

# Stability of bcc and fcc structures in alkaline and earth-alkaline elements. Dipolar corrections to metallic bonding potential

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## Abstract

The purpose of this article is to study the dipolar interactions in alkaline and alkaline-earth crystals and to build a model that allows us to predict crystalline structure. The analysis is extended to binary alloys, to propose average behavior of the different coefficients involve in the bonding potential energy.

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## 1 Introduction

In different reference books used in Solid State Physics, metallic bonding unlike ionic and molecular bonding is briefly described [1], and in general it is assumed that metal stability should be properly described under the Bloch-theory of electrons in solids. However, the simple view offered by the isotropic bonding potential is worthy to consider and, in fact, it is useful to describe the stability and properties of binary and multielement systems, including high entropy alloys [2].

Bonding in metals is described, as a first approach, under the average electron cloud model [1], where we only take into account the self-stabilization of a metallic atom understood as composed by a positive core and an average number of conduction electrons released to the electron cloud of the metal. Therefore, two energy terms are considered: the electrostatic attraction between the positive core and the average conduction electrons (attractive term) and the quantum energy due to confinement of the fermionic gas in the Wigner-Seitz (W-S) cell (repulsive term):

$$U_m(d) = -\frac{A}{d} + \frac{B}{d^2} \quad (1.1)$$

Where  $d$  is the distance between near neighbors in the metal and  $A$  and  $B$  are coefficients that can be phenomenologically obtained from the lattice parameter and the bulk modulus [3].

The equilibrium between these two forces will allow us to set an equilibrium distance between the neighbor atoms. In this model, the crystal lattice is not taken into account, only the volume of the W-S cell.

Due to this circumstance, it would be more stable to have a crystal structure that minimizes the repulsive interaction for a fixed distance between neighbors. In fact, open structures would be preferred with respect to denser ones (bcc preferred with respect to fcc) as the attractive term is not seriously affected but the confinement energy would be diminished. Therefore, a contradictory result is observed when using this simple model because many pure metals exhibit compact structures (fcc or hcp).

The dipolar interactions between neutral units (formed by the core metal and the conduction electron in the W-S cell) are needed to explain the presence of such compact structures. First, dipolar forces appear, because the atomic centers of charge of the metallic core and the corresponding conduction electrons do not coincide, and thus, as it occurs in solids of noble gases, we will have a dipolar interaction between an atom and their neighbors. This dipolar force is attractive, following the Lennard-Jones interaction potential:

$$U_{dip}(d) = \varepsilon \left( -f_6 \left( \frac{\sigma}{d} \right)^6 + f_{12} \left( \frac{\sigma}{d} \right)^{12} \right) \quad (1.2)$$

where  $\sigma$  and  $\varepsilon$  are parameters of the potential and  $f_6$  and  $f_{12}$  are coefficients that depend on the lattice structure (For fcc  $f_6=14.45$ ,  $f_{12}=12.13$ ; and for bcc  $f_6=12.25$ ,  $f_{12}=9.11$ ) and, for a constant neighbor distance, favors compact structures. The balance between the self-stabilization of the metallic atom and the dipolar interactions will define the crystalline structure of the system. This work is devoted to understand this phenomenon in the frame of a very simple model.

## 2 Theoretical Model

In order to build the metallic interaction model assuming dipolar interaction we will consider several assumptions:

We will suppose that the atom is decomposed in two parts: an effective core, which will be composed by the nucleus and the inner electrons; and an average (fixed) number of conduction electrons located within the volume of the W-S cell excluding that of the effective core.

We will assume free-electron model for the conduction electrons but constrained to a volume which is the difference between the W-S volume and that of the core.

We will consider a finite size of the effective positive core from which the conduction electrons will be excluded. Therefore, we consider a spherical positive charge formed by  $+Z$  placed at the center of W-S cell and  $-(Z - N)$  electron units where  $Z$  is the atomic number and  $N$  is the number of valence electrons. Moreover, we will neglect the possible dipole character of the core, and we assume that the center of charge of the core electrons is always coincident with that of the positive charge. This approach could be supported by the higher mobility of the free electrons.

The approach that restrict the core electrons to the core volume and the free electrons to the rest of the W-S volume will assure orthogonality between conduction electrons and core electrons waves.

