

Bulk Hydrostatic Properties of Binary Liquid Alloys

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Abstract: *The energetic and ground state structures of the elemental metals combined with density- functional theory and the local density approximation now able not only the computation of the cohesive energy of the elemental metals but also the particular symmetry of the ground-state lattice Previously it has been shown that a model based on the electron gas explains the trends in the cohesive energies of the elemental metals. In this paper we show that a simple extension of this uniform electron gas model also explains the trends in the elastic constants of the simple and transition metals and binary alloys at different concentration*

Key Word: *Cohesive Energy | Electron Gas Model | Elastic Constants | Binary Alloys|*

I. Introduction

The last two decades have seen a great advance in our ability to compute the energetic and ground – state structures of the elemental metals. The digital computer combined with density- functional theory and the local density approximation now able not only the computation of the cohesive energy of the elemental metals, but also the very small differences in energies that determine the particular symmetry of the ground state lattice. Our ability to compute such detailed properties continues to expand rapidly and is paying great dividends. However, as remarked by Wigner and Seitz in their famous quote concerning a great calculating machine. "It would be preferable instead to have a vivid picture of the behavior of the wave functions. A simple description of the essence of the factors which determine cohesion and an understanding of the origins of variation in properties from metal to metal." It is the purpose of this paper to contribute to the qualitative picture envisioned in the quote. Previously it has been shown that a model based on the electron gas explains the trends in the cohesive energies of the elemental metals. In this paper we show that a simple extension of this uniform electron gas model also explains the trends in the elastic constants of the simple and transition metals.

FORMULISM:

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

$$V_{\text{ext}}(r) = \phi(r) + V_0 \eta_b(r) / \eta. \quad (1)$$

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 η 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 η . 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

$$V_0 = \eta(\partial e_{\text{jell}}/\partial \eta)\eta. \quad (2)$$

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

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

$$H = -\hbar^2/2m \sum_i \nabla_i^2 + e^2/2 \sum_{i \neq j} (1/r_i - r_j) + e^2/2 \iint d^3r d^3r' [\eta_b(r')/r - r'] - e^2 \sum \int d^3r [\eta_b(r)/r_i - r_j] + V_0 \sum_i [\eta_b(r_i)/\eta] \quad (3)$$

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

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

Here, $\rho = \eta_e - \eta_b$ 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

$$E_{ei}[\eta_e, \eta_b] = V_0/\eta \int d^3r \eta_b(r) \eta_e(r). \quad (5)$$

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

$$E_{ei}[\eta_e, \eta_b] \approx \int d^3r \eta_e(r) [V_0 \{ \eta_b(r)/\eta \} \{ 1 - 1/2\beta^2 \{ \eta_e(r) - \eta \}^2 \}] \quad (6)$$

Here β 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 I_s therefore given as

$$E_{\text{eff}}(r) = \delta E_{xc} / \delta \eta_e + \delta E_{ei}[\eta_e, \eta_b] / \delta \eta_e \quad (7)$$

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. χ

$$\chi^{\text{sc}}(q) \approx \chi^0(q) / [1 - (8\pi/q^2 + \delta^2 E_{xc} / \delta \eta_e^2 | \eta + \delta^2 E_e / \delta \eta_e^2 | \eta) \chi^0(q)] \quad (8)$$

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

$$[\delta^2 E_{xc} / \delta \eta_e^2 | \eta = d^2/d\eta_e^2 \{ \eta_e e_{xc}(\eta_e) \} | \eta \quad (9)$$

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 (4.6)

$$\delta^2 E_{e-i} / \delta \eta_e^2 | \eta = V_0 \eta_b / \eta d^2 / d\eta_e^2 \{ \eta_e [1 - 1/2\beta^2 (\eta_e - \eta)^2] \} \quad (10)$$

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

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

and

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

In the following. We will consider background densities that can be formed as

$$\eta_b(r) = \eta \sum_{R_i} \gamma(r - R_i) \quad (12)$$

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

$$E_{eq}(\eta) = N [e_{jell}(\eta) + V_0] \quad (13)$$

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 ϵ_{ij} and the elastic constants C_{ijkl} . via

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

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

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

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} .

Vartsov. 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

$$B = \{ [1 + \eta(V_2/V_1 - 1)] / \{1 + \eta(B_1V_1 / B_2V_1 - 1)\} \} B_1 \quad (16)$$

In this expression η 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} and 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} and 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 Θ_r and Θ_s of ionic compounds r and s having molecular fractions p and q respectively, which is

$$M_{rs(pq)} \Theta_{rs(pq)}^2 = pM_r \Theta_r^2 + qM_s \Theta_s^2 \quad (17)$$

Here $M_{rs(pq)} = pM_r + qM_s$. 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 neighbor central constant f_1 is related to Debye temperature Θ through the relation. Shirly, 1975;

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

Where.

$$Y = C K^2 A / 9 \hbar^2;$$

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.

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

$$f_2^{rs(pq)} = p f_3^r + q f_3^s \quad (24)$$

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

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

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

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 as

$$B = (1/3) (C_{11} + 2C_{12})$$

In the present work we have calculated the values of C_{11} , C_{12} and C_{44} for the reference alloys Na-K; K-Cl; K-Br system at different concentration, which are tabulated in the table 1-3.

TABLES-1
ELASTIC CONSTANTS OF Na-K AT EQUI-CONCENTRATION

q/2K _f	values of elastic constants (10 ₁₀ N/m ²)			Values of bulk Modulii B (10 ¹⁰ N/m ²)	
	C ₁₁	C ₁₂	C ₄₄	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

TABLES - 2
ELASTIC CONSTANTS OF K-Cl AT EQUI-CONCENTRATION

q/2K _f	values of elastic constants (10 ₁₀ N/m ²)			Values of bulk Modulii B (10 ¹⁰ N/m ²)	
	C ₁₁	C ₁₂	C ₄₄	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	

TABLES -3
ELASTIC CONSTANTS OF K-Br AT EQUI-CONCENTRATION

q/2K _f	values of elastic constants (10 ₁₀ N/m ²)			Values of bulk Modulii B (10 ¹⁰ N/m ²)	
	C ₁₁	C ₁₂	C ₄₄	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	

II. Conclusion

It has been shown that a model based on electron gas explains the trends in the cohesive energies of elemental metals. The simple extension of uniform electron gas model explains the trends in the elastic constants of the simple and transition metals. By this methods the various elastic constants of some metals have been calculated which agrees well with the data available in literatures within the range of experimental errors. This validates the efficiency and importance of the methods.

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