

# Pseudo Elastic Behaviour of Liquid Binary Alloys

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**Abstract-** The trend in the elastic constants of simple and transition elemental cube metals are explained in terms of a uniform electron gas theory. Previously this new model was used to show that the cohesive energies of the elemental transition metals depend primarily on the bonding valence and the average electron density at the boundary of the unit cell. In the present work we shall study the pseudo elastic behavior of liquid binary alloys using pseudo potential model based on the density functional theory with both the local density approximation and the generalized gradient approximation for the exchange correlation function. Here we use a slight modification of the same model to show that the elastic constants of the elemental cubic metal depend primarily on the bonding valence, the density at the cell boundary and the symmetry of the lattice.

**Index Terms-** Elastic Constants, Cohesive Energy, Pseudopotential Model, Density Functional Theory, Generalized Gradient Approximation, Exchange Correlation Function, Bonding Valence

## 1 INTRODUCTION

THE effect of strain on electron properties require knowledge of the materials mechanical properties and specifically the elastic constants which describe the response to an applied macroscopic stress. To this purpose the elastic constants of the material under study are of particular interest and has been calculated at different composition by computing the compounds of the stress tensor  $\delta$  for small strain. It is well known that a cubic crystal has only three independent elastic constants. When a vacancy is thermally created in a solid, the latter's volume changes thus defining a vacancy formation volume. In other cases a defect is produced by exchange one of the foreign atom or molecule. A defect volume  $V^d$  can be define as the difference between the volume  $V$  of the host material containing defect (d) and the volume  $V^o$  of the perfect crystal, provided that the volume  $V$  and  $V^o$  contain the same number of particles. The theoretical pressure volume relations for metals were studied by Soma et al. By using a model potential due to Kulshrestha et al. Pandya et al. have also studied the pressure volume relation for fcc transition metals using the model proposed by Antanov et al. Some rigorous methods to calculate the cubic and hexagonal elastic constants have been well described in previous studies.

The main purpose of the present work is the determination of the elastic constants of liquid binary alloys at different concentration using pseudopotential model by means of the Cambridge Serial total Energy Package Soft Ware(CASTEP) Employing the generalized gradient approximation within density functional theory (DFT).

## 2 Theoretical formalism

In the present work Varotsos and Alexopoulos model has been applied using slight modification in volume due to concentration.

Varotsos had derived an expression for the bulk modulus of mixed system in terms of constituent ionic compounds, their molar volumes and their molecular fractions. According to him the bulk modulus of the mixed system is given by

$$B = [1 + x (V_2/V_1 - 1)/1 + (B_1V_2/B_2V_1 - 1)] B_1$$

In this expression  $x$  is the molecular fraction of compound 1 having Bulk modulus and molar volume  $B_1$  and  $V_1$  respectively.  $B_2$  and  $V_2$  are the Bulk modulus and the molar volumes of compound 2 respectively.

The molecular volume of the alloy is determine in ideal sense using the relation

$$\Omega_{\text{alloy}}^{\text{ideal}} = (1 - C) \Omega_1 + C \Omega_2$$

Here  $\Omega_1$  and  $\Omega_2$  are the atomic volume of the compounds species of the alloy and  $C$  is concentration of the second compound.

With the increasing power of modern work stations pseudopotential calculation of elastic constants have become possible. These investigations are all based on density functional theory; differ however, in the treatment if tightly bound core electrons.

Our calculations were made using the plane wave pseudopotential method as invoked by the CASTEP. Castep is the total energy code that allows one to easily compute atomic forces and stress as well as the energy and electronic properties and it is thus most suitable for structural studies.

The Jellium model of the electron gas has long been used to understand the qualitative trends in the plasma ion and electron hole excitation spectra of elemental metals. The calculated spectra agree semiquantitatively with experiment for simple metals, and are qualitatively useful for the transition metals. One is used to thinking that the excitations of quantum systems are harder to predict than ground-state properties. From this point of view, it is surprising that the Jellium model has not provided a similarly simple explanation for the trends in the ground state energetic of the elemental metals. For non-uniform systems the

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background density varies with position and the new potential gives rise to force. The total external electron potential  $V_{ext}(r)$  is given explicitly by

$$V_{ext}(r) = \phi(r) + v_0 n_b(r)/n, \quad (1)$$

Where  $\phi(r)$  is the usual electrostatic potential. The strength of the ad hoc interaction  $v_0$  is uniquely fixed by the condition of zero forces for the uniform state and is given in terms of the energy of bulk Jellium and  $n$  is the uniform equilibrium electron density.