We will admit as an extra simplification that the effective core radius is proportional to the distance to the first neighbor. This will be useful to model how the core radius depends on the size of the atoms. We will define the parameter  $x$ , as the ratio between the effective core radius,  $r_0$ , and the first neighbor distance,  $d$ . As free electrons, the distribution of the valence electrons is supposed to be uniform through the W-S volume excluded the core volume.

With these assumptions we can construct a theoretical description of equation (1.1). The attractive term of  $U_m$  is produced because of a Coulomb force between the core and the valence electrons. As a simplification, we will consider these electrons as a spherical charge of  $N$  electrons placed at the average distance to the center of the W-S cell restricted for free electrons.

The attractive term of  $U_m$  we will use is:

$$U_m^a = -\frac{e^2 N^2}{4\pi\epsilon_0 r_{eff}(d, x)} \quad (2.1)$$

where  $N$  is the number of conduction electrons;  $d$  is the equilibrium distance with its first neighbor;  $r_{eff}(d, x)$  is a function of  $d$  and  $x$  ( $r_0 = xd$ , where  $r_0$  is the effective core radius).  $r_{eff}$  gives us the effective distance from the center of W-S cell of the free electrons, with a uniform distribution of charge. This  $r_{eff}$  depends on the form of the W-S cell and the volume available to the free electrons, and thus depends on the structure.

According to the statistics of fermions, we could estimate the energy of free electrons due to confinement to a volume  $V$ :

$$U_m^r = \frac{3}{5} N \left( 3\pi^2 \frac{N}{V(d, x)} \right)^{\frac{2}{3}} \quad (2.2)$$

Where  $V(d, x)$  is the volume available to the free electrons, which depends on the distance of equilibrium and structure.  $V(d, x)$  has the form:

$$V(d, x) = V_{WS}(d) - \frac{4}{3}\pi x^3 d^3$$

where  $V_{WS}(d)$  is the volume of the W-S cell, which depends on  $d$  and on the structure.

We will add the Lenard-Jones potential to these two terms in order to model dipolar interactions.

Under these assumptions, the potential energy of the metallic bonding we will use can be written as:

$$U(d) = -\frac{e^2 N^2}{4\pi\epsilon_0 r_{eff}(d, x)} + \frac{3}{5} N \left( 3\pi^2 \frac{N}{V(d, x)} \right)^{\frac{2}{3}} + \varepsilon \left( -f_6 \left( \frac{\sigma}{d} \right)^6 + f_{12} \left( \frac{\sigma}{d} \right)^{12} \right) \quad (2.3)$$

## 3 Conditions for the adjustment with experimental results

In the model, we have several parameters to identify a metal: number of conduction electrons per atom,  $N$ , as well as  $\varepsilon$ ,  $\sigma$  and  $x$ . In order to adjust these parameters we will use the following experimental data:

The equilibrium distance, taken from the lattice parameter and the corresponding crystalline structure [3]. For  $d = d_0$ :

$$\left. \frac{\partial U}{\partial d} \right|_{d_0} = 0 \quad (3.1)$$

Bulk Modulus, which we can relate to the second derivative of the potential energy [4].

$$B = V \left. \frac{\partial^2 U}{\partial V^2} \right|_{d_0} \quad (3.2)$$

Coefficient of thermal expansion,  $\alpha$ . Using a Taylor expansion of anharmonic terms of the potential, we can write [5]:

$$\alpha = \frac{-1}{2} \frac{k_B (\partial^3 U / \partial d^3)}{d (\partial^2 U / \partial d^2)^2} \Big|_{d_{eq}} \quad (3.3)$$

## 4 Application of the model

Using the data available in [3], we can adjust the different values for  $x, \varepsilon, \sigma$  for the alkalines and alkaline-earth ( $N = 1$  and  $2$ , respectively), aluminium ( $N = 3$ ) and lead ( $N = 4$ ).

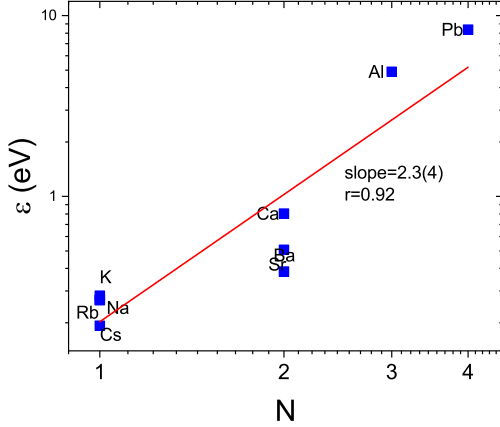


Figure 1: Logarithmic plot of  $\varepsilon$  vs  $N$  for different metals. The red line corresponds to the linear fitting.

