Advances in Physics Theories and Applications
ISSN 2224-719X (Paper) ISSN 2225-0638 (Online)
Vol 10, 2012

Effects of Deformation on the Energies of Metals

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Abstract

In this work, a model for computing the correlation, binding and cohesive energy of deformed and undeformed metals was developed based on the structureless pseudopotential formalism. Using the developed model, the correlation, binding and cohesive energy of metals were computed and studied. Also, the computed binding and cohesive energy of metals were compared with available experimental values. The results obtained showed that correlation energy increases with increase in electron density parameter. An increase in deformation was found to cause corresponding increase in the correlation energy. The computed binding energy and cohesive energy of metals were in good agreement with experimental values. The results obtained further showed that deformation causes a decrease in the binding energy of metals and it does not cause a significant change in the cohesive energy of metals, although transition metals have high values of cohesive energy compared to alkaline and simple metals.

Keywords: Metals, pseudopotential model,cohesive, binding and correlation energy.

1.Introduction

Solid metals has a crystalline structure, the nuclei of the atoms which constitute a metal are arranged on a space lattice in a regular spatial pattern which repeats itself throughout the volume of the metal. A lump of metal of macroscopic dimensions generally consists of a mass of tiny crystals tightly packed together or has an irregularities in its crystal structure. The mechanical properties of metals depend strongly upon these crystal imperfections. In computing the energy of a metal, the Hamiltonian operator for the system of nuclei and electrons containing the kinetic energy of the electrons, the potential energy of the electrons in the field of the nuclei, the energy due to coulomb interaction of the electron and the potential energy due to the coulomb interaction of the nuclei is set up (Raimes, 1963).

The pseudopotential formalism is a versatile tool used to compute different properties of solids. The pseudopotential theory uses the valence electrons to explain physical properties of atoms, molecules and solids. Usually, an effective potential that is weaker than the true potential between the valence electrons and the atomic core is introduced to avoid complicated all electron problem (Harrison, 1966). Over the years, models based on the pseudopotential formalism have been used to explain different phenomenon in solids. For example, the pseudopotential formalism provides a useful description of binding energy, cohesive energy and surface properties of the simple metal (Perdew et al., 1998).

Vackar et al., (1998), developed an all-electron pseudopotential and used it to calculate lattice constant and bulk modulus of silicon, diamond, cobalt and titanium and the results they got were in good agreement with experimental value. Pseudopotential calculations gave good account of crystal structure, bulk modulus and lattice dynamics of simple metals (Pollack, et al., 1998).

The structureless pseudop[otential formalism evolved from the variational-consistent treatment of the ground state properties of metals (Lang and Kohn, 1971). The structureless pseudopotential formalism requires mechanical stability and neglects the crystal structure of the metals. Its advantages include computational simplicity, physical transparency, require fewer input parameters and can be used with the density functional theory. In the structureless pseudopotential, the input parameters are the valence, the core radius and the electron density parameter. The structureless pseudopotential formalism have been applied in computing different metallic properties (Kiejna, 1993, Osiele and Edema, 2009, Sidl et al., 1998).

The exchange-correlation energy is the correction to the Hartree approximation for the ground-state total energy of a many-electron system. One contribution to this correction is the exchange energy which removes the spurious interaction of an electron with itself and also accounts for the fact that two electrons of the same spin avoid one another due to the Pauli's exclusion principle. The other contribution to this correction is the correlation energy which accounts for the fact that two electrons of opposite or the same spin move within the density to avoid one another because of their mutual coulomb repulsion. In the deformable jellium model, all valence-electron binding electrons to atoms arise from exchange and correlation alone. Two electrons of opposite or the same spin stay apart because of coulomb repulsion, and this effect yields the correlation energy per electron which is smaller in magnitude than exchange energy and has more complicated electron density dependence. The exchange-correlation energy is sometimes called "nature's glue" because it holds material together (Tran and Perdew, 2003).

The cohesive energy is the energy required to dissociate a given mass of solid metal at the absolute zero temperature into free atoms. Cohesive energy is a measure of the strength of the forces which bind the atoms together in the solid state (Raimes, 1963). It arises fro the electronic energy, the electron-electron interaction energy and the interaction between the core and the valence electrons.