The theory of ideal metals can be understood by starting with an electron gas that has a uniform electron and background density  $n$ . The zero-force condition is achieved by introducing an additional ad hoc electron-ion potential, which at a point  $r$  is proportional to the background density at that point. The strength of the additional potential is determined by the zero-force condition, and is given by

$$v_0 = -n(\partial e_{jell}/\partial n)_n \quad (2)$$

Here  $e_{jell}$  is the energy per electron in uniform Jellium of density  $n$ .

The Born-Oppenheimer approximation yields the following many-body Hamiltonian for the unmodified theory of ideal metals:

$$H = -\hbar^2/2m \sum_i \nabla_i^2 + e^2/2 \sum_{i \neq j} (1/r_{ij}) + e^2/2 \iint d^3r d^3r' [n_b(r) n_b(r') / r - r'] - e^2 \sum_i d^3r [n_b(r) / r_i - r_j] + v_0 \sum_i [n_b(r_i)/n] \quad (3)$$

A density function for the energy can also be used to describe the theory of ideal metals in the Born-Oppenheimer approximation. Formally,

$$E[n_e, n_b] = T_s[n_e] + \int d^3r \int d^3r' [\rho(r) \rho(r') / r - r'] + E_{xc}[n_e] + E_{ei}[n_e, n_b] \quad (4)$$

Here,  $\rho = n_e - n_b$  denotes the net charge.  $E_{xc}$  denotes the exchange-correlation energy, while  $T_s$  denotes the kinetic energy of non-interacting electrons. The second term on right hand side denotes the classical electrostatics energy. Finally, the last term on the right hand side models electron-ion interactions beyond the classical electrostatic interaction. It is expressed, for the unmodified ideal metal as

$$E_{ei}[n_e, n_b] = v_0/n \int d^3r n_b(r) n_e(r) \quad (5)$$

We modify the theory of ideal metals by introducing the following, more general form for the electron ion interaction.

$$E_{ei}[n_e, n_b] \approx \int d^3r n_e(r) [v_0 \{n_b(r)/n\} \{1 - 1/2 \beta^2 (n_e(r) - n)^2\}] \quad (6)$$

Here  $\beta$  is an ad hoc parameter that is chosen once to give agreement with experiment for all metals.

Solution for the energy can be obtained from the energy-density function by following the procedure of Kohn and Sham. The self-consistent equations with an effective potential is therefore given as

$$v_{eff}(r) = \delta E_{xc} n_e / \delta n_e + \delta E_{ei}[n_e, n_b] / \delta n_e \quad (7)$$

Density-functional theory can also be used to compute the response of the electron gas to a perturbation. The screened potential-density linear response function can be obtained in the random-phase approximation Shore et al,  $\chi$

$$\chi^{sc}(q) \approx \chi^0(q) / [1 - (8\pi/q^2 + \delta^2 E_{xc} / \delta n_e^2) \chi^0(q) + \delta^2 E_{ei} / \delta n_e^2] \chi^0(q) \quad (8)$$

Here  $\chi^0$  is the Lindhard function. The functional derivative of the exchange-correlation energy can be evaluated in the local-density approximation, as

$$[\delta^2 E_{xc} / \delta n_e] \Big|_n = d^2/d n_e^2 \{n_e e_{xc}(n_e)\} \Big|_n \quad (9)$$

Here,  $e_{xc}$  denotes the exchange-correlation energy of Jellium per unit volume. The functional derivative for the electron-ion interaction can be evaluated from (6)

$$\delta^2 E_{e-i} / \delta n_e \Big|_n = v_0 n_b/n d^2/d n_e^2 \{n_e [1 - 1/2 \beta^2 (n_e - n)^2]\} \quad (10)$$

If the transition metal is compressed, the rigid positive backgrounds of the various Wigner-Seitz cells overlap and the background becomes inhomogeneous, the Wigner-Seitz cell centered about the origin of coordinates and define the characteristic function as,

$$\Upsilon(r) = 1 \quad r \in \text{Wigner-Seitz cell}$$

and,

$$\Upsilon(r) = 0 \quad r \notin \text{Wigner-Seitz cell} \quad (11)$$

In the following, we will consider background densities that can be formed as

$$n_b(r) = n \sum_{R_i} \Upsilon(r - R_i) \quad (12)$$

Where  $R_i$  denotes the set of vectors.

