# Calculation of parameters of Heine and Abarenkov model potential for bcc crystals

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## Abstract

Parameters of Heine and Abarenkov model potential (HAP) have been computed in this paper for sixteen body centered cubic (bcc) closed pack crystals. From the minimization of structure dependent energy of the pure crystal the inter-relation between the two parameters is first determined. Calculation uses pseudopotential technique with nine different exchange and correlation functions (ECF) and either only available experimental value of vacancy formation energy (VFE) or that obtained from an empirical relation based on other experimental parameters (Melting temperature, cohesive energy or activation energy) as tool. The variation of VFE with one parameter of HAP and different ECF show sharp fall in VFE near very small value of it after which it shows constancy for all bcc crystals. Comparison is made with parameter of Ashcroft model also. For increase in valency this parameter of HAP increases and show distinct different curves.

## KEYWORDS

Point defect, vacancy, Heine and Abarenkov model pseudopotential, bcc crystal, exchange and correlation function.

## PACS NUMBERS

61.72, 66.30, 02.70, 65.40, 71.15

## 1. Introduction

Here I shall use a simplified way of pseudopotential approach which is comparatively easier to get some insight into some bcc crystals. This is for recent studies of the mechanism of melting [1-2] by considering the role of surfaces with regard to the concentration and migration of vacancies, provides valuable input for this type of work. Necessity of this work is due to the fact that a database for fcc and hcp crystals was demonstrated using ab initio calculations by Angsten et. al. [3] and seven interatomic potentials were discussed by Li et. al. [4].

The two parameters $(\mathrm{A}, \mathrm{r_c})_{\mathrm{HA}}$ of simple Heine and Abarenkov model pseudopotential (henceforth called HAP) is used for this purpose. The Fourier transform of it is given by [5]

$$\omega(q) = \frac{4\pi A}{\Omega q^3}(q r_c \cos q r_c - \sin q r_c) - \frac{4\pi z e^2}{\Omega q^2} \cos q r_c \qquad (1)$$

Here $z$ is the valency, $\Omega$ the atomic volume, $e$ the electronic charge, and $q$ the wave number. Earlier these two values calculated using fittings to several experimental values of atomic properties, viz. phonon dispersion curves, resistivity, elastic constants, lattice parameter, etc. But here only the experimental value of vacancy formation energy (VFE) will be used for the calculation.

## 2. Results and discussions

The expression for VFE uses pseudopotential method [6-7] and computation uses integration and summation. The integration over quasi-continuous wave numbers $\vec{q}$ uses Gauss-

Legendre quadrature method within the limit from 0 to 1 in 100 divisions and Gauss-Laguerre quadrature integration in the limit from 1 to infinity [8].

$$\int_0^\infty \rightarrow \int_0^1 \mathrm{Gauss-Lagendre} + \int_1^\infty \mathrm{Gauss-Laguerre} \qquad -(2)$$

The discrete sum over lattice wave numbers defined as $\vec{q}_0 = \frac{m_1}{N_1} q_1 + \frac{m_2}{N_2} \vec{q}_2 + \frac{m_3}{N_3} \vec{q}_3$ where the maximum value of $\frac{m_i}{N_i} = 14$ with i=1,2,3 and the lattice wave numbers are generated in the cubic Brillouin zone with the reciprocal lattice vectors respectively as $\vec{q}_1 = \frac{2\pi}{a}(\hat{j} + \hat{k})$, $\vec{q}_2 = \frac{2\pi}{a}(\hat{k} + \hat{\imath})$ and $\vec{q}_3 = \frac{2\pi}{a}(\hat{\imath} + \hat{j})$, $(\hat{\imath}, \hat{j}, \hat{k})$ being unit vectors along three coordinates. The input parameters used in this calculation are lattice constant a and experimental or theoretical mean value of VFE. The necessity of $(\mathrm{VFE})_{\mathrm{theo}}$ is due to the fact that in most of the cases the experimental value of VFE is not available and so $(\mathrm{VFE})_{\mathrm{theo}}$ is determined from an empirical relation among the melting temperature ($T_m$), the cohesive energy ($E_{coh}$) and the activation energy for self diffusion ($Q_0$) .