In this work, the structureless pseudopotential formalism is extended to the computation of the correlation energy, binding energy and cohesive energy of deformed metals in order to give us an insight into how these different energies of metals vary as a result of the deforming force acting on the metal. The results obtained form the computation for different metals will be compared with the available experimental results. The metals used to test the model were chosen based on the availability of some physical constant that is require for computation and availability of experimental values.

2. Theoretical consideration

For a crystal in the undeformed state, all of its faces are equivalent. It is assumed that deformation is a measureable quantity and a metallic crystal can be considered as assembled from a number of simple crystallites. Qualitatively, the problem can be reduced to the consideration of tension or compression applied to a single crystal.

The average electron density in a metal as a function of deformation is given as;

$$n = n_0\left[1-(1-2\upsilon)u_{xx}\right]+0(u_{xx}^2) \tag{1}$$

where u_{xx} is the uniaxial strain, υ is the poisson ratio relating the transversal compression to elongation in the direction of applied deformation and n_0 is the average electron density in the bulk of undeformed metal given as;

$$n_0 = \frac{3}{4\pi r_s^3} \tag{2}$$

where r_s is the electron density parameter defined as the radius of a sphere containing one electron on average. In the presence of deformation, the spacing between the lattice planes perpendicular to the y and z directions and is expressed as;

$$d_u = d_0(1-\upsilon u_{xx}) \tag{3}$$

where d_0 is the interplanar spacing in an undeformed crystal (Sidl et al., 1998; Kiejna and Pogosov, 1999). Similarly, the corresponding electron density parameter of a deformed metal is

$$r_{su} = r_s\left[1+(1-2\upsilon)u_{xx}\right]^{\frac{1}{3}} \tag{4}$$

In a metal, the average binding energy per valence electron in the bulk based on the structureless pseudopotential approach is

$$\varepsilon = \varepsilon_j\left(n\right)+\varepsilon_m+W_R \tag{5}$$

where the first term in equation (5) is the jellium energy given as

$$\varepsilon_j(n) = \frac{3}{10}k_f^2(n) - \frac{3}{4\pi}k_f(n) + \varepsilon_{cor}(n) \tag{6}$$

This consist of the average kinetic and exchange-correlation energy per electron and k_f is the Fermi momentum expressed as $k_f^3 = 3\pi^2 n$. In equation (5), ε_m is the Madelung energy, W_R is the repulsive part of the Ashcroft core potential and n is the average electron density in the deformed metal. The binding energy per electron can be written as

$$E = t_s + \varepsilon_{xc} + W_R + \varepsilon_m \tag{7}$$

where t_s is the kinetic energy, ε_{xc} is the exchange-correlation energy, Ecorr is the correlation energy, W_R is the repulsive part of the Ashcroft model potential and ε_m is the Madelung energy (Kiejna and Pogosov, 1999). Based on the density functional theory in the low density approximation, the kinetic and exchange of a deformed metal can be written as

$$t_s = \frac{1.105}{r_{su}} \quad \text{and} \quad \varepsilon_x = \frac{-0.458}{r_{su}} \tag{8}$$

where ε_x is the average exchange energy while ε_c is the correlation energy of deformed metal. The correlation energy of deformed metals can be obtained from that of undeformed metals proposed by Carpeley and Alder (1980) and parameterized by Perdew and Zunger (1981) and is obtained (Kiejna and Wojciechowski, 1996) as

$$\varepsilon_c = \frac{-0.1423}{1 + 1.0529 r_{su}^{\frac{1}{2}} + 0.3334 r_{su}} \tag{9}$$

where r_{su} is the electron density parameter of deformed metal. From equation (7) which gives the expression for the binding energy according to the structureless pseudopotential model, the binding energy of deformed metal per electron according to the structureless pseudopotential model is

$$BE = \frac{1.105}{r_{su}^2} - \frac{0.458}{r_{su}} - \frac{0.1423}{1 + 1.0529 r_{su}^{\frac{1}{2}} + 0.3349 r_{su}} + 2\pi n r_c - \frac{9z}{10 r_0} \tag{10}$$