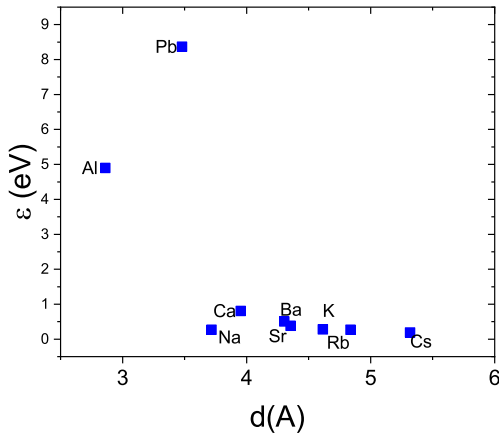


Figure 2:  $\varepsilon$  vs  $d$  for different metals.

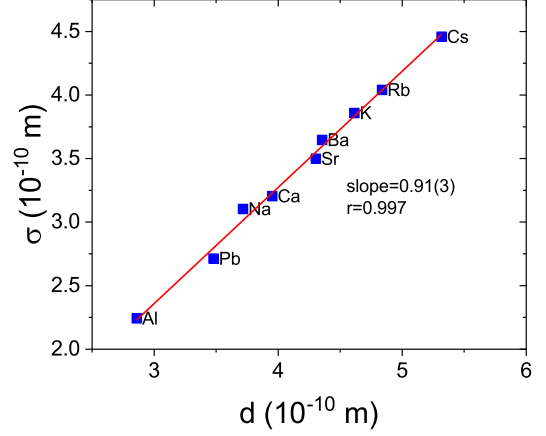


Figure 3:  $\sigma$  vs  $d$  for different metals. The red line corresponds to the linear fitting.

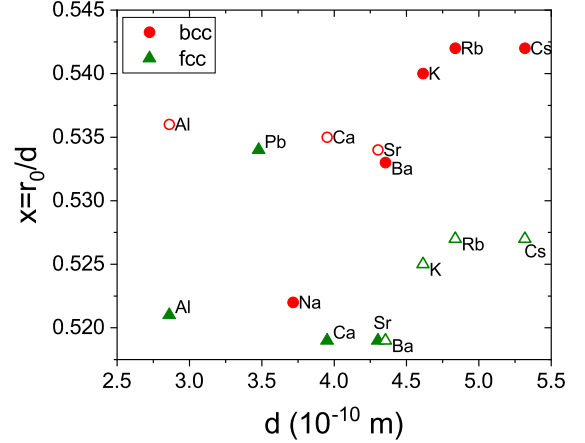


Figure 4:  $x$  vs  $d$  for different metals in their stable structure (solid symbols) and in their unstable structure (hollow symbols).

The parameter  $\varepsilon$  seems to increase with the number of conduction electrons, which makes sense as dipolar effects must be proportional to the product of the dipolar moments (i.e. to the square of the charge of the conduction electrons). In fact representing,  $\varepsilon$  in logarithmic scale shows a slope close to 2 (See figure 1). However, there is not a clear dependence of  $\varepsilon$  with  $d$  (See figure 2). This linearity is better fulfilled for  $\sigma$  (See figure 3).

As we can see, except for Na and Pb, the parameter  $x$  is clearly lower for fcc metals (Ca, Sr and Al) than for bcc ones. It is remarkable the difference in  $x$  between Ba (bcc) and Ca and Sr (fcc), which share similar chemical properties.

## 5 Binary alloys and Stability

In order to study the stability of the different structures, we need to test the model for both structures (stable and unstable) and check whether the energies at the equilibrium favors the presence of the stable structure.

We will suppose that  $\varepsilon$  and  $\sigma$  do not depend on the structure. The change in the structure will affect the parameters  $f_6$  and  $f_{12}$ . The parameter  $x$ , that also depends on the structure, needs to be adjusted for each one.