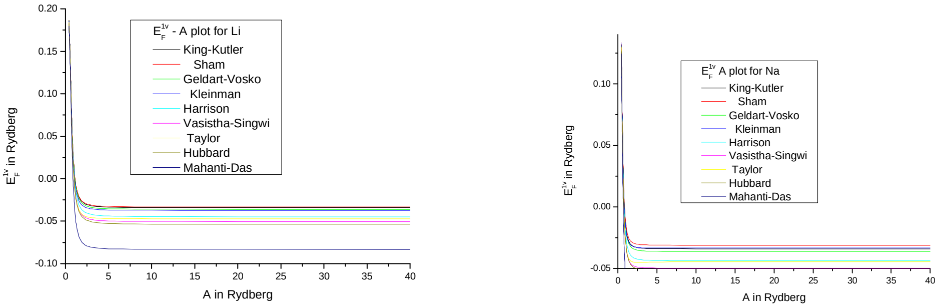

Figure 1 : $E_F^{1v} - A$ plot for Lithium (Li) and Sodium (Na) type bcc metals

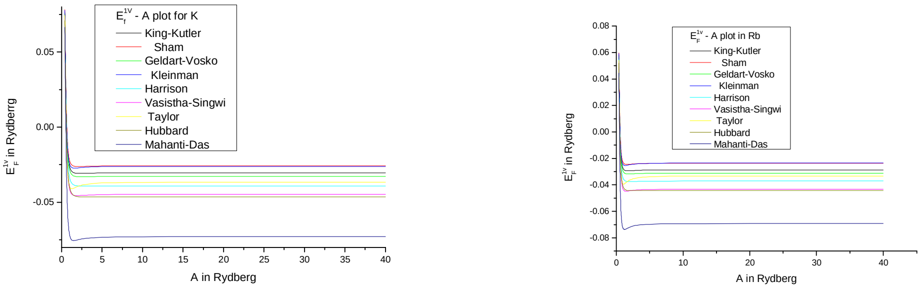

Figure 2 : $E_F^{1v} - A$ plot for Potassium (K) and Rubidium (Rb) type bcc metals

