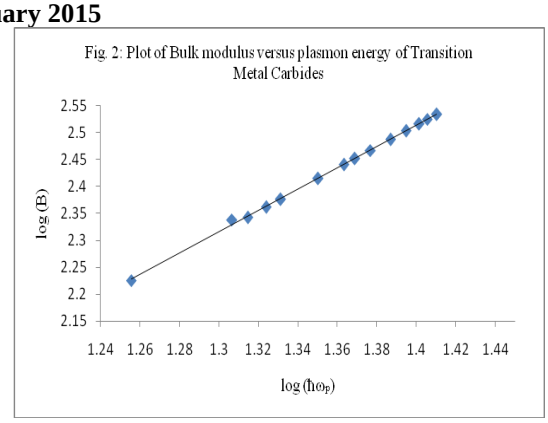

Table 2: The calculated values of bulk-modulus of 3d-, 4d-, and 5d-transition metal mono-carbides

TMC	$\hbar\omega_p$	Bulk modulus [GPa]		
	[in eV]	$B_{[Calc.]}$	$B_{[Expt.]}$	$B_{[Theo.]}$
ScC	20.25	218		153[e], 173.6[k]
TiC	23.38	283	242[l], 232-290[i]	281[m], 248[e], 253[i]
VC	24.82	319	308-390[i]	321[d], 311[e], 320.67[k]
CrC	25.2	328		322[f], 262[e], 351[d]
FeC	25.44	335		
NbC	22.4	260	266.7-340[g]	298[e], 300[o], 290[i]
HfC	21.08	230	241[i], 242[l]	237[e], 238[l]
TaC	24.37	307	344[l], 214-404[i]	316[i], 304[l]
ZrC	20.63	220	208.7[l], 159-224[i]	219[e], 220[o], 221[l], 214[i]
YC	18.01	168		124.3[o], 128[f]
WC	25.72	342		329-387[g], 357[j]
MoC	23.8	293		312[i]
PtC	21.44	238		331-339[g]
RhC	23.08	276		280[o]

a-[50], b-[51], c-[22], d-[52], e-[27], f-[23], g-[36], h-[25], i-[48], j-[46], k-[47], l-[49], m-[53], n-[54], o-[45] p-[55].