For this purpose, we will use the transition between fcc and bcc structures in the Ba-Ca binary alloy. We can extend the potential energy proposed to binary alloys using average values of  $\varepsilon$  and  $\sigma$  which will be assumed linear with the fraction of each metal. Using the transition point between the structures (28 at. %, of Ba, according to [6]), we can adjust  $x$  to fit the data to obtain the diagram shown in figure (5).

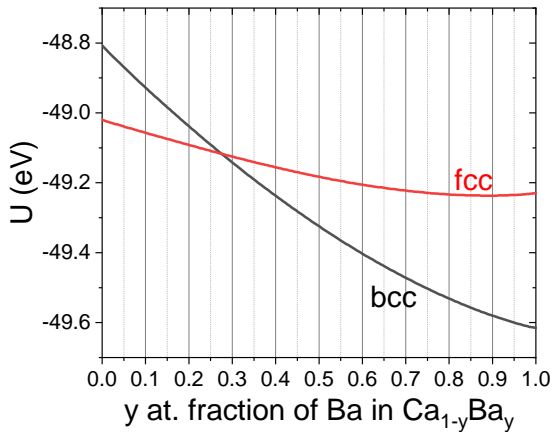


Figure 5: Energies of bcc and fcc structures as a function of the barium content in Ba-Ca binary alloy.

The obtained  $x$  values are collected in table 1, where the difference between bcc and fcc is also collected as  $\Delta x$ .

	$x_{bcc}$	$x_{fcc}$	$\Delta x$
Ba	0.533	0.519	0.0147
Ca	0.535	0.519	0.0155

Table 1: Table of values of  $x$  for Barium and Calcium.

We will use the difference between the structures,  $\Delta x$ , to approximate the value of  $x$  of both stable and unstable structures. For the studied metals we calculate the difference in energy between them,  $U_{bcc} - U_{fcc}$  (See Figure 6):

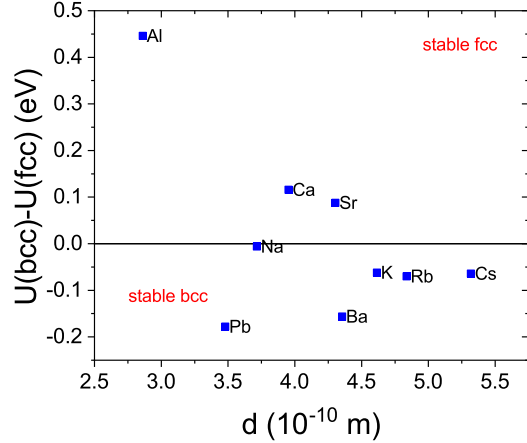


Figure 6: Difference in Energy in equilibrium for the different elements.

Under the frame of the present model we are able to predict the stable crystalline structure for the different studied metals except for Pb. We get that all the alkaline metals crystallize in bcc structures, whereas alkaline-earth have a transition between fcc to bcc structures which depends on the size of the atom.

A note about this model is that the data used to obtain the parameters correspond to room temperature. This limits the capability of the model to predict bcc-fcc transition as a function of temperature. A more complex model could include the temperature dependence of lattice parameter and bulk modulus.

As a perspective for extending this work, we will consider the application of the present model to transition metals and alloys (where the number of conduction electrons and the free electron approximation is not so effective). This will supply a simple frame to predict the microstructure of much complex systems as the high entropy alloys.

## 6 Conclusion

In this study, we have incorporated dipolar interactions to the metallic bonding potential model based on the simple self-stabilization of the metallic atom, which is generally described in reference handbooks of Solid State Physics.

The different parameters involved in the energy potential were obtained phenomenologically by using the lattice parameter, the bulk modulus and the thermal expansion coefficient.

The research reveals that the stability of crystal structures is linked to the balance between attrac-

tive and repulsive forces. By introducing the dipolar interactions into the model, we are able to predict stability of fcc structures in some alkaline-earth metals and binary Ba-Ca systems.

Despite the success of our model in predicting the stability of different structures, it is important to note its limitations. The current model is based on room-temperature data and does not account for temperature-dependent transitions.

Our study has been delimited to the examination of alkaline, alkaline-earth elements, aluminium and lead. The extension to transition metals and alloys would be particularly interesting due to the boost research on high entropy alloys in order to supply a simple way to predict the crystalline structure of more complex systems.

In conclusion, our research provides a simple phenomenological framework for exploring the stability of crystal structures in metallic systems.

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