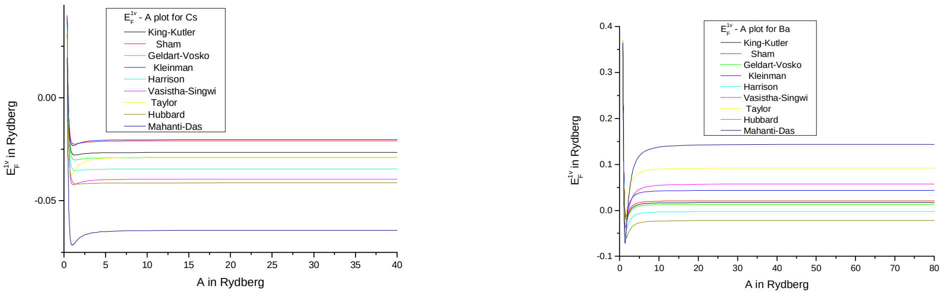

Figure 3 : $E_F^{1v} - A$ plot for Cesium (Cs) and Barium (Ba) type bcc metals

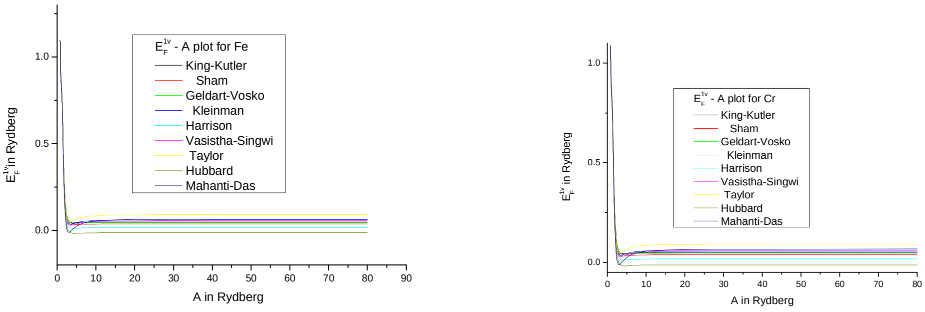

Figure 4 : $E_F^{1v} - A$ plot for Iron (Fe) and Chromium (Cr) type bcc metals

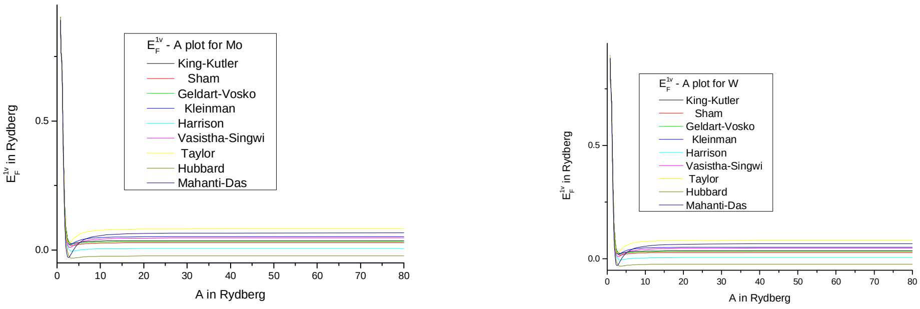

Figure 5 : $E_F^{1v} - A$ plot for Molybdenum (Mo) and Tungsten (W) type bcc metals

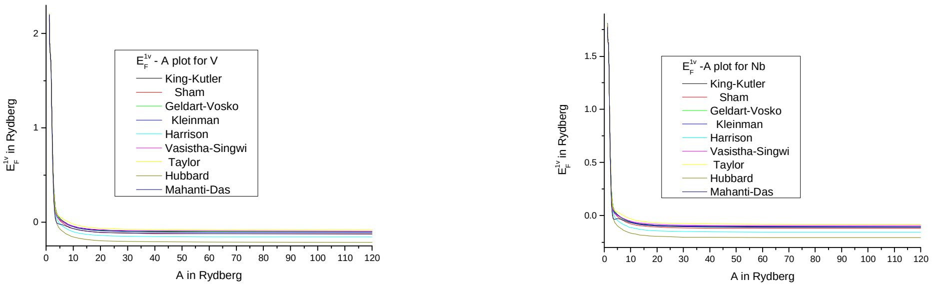

Figure 6 : $E_F^{1v} - A$ plot for Vanadium (V) and Niobium (Nb) type bcc metals

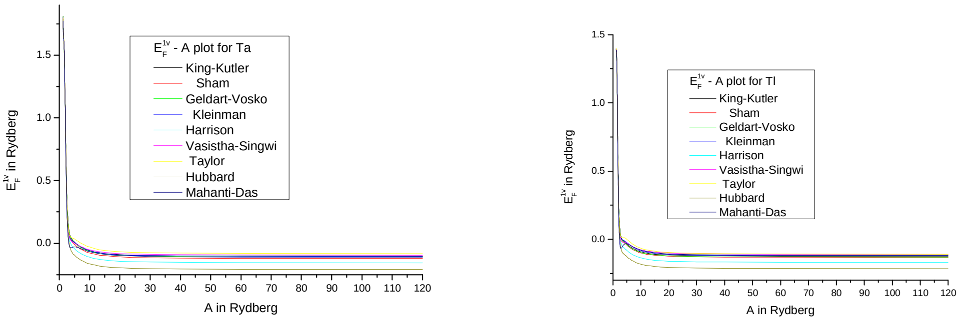

Figure 7 : $E_F^{1v} - A$ plot for Tantalum (Ta) and Thallium (Tl) type bcc metals