But $r_o = z^{\frac{1}{3}} r_{su}$ and $n = {4\pi r_{su}}/{3}$ where r_c is the Ashcroft core radius, r_{su} is the electron density parameter of deformed metal and z is the valency, hence

$$BE = \frac{1.105}{r_{su}^2} - \frac{0.458}{r_{su}} - \frac{0.1423}{1 + 1.0529 r_{su}^{\frac{1}{2}} + 0.3334 r_{su}} + \frac{3r_c^2}{2r_{su}^3} - \frac{9z^{\frac{2}{3}}}{10 r_{su}} \tag{11}$$

The Ashcroft core radius for deformed metals can be obtained from the bulk stability condition and is given as

$$r_c = \left[-\frac{2}{15}\left(\frac{9\pi}{4}\right)^{\frac{2}{3}} r_{su} + \frac{1}{6\pi}\left(\frac{9\pi}{4}\right)^{\frac{1}{3}} r_{su}^2 + \frac{1}{5} z^{\frac{2}{3}} r_{su}^2 + \frac{2}{9} r_{su}^4 \frac{\partial E_c}{\partial r_{su}} \right]^{\frac{1}{2}} \tag{12}$$

The cohesive energy is the energy required to dissociate a given mass of solid metal at the absolute zero of temperature into free atoms. The total energy of the Fermi gas in atomic unit for a deformed metal is obtained from that of undeformed metals (Eliott, 1997) and is expressed as

$$U_{Fg} = \frac{2.21}{r_{su}^2} - \frac{0.916}{r_{su}} - \left(0.115 - 0.0313 \ln r_{su}\right) \tag{13}$$

The inter-electron repulsion within the cell is

$$U_{WS} = U_{ei} + U_{ee} \tag{14}$$

where U_{ei} is the electron-ion attractive interaction given (Eliott,1997) as

$$U_{ei} = \frac{-3z^2e^2}{8\pi\varepsilon_0 r_{su}}\left[1 - \left(\frac{r_c}{r_{su}}\right)^2\right] \tag{15}$$

and U_{ee} is the electron-electron attractive interaction given as

$$U_{ee} = \frac{3z^2e^2}{20\pi\varepsilon_0 r_{su}} \tag{16}$$

hence

$$U_{WS} = \frac{-3z^2e^2}{8\pi\varepsilon_0 r_{su}} + \frac{3z^2e^2}{20\pi\varepsilon_0 r_{su}} \tag{17}$$

The total expression for the cohesive energy is

$$U_{coh} = zU_{Fg} + U_{WS} \tag{18}$$

where z is valency

In atomic units cohesive energy of deformed metals is obtained as

$$U_{Coh} = z\left[\frac{2.21}{r_{su}^2} - \frac{0.916}{r_{su}} - (0.115 - 0.0313 \ln r_{su})\right] - \frac{3Z^2}{r_{su}}\left[1 - \left(\frac{r_c}{r_{su}}\right)^2\right] + \frac{1.2Z^2}{r_{su}} \tag{19}$$

In this work, the correlation energy, binding energy, cohesive energy of undeformed and deformed metals were computed and studied in order to get an insight into the effect of deformation on the different types of energy of metals.

3. Results and Discussion

Figure 1 shows the variation of the correlation energy with electron density parameter for deformed and undeformed metals. The correlation energy was calculated for some elemental metals consisting of alkaline, alkaline earth, transition and noble metals. The correlation energy computed for the undeformed metals using structureless pseudopotential model varies directly with electron density parameter rs. As shown in the figure, the lower the value of electron density parameter the higher the correlation energy and the higher the value of the electron density parameter the lower the correlation energy. In the low-density limit, we have transition and inner transitions. The results obtained suggest that the correlation energy is high in metals that have high electron concentration as interaction between the electrons is high. For rs > 3.0 a.u, the contribution of correlation energy is smaller to that contributed for rs < 3.0 a.u. The alkaline metals fall within this range of rs. The properties of these metals can be explained with the structureless pseudopotential model. The trend exhibited by the correlation energy depends inversely on electronic concentration of metals.