Now the change in energy to second order  $E^{(2)}$  is obtained by comparing three states. Which is

$$E_{eq}(n) = N [e_{jell}(n) + v_0] \quad (13)$$

Where  $N$  is the total number of electrons.

The extraction of elastic constants is straightforward once the energy changes have been calculated. The change in energy is related to the strain  $\epsilon_{ij}$  and the elastic constants  $C_{ijkl}$ , via

$$\delta E = 1/2 C_{ijkl} \epsilon_{ij} \epsilon_{kl} \quad (14)$$

We computed the energy changes for the fcc and bcc cubic metals using following strains:

$$\begin{pmatrix} \delta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & 0 \end{pmatrix}, \begin{pmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \delta \end{pmatrix} \& \begin{pmatrix} 0 & \delta & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (15)$$

The axes of strain tensor are aligned with the set of [100] direction of the cubic crystal. These strains over determine  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ .

Vartsos, 1980; had derived an expression for bulk modulus of mixed systems in terms of those of constituent ionic compounds, their molar volumes, and their molecular fractions. This is given by

$$B = \left\{ \frac{1 + \eta (V_2/V_1 - 1)}{1 + \eta (B_1 V_2/B_2 V_1 - 1)} \right\} B_1 \quad (16)$$

In this expression  $\eta$  is the molecular fraction of compound 1 having bulk modulus and molar volume  $B_1$  and  $V_1$ , respectively.  $B_2$  and  $V_2$  are the bulk modulus and the molar volume of compound 2, respectively.  $B$  is the bulk modulus of the mixed system. This expression yields very satisfactory results. Moreover from the above expression we get the values for bulk moduli such, not the three independent elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ . Which are sometimes necessary to enable one to predict the values of Young's modulus, Poisson's ratio, etc. in different directions.

The aim of this work is to derive expression to predict the values of  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$  for mixed systems when those for constituent ionic compounds and their molecular fractions are known.

Giri and Mitra, 1985; have derived an expression for Debye temperatures  $\Theta_{rs(pq)}$  of mixed system  $rs(pq)$  in terms of those  $\Theta_r$  and  $\Theta_s$  of ionic compounds  $r$  and  $s$  having molecular fractions  $p$  and  $q$  respectively, which is

$$M_{rs(pq)} \Theta_{rs(pq)}^2 = p M_r \Theta_r^2 + q M_s \Theta_s^2 \quad (17)$$

Here  $M_{rs(pq)} = p M_r + q M_s$ ,  $M_r$  and  $M_s$  are the molecular weights of the mixed system, compound  $r$ , and compound  $s$ , respectively. They have shown that the above equation is valid for number of mixed system at all proportions. For the cubic lattices the nearest neighbour central constant  $f_1$  is related to Debye temperature  $\Theta$  through the relation, Shirly, 1975;

$$f_1 = Y M \Theta^2 \quad (18)$$

Where,

$$Y = C k^2 A / 9 h^2 ;$$

$A$  is the atomic mass unit,  $M$  the mass,  $C$  is a constant depending on the lattice type, having value 2.515 for f. c. c lattices.

If  $f_1^{rs(pq)}$ ,  $f_1^r$ ,  $f_1^s$  are the nearest neighbor central force constants for the mixed system, for compound  $r$ , and compound  $s$ , We may, therefore write

$$f_1^{rs(pq)} = Y M_{rs(pq)} \Theta_{rs(pq)}^2 \quad (19)$$

$$f_1^r = Y M_r \Theta_r^2 \quad (20)$$

$$f_1^s = Y M_s \Theta_s^2 \quad (21)$$

$$f_1^{rs(pq)} = p f_1^r + q f_1^s \quad (22)$$

Similarly,

$$f_2^{rs(pq)} = p f_2^r + q f_2^s \quad (23)$$

$$f_3^{rs(pq)} = p f_3^r + q f_3^s \quad (24)$$

So we get three equations for three types of force constants for mixed systems in terms for these constituent ionic compounds.