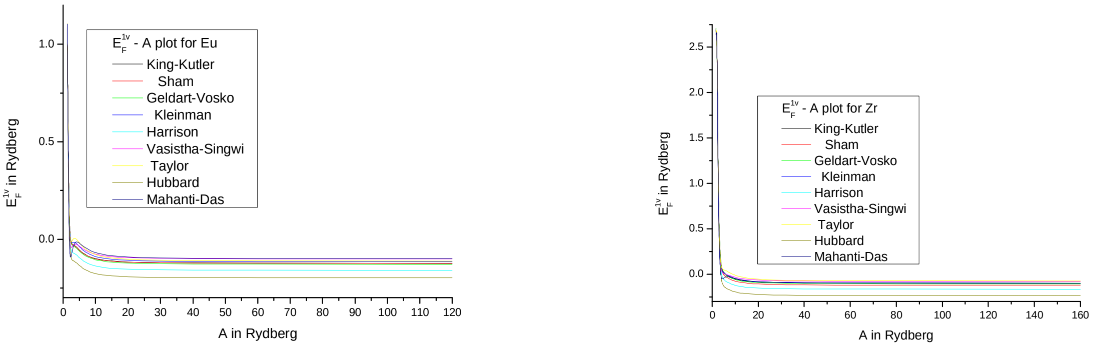

Figure 8 : $E_F^{1v} - A$ plot for Europium (Eu) and Zirconium (Zr) type bcc metals

**Table 1**

Input parameters [1 Rydberg = 13.605 eV] and [1 Atomic Unit (AU) = 0.0529177 nm]