The variation of the correlation energy with electron gas parameter for deformed and undeformed metals follows the same trend. For the deformed metals, the correlation energy of the metals decreases as deformation increases. The trend exhibited by metals in Figure 1 revealed that the correlation energy of an undeformed metal is the highest, followed by the correlation energy of metals subjected to a deforming force of 0.1dyn, then the correlation energy of metals subjected to a deforming force of 1.0 dyn. The trend exhibited by the metals suggest that the higher the deformation, the higher the inter atomic distance in the metals and this lowers the correlation energy, as the Coulomb correlation effects in the metals and the exchange energy of interaction between the electrons in the metals reduce.

As shown in Figure 2, the binding energy per electron calculated using the structureless pseudopotential model does not show a definite trend with the electron density parameter, rs this may be due to the different valencies of the metals whose binding energies were computed. The model gave negative values of binding energy for some metals in the high density limit ($rs \leq 2$). The binding energy per electron for different metals computed using the structureless pseudopotential model is in good agreement with available experimental values, which shows that the model can be used to predict the binding energy of metals.

The discrepancy between the binding energy per electron according to the structureless pseudopotential model and available experimental values may be due to crystal structures which play an important role in electronic properties of metals. The calculated binding energy per electron according to the structureless pseudopotential model and available experimental values show that transition metals have large values of binding energies per electron. This may be due to additional binding from the inner valence electron shells as a result of large d–electron shells and a contribution from the Van der Waals interaction of the cores (Kittel, 1976). Figure 3 shows the variation of binding energy with deformation for some elemental metals. The figure revealed that the binding energy of metals decreases as deformation increases. The decrease in the binding energy as a result of the applied deforming force may be due to the fact that the applied deformation causes an increase in the separation between the atoms in the metals. Also, the applied strain (or deformation) causes a reduction in the interactions between the electrons in the metals.

Figure 4 shows the variation of computed and experimental cohesive energy of metals with electron gas parameter. In the low density limit $rs \geq 3.0$, the computed cohesive energy is in good agreement with experimental values. The computed cohesive energy is generally lower than experimental values. The agreement between the experimental and computed values of cohesive energy suggest that cohesive energy is a measure of the strength of the forces which bind the atoms in the metal together and the difference between the computed and experimental values may be due to the repulsion between core and valence electrons which may not have been properly accounted for in the model.

The experimental values of the cohesive energy of metals do not vary so much with the electron gas parameter unlike the computed values. As rs increases, the agreement between the experimental values and computed values increases. Furthermore, the trend exhibited by metals in Figure 4 revealed that the cohesive energy of metals in the high density region is higher than at the low density region. In the high density limit, $rs \leq 3.0$ a.u, there is disagreement between calculated and experimental values, although there are some metals in this density region whose cohesive energy agree quite well with experimental values.

Figure 5 shows the variation of cohesive energy with deformation for some elemental metals. As shown in the figure, the cohesive energy decreases with an increase in deformation. The cohesive energy of the transition metals is high while that of the alkaline and simple metals is low. The trend exhibited by different metals in figure 5 revealed that the cohesive energy of metals is greatly influence by deformation. This suggests that the energy required to dissociate a given metal into free atoms depends on the electronic concentration and the crystal strength of the metals.

4. Conclusion

A model based on the structureless pseudopotential formalism was developed and used to investigate the effect of deformation on the energy of metals. The work revealed that the binding energy of metals decreases with increase in deformation, while correlation energy of metals increases with increase in deformation. Deformation does not cause a significant change in the cohesive energy of a metal but the transition metals have high cohesive energy compared to simple and alkaline metals. The results obtained for the binding energy and cohesive energy of metals compares very well with experimental values which indicate that the developed model can be used to predict the different energies of metals and the effect of deformation.