According to Niu and Shimizu, force constants  $f_1$ ,  $f_2$  and  $f_3$  are related to elastic constants  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  for f.c.c lattice through these three equations. They are

$$f_1 + 3 f_3 = a C_{44} \quad (25)$$

$$f_1 + 4 f_2 - f_3 = a (C_{11} - C_{44}) \quad (26)$$

$$2 (f_1 - f_3) = a (C_{12} + C_{44}) \quad (27)$$

Here  $a$  is the lattice constant. For mixed system it can be expressed as

$$a_{rs(pq)} C_{44}^{rs(pq)} = f_1^{rs(pq)} + 3 f_3^{rs(pq)} \quad (28)$$

$$a_{rs(pq)} C_{44}^{rs(pq)} = p f_1^r + q f_1^s + 3 p f_3^r + 3 q f_3^s = p (f_1^r + 3 f_3^r) + q (f_1^s + 3 f_3^s). \quad (29)$$

Finally,

$$a_{rs(pq)} C_{44}^{rs(pq)} = p a_r C_{44}^r - q a_s C_{44}^s \quad (30)$$

$C_{44}^r$  and  $C_{44}^s$  are the values of  $C_{44}$  for ionic compounds  $r$  and  $s$  having lattice constants  $a_r$  and  $a_s$  respectively.  $C_{44}^{rs(pq)}$  is that of the mixed system.  $a_{rs(pq)}$  is the lattice constant of the mixed system with similar calculation for  $C_{11}$  and  $C_{12}$  we get

$$a_{rs(pq)} C_{11}^{rs(pq)} = p a_r C_{11}^r - q a_s C_{11}^s \quad (31)$$

$$a_{rs(pq)} C_{12}^{rs(pq)} = p a_r C_{12}^r - q a_s C_{12}^s \quad (32)$$

Thus we can derive  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  for mixed systems, if the constituent ionic compounds along with their lattice constants are known. These parameters of the reference binary alloys are not easily available, so we have used Vegard's law. Once by knowing the value of  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ , the value of  $B$  can be calculated.

### 3 Results and discussion

In the present work we have calculated the values of  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  for the reference alloy system at different concentration, which are tabulated in the table 1 – 3.

TABLE – 1

#### ELASTIC CONSTANTS OF Na–K AT EQUI-CONCENTRATION

q / 2k <sub>r</sub>	Values of elastic constants (10 <sup>10</sup> N/m <sup>2</sup> )			Values of bulk Modulii B (10 <sup>10</sup> N/m <sup>2</sup> )	
	C <sub>11</sub>	C <sub>12</sub>	C <sub>44</sub>	Calc. (Present.)	Calc.(1.)
0.00	3.962	0.687	0.607	1.782	1.766
0.50	3.822	0.657	0.581	1.716	1.692
1.00	3.702	0.632	0.554	1.654	1.631
1.50	3.578	0.612	0.531	1.596	1.593
2.00	3.432	0.601	0.522	1.573	1.542

TABLE – 2

ELASTIC CONSTANTS OF K–Cl AT  
EQUI–CONCENTRATION

q / 2k <sub>f</sub>	Values of elastic constants (10 <sup>10</sup> N/m <sup>2</sup> )			Values of bulk Modulii B (10 <sup>10</sup> N/m <sup>2</sup> )	
	C <sub>11</sub>	C <sub>12</sub>	C <sub>44</sub>	Calc. (Present.)	Calc.(1.)
0.00	14.201	6.354	7.234	8.890	
0.50	13.365	6.001	6.935	8.732	
1.00	12.234	5.932	6.003	8.695	
1.50	11.759	5.634	5.443	8.235	
2.00	11.663	5.320	5.213	8.125	

TABLE – 3

ELASTIC CONSTANTS OF K–Br AT  
EQUI–CONCENTRATION

q / 2k <sub>f</sub>	Values of elastic constants (10 <sup>10</sup> N/m <sup>2</sup> )			Values of bulk Modulii B (10 <sup>10</sup> N/m <sup>2</sup> )	
	C <sub>11</sub>	C <sub>12</sub>	C <sub>44</sub>	Calc. (Present.)	Calc.(1.)
0.00	18.885	9.334	6.373	4.321	
0.50	17.732	9.363	6.125	4.221	
1.00	17.321	9.321	5.987	4.132	
1.50	16.421	9.233	5.635	4.110	
2.00	15.321	9.121	5.334	4.009	

Giri and Mitra 1986, which are in good agreement to the experimental values, have also applied this technique to KCl and KBr system for a number of compositions. Our theoretical study of binary liquid alloys at equi-concentration not only reproduces the concentration dependence of various elastic constants and microscopic properties but also throw light on the phenomenon of compound formation in its melt.

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