| Metal | Atomic number | Configuration | Valency | Lattice Constant (nm)[a] | Vasistha-Singwi parameters in au | | $T_m$ (K)[a] | $E_{coh}$ (eV)[a] | $Q_0$ (eV)[b] | $(VFE)_{exp}$ (eV) | $(VFE)_{theo}$ theoretical range in (eV) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | 3 | He2s$^{1}$ | 1 | 0.3491 | 1.00529 | 0.29979 | 453.7 | 1.63 | 0.55<br>0.585 | 0.34[c] 0.4[c] 0.48[c] | 0.302-0.489 |
| Na | 11 | Ne3s$^{1}$ | 1 | 0.4225 | 1.07771 | 0.2846 | 371 | 1.113 | 0.499<br>0.438 | 0.36[c] 0.39[c] 0.42[c]<br>0.35[d] | 0.24-0.334 |
| K | 19 | Ar4s$^{1}$ | 1 | 0.5225 | 1.16737 | 0.26925 | 336.3 | 0.934 | 0.418<br>0.409 | 0.39[c] 0.3[c] 0.31[d] | 0.23-0.28 |
| Rb | 37 | Kr5s$^{1}$ | 1 | 0.5585 | 1.19566 | 0.26981 | 312.6 | 0.852 | 0.408<br>0.409 | 0.27[c,d] | 0.224-0.261 |
| Cs | 55 | Xe6s$^{1}$ | 1 | 0.6045 | 1.23419 | 0.2605 | 301.6 | 0.804 | 3.998 | 0.28[c] 0.26[d] | 0.241-2.199 |
| Ba | 56 | Xe6s$^{2}$ | 2 | 0.502 | 1.14962 | 0.27321 | 1002 | 1.9 | | | 0.57-0.835 |
| Fe | 26 | Ar3d$^{6}$4s$^{2}$ | 2 | 0.287 | 0.93847 | 0.31221 | 1811 | 4.28 | 2.658<br>2.488 | 1.6[e] | 1.284-1.509 |
| Cr | 24 | Ar3d$^{4}$4s$^{2}$ | 2 | 0.288 | 0.93937 | 0.31294 | 2133 | 4.1 | 3.196<br>4.572 | 2.0[f] 2.27[f] 2.08[f] | 1.23-2.51 |
| Mo | 42 | Kr4d$^{5}$5s$^{1}$ | 2 | 0.315 | 0.97098 | 0.30512 | 2895 | 6.82 | 3.998<br>3.997 | 2.24[d] 3.0[f] 3.2[f] | 2.046-2.413 |
| W | 74 | Xe4f$^{14}$5d$^{2}$6s$^{2}$ | 2 | 0.316 | 0.9713 | 0.30548 | 3695 | 8.9 | 6.076 | 3.15[d] 4.0[f]<br>4.1[f] 3.6-4.0[f] | 2.670-3.34 |
| V | 23 | Ar3d$^{3}$4s$^{2}$ | 3 | 0.303 | 0.95586 | 0.30939 | 2202 | 5.31 | 4.58<br>4.083 | 2.2[f] | 1.593-2.519 |
| Nb | 41 | Kr4d$^{4}$5s$^{1}$ | 3 | 0.33 | 0.98576 | 0.30406 | 2750 | 7.57 | 4.163<br>4.164 | 2.04[d] 2.6[f]<br>2.7-3.0[f] | 2.271-2.292 |
| Ta | 73 | Xe4f$^{14}$5d$^{2}$6s$^{2}$ | 3 | 0.33 | 0.98576 | 0.30406 | 3293 | 8.1 | 4.28<br>4.281 | 2.9[d] 2.8[f]<br>2.9[f] 3.1[f] | 2.354-2.744 |
| Tl | 81 | Xe4f$^{14}$5d$^{2}$6s$^{2}$ | 3 | 0.387 | 1.04372 | 0.29327 | 577 | 1.88 | 6.639 | | 0.48-3.651 |
| Eu | 63 | Xe4f$^{7}$5d$^{0}$6s$^{2}$ | 3 | 0.458 | 1.11056 | 0.28079 | 1091 | 1.86 | 1.489 | | 0.558-0.909 |
| Zr | 40 | Kr4d$^{2}$5s$^{2}$ | 4 | 0.361 | 1.01502 | 0.29717 | 2128 | 6.25 | 0.85<br>0.88 | 1.75[d] | 0.468-1.875 |

[a] Ref. [10]; [b] Ref. [11]; [c] Ref. [12]; [d] Ref. [1]; [e] Ref. [13]; [f] Ref. [14].

In the first step, the two parameters $(\mathrm{A}, \mathrm{r_c})_{\mathrm{HA}}$ of HAP suggest a minimization of structure dependent energy of the pure crystal and yield a relation $\mathrm{A} = \frac{\mathrm{ze^2}}{\mathrm{r_c}}$. The value of VFE is computed for different values of parameter A of HAP and it is now plotted for nine ECFs [9] for sixteen different body centered cubic (bcc) closed pack crystals, viz. lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), barium (Ba), iron (Fe), chromium (Cr), molybdenum (Mo), tungsten (W), vanadium (V), niobium (Nb), tantalum (Ta), thallium (Tl), europium (Eu) and zirconium (Zr). There is a sharp fall in VFE near very small value of A in the VFE-A plot and with increase in A VFE shows constancy for all bcc crystals as shown in figure 1 to figure 8.

The value of A and hence $\mathrm{r_c}$ are determined from fitting to all the experimental values of $(\mathrm{VFE})_{\mathrm{exp}}$ or theoretical mean value of $(\mathrm{VFE})_{\mathrm{theo}}$. Thus a plot of VFE-$\mathrm{r_c}$ with fixed value of A will be expected to show definite convergence. The theoretical estimation using an empirical relation [8] is also very close to ab initio calculations by Angsten et. al. [3]. This is shown in the table 1. However there is a systematic change in the fitted value of A for every bcc metal from one ECF to other so also there is a change in the value of $\mathrm{r_c}$ from one ECF to other.