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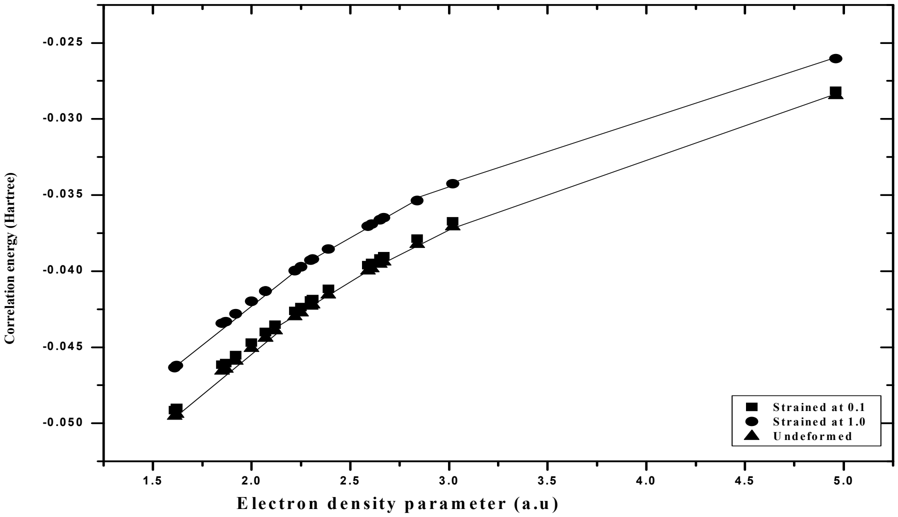

Figure1. Variation of correlation energy with electron gas parameter for deformed and undeformed metals.

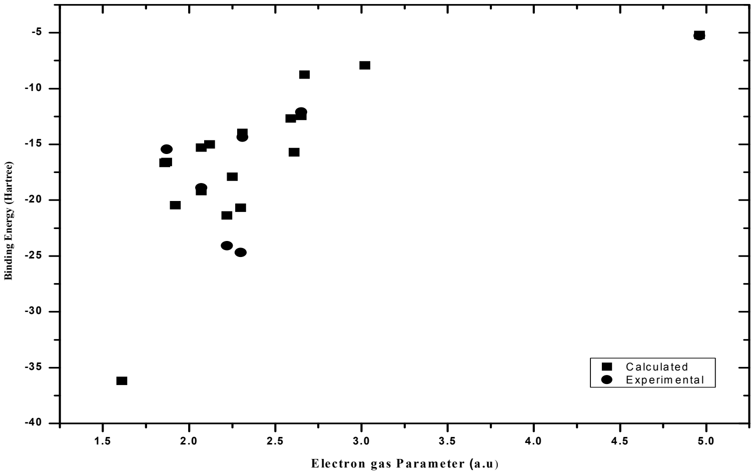

Figure 2. Variation of binding energy with electron gas parameter for some undeformed metals. The experimental values were obtained from Introduction to solid state Physics by Kittel, (1976), Ashcroft and Mermin (1976).

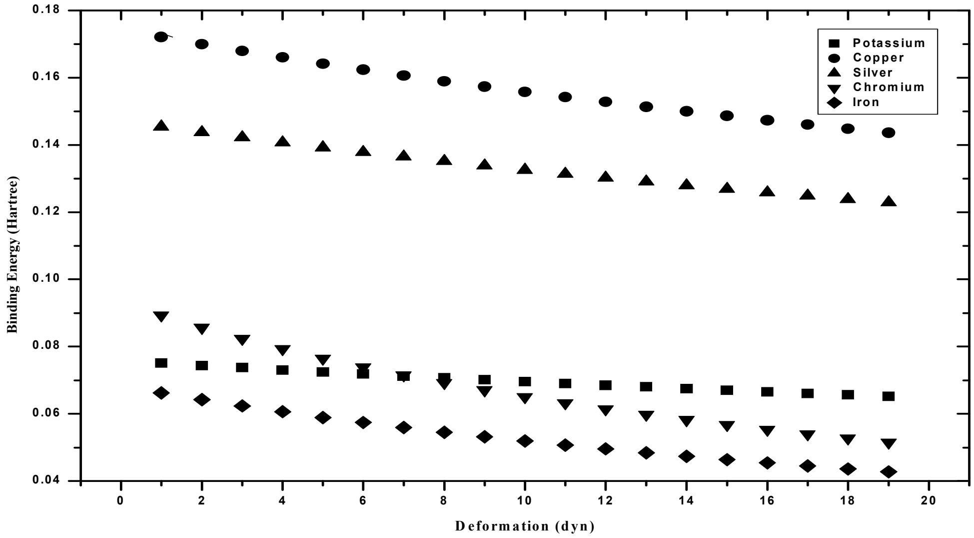

Figure 3. Variation of binding energy with deformation for some metals.

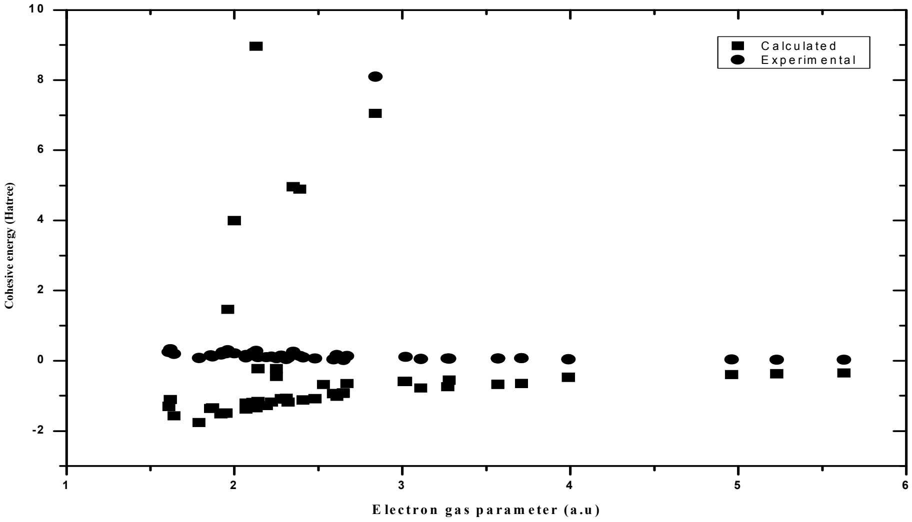

Figure 4. Variation of cohesive energy with electron gas parameter for some metals. The experimental values were obtained from Kittel (1976), Ashcroft and Mermin (1976)

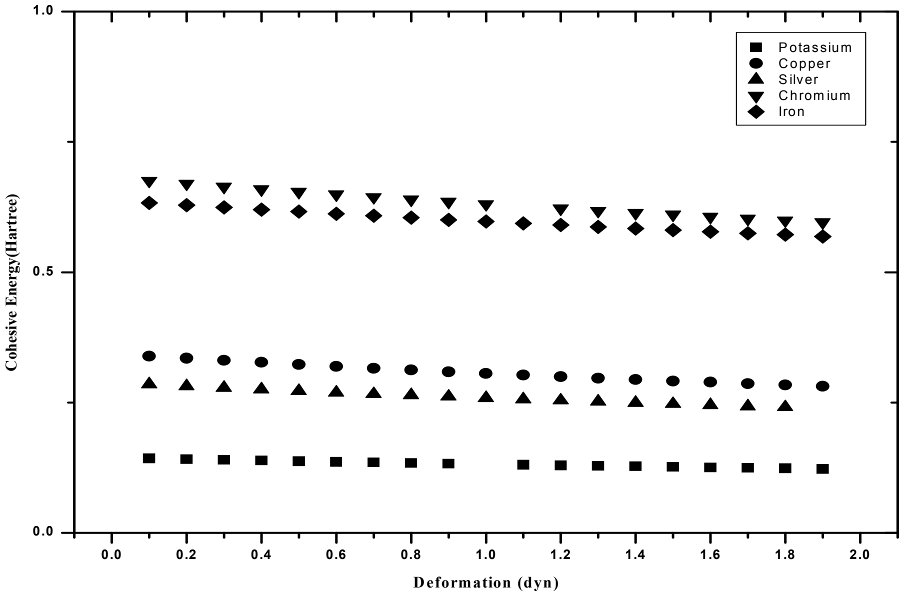

Figure 5. Variation of cohesive energy with deformation for some metals