**Table 2**
Input parameters [1 Rydberg = 13.605 eV] and [1 Atomic Unit (AU) = 0.0529177 nm]

| Metal | $\Delta A$ for different ECF in eV | $\Delta \mathrm{r_c}$ for different ECF in nm | Ashcroft $(\mathrm{r_c})_{\mathrm{Ash}}$ (nm) | | Heine-Abarenkov $(A, r_c)_{\mathrm{HA}}$ parameters | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $(\mathrm{r_c})_{\mathrm{Ash}}{}^{a}$ | Mean $(\mathrm{r_c})_{\mathrm{Ash}}{}^{b}$ | Mean $(\mathrm{r_c})_{\mathrm{HA}}$ nm | Other $(\mathrm{r_c})_{\mathrm{HA}}$ | Mean $(A)_{\mathrm{HA}}$ eV | Other $(A)_{\mathrm{HA}}$ eV |
| Li | 2.03 | 0.023 | 0.06-0.11 | 0.071$^{b}$ | 0.1248 | | 11.5626 | |
| Na | 1.10 | 0.022 | 0.09 | 0.090$^{b}$ | 0.1616 | | 8.9245 | |
| K | 0.68 | 0.022 | 0.12 | 0.117$^{b}$ | 0.2135 | | 6.7499 | |
| Rb | 0.81 | 0.029 | 0.11-0.14 | 0.126$^{b}$ | 0.2215 | | 6.5085 | |
| Cs | 0.68 | 0.030 | 0.11-0.16 | 0.157$^{b}$ | 0.2469 | | 5.8383 | |
| Ba | 0.83 | 0.007 | | 0.124$^{b}$ | 0.2055 | | 14.0172 | |
| Fe | 3.80 | 0.006 | | 0.061$^{c}$ | 0.0959 | | 30.0761 | |
| Cr | 3.06 | 0.016 | | 0.063$^{d}$ | 0.1022 | 0.13$^{e}$ | 28.2060 | 21.77$^{e}$ |
| Mo | 1.67 | 0.005 | | 0.074$^{d}$ | 0.1265 | 0.11$^{e}$ | 22.7786 | 31.29$^{e}$ |
| W | 0.89 | 0.003 | | 0.077$^{d}$ | 0.1337 | 0.11$^{e}$ | 21.5442 | 31.29$^{e}$ |
| V | 6.02 | 0.005 | | 0.068$^{d}$ | 0.0980 | 0.08$^{e}$ | 44.1535 | 44.22$^{e}$ |
| Nb | 4.36 | 0.005 | | 0.079$^{d}$ | 0.1168 | 0.11$^{e}$ | 37.0047 | 23.13$^{e}$ |
| Ta | 3.76 | 0.004 | | 0.079$^{d}$ | 0.1182 | 0.11$^{e}$ | 36.5779 | 23.81$^{e}$ |
| Tl | 1.56 | 0.003 | | 0.096$^{d}$ | 0.1550 | | 27.8773 | |
| Eu | 2.27 | 0.005 | | 0.118$^{d}$ | 0.1713 | | 25.2297 | |
| Zr | 5.49 | 0.004 | | 0.081$^{d}$ | 0.1216 | | 47.4232 | |

[a]Ref. [15]; [b]Ref. [16]; [c]Ref. [13]; [d]Ref. [14]; [e]Ref. [17].

Since the difference is about 10% so the variation of HAP parameters A and $\mathrm{r_c}$ for all nine ECFs are not shown but only their mean value A and $\mathrm{r_c}$, and the difference (ΔA) and $\Delta\mathrm{r_c}$ are shown in table 2 along with AP for comparison together with other calculated values. The graph between A and $\mathrm{r_c}$ is obviously four different rectangular hyperbolae for four valency values.

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