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A new look towards the determination of parameters of Heine and Abarenkov model potential using only vacancy formation energy in fcc crystals

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Abstract

The Heine and Abarenkov model potential (HAP) parameters (r_c, A) have been calculated in this paper for twenty face-centered cubic (fcc) closed pack crystals. From the minimization of the structure dependent energy of the pure crystal the inter-relation between the two parameters of HAP has been initially determined. The calculation uses pseudopotential technique with nine different exchange correlation functions (ECF), either the available experimental value of the vacancy formation energy (E_F^{1v}) or that obtained from an empirical relation based on other experimental parameters (melting temperature, cohesive energy or activation energy) as tool. The variation of E_F^{1v} with the parameter A of HAP and ECF shows a sharp fall in E_F^{1v} near a very small value of A after which it shows constancy for all fcc crystals, and the parameters (r_c, A) are determined near the bend. Comparison is made with other calculations and parameters of the Ashcroft model also. For increase in valency the parameter A of HAP increases and shows distinctly different curves.

Keywords

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

1. Introduction

In this paper the pseudopotential technique [1] has been utilized for the calculation of HAP parameters (r_c, A) although there are modern sophisticated techniques (ab initio, dft, molecular dynamics, Monte-Carlo, etc.). Pseudopotential method does not require rigorous computation and was tested earlier several times [2-12]. In this method, the change in the structure-dependent total energy of the lattice after and before the defect creation will give the defect formation energy. Model pseudopotential is necessary for this purpose. Heine and Abarenkov model potential (henceforth called HAP) [13-14] is used here and its parameters are calculated using only monovacancy formation energy E_F^{1v}.

2. Theory

The monovacancy formation energy (E_F^{1v}) in the pseudopotential approach of Harrison is given by [15-17] $E_F^{1v} = \sum'_{q_0} \frac{q_0}{3} \frac{\partial U(q_0)}{\partial q_0} + \frac{\Omega}{2\pi^2} \int_0^\infty U(q)\, q^2 dq$ - (1)

$$U(q) = \lim_{\eta \to \infty} \frac{2\pi z^2 e^2}{\Omega q^2} e^{-\frac{q^2}{4\eta}} + w^2(q)\varepsilon(q)\chi(q) \quad - (2)$$

Here e is the electronic charge, η the convergence factor, z the valency, Ω the atomic volume, q_0 the lattice wave number, q the quasi-continuous wave number, $\varepsilon(q)$ the dielectric function and $\chi(q)$ the perturbation characteristics defined earlier several times [16,17]. The term $w(q)$ contains the simplest form of the Fourier transform of HAP which is written as

$$w(q) = \frac{4\pi A}{\Omega q^3}[q r_c \cos q r_c - \sin q r_c] - \frac{4\pi z e^2}{\Omega q^2} \cos q r_c \quad - (3)$$

The values of its parameters (r_c, A) have been calculated earlier from the fittings to several experimental values of atomic properties, viz. phonon dispersion curves, resistivity, elastic constants, lattice parameter, etc. But here a unique and new process is developed where only the experimental value of the vacancy formation energy $(E_F^{1v})_{expt}$ or the theoretical mean value of $(E_F^{1v})_{theo}$ will be used for the calculation of these two parameters. The necessity of $(E_F^{1v})_{theo}$ is due to the fact that an experimental value of E_F^{1v} is not available in all cases.

3. Procedure

Computation has been done by integration over quasi-continuous wave numbers $\vec{q}$ using Gauss-Legendre quadrature integration within the limit from 0 to 1 in 100 divisions and Gauss-Laguerre quadrature integration in the limit from 1 to infinity as follows

$$\int_0^\infty \to \int_0^1 Gauss - Lagendre + \int_1^\infty Gauss - Laguerre \quad - (4)$$

Computation also has a discrete sum over lattice wave numbers $\vec{q}_0$ with primitive and reciprocal lattice vectors being defined, respectively, as

$$\vec{q}_1 = \frac{2\pi}{a}(-\hat{\imath} + \hat{\jmath} + \hat{k}) \qquad \vec{q}_2 = \frac{2\pi}{a}(\hat{\imath} - \hat{\jmath} + \hat{k}) \qquad \vec{q}_3 = \frac{2\pi}{a}(\hat{\imath} + \hat{\jmath} - \hat{k}) \quad - (5)$$

With $\vec{q}_0 = \frac{m_1}{N_1}\vec{q}_1 + \frac{m_2}{N_2}\vec{q}_2 + \frac{m_3}{N_3}\vec{q}_3$ - (6)

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. Here a is the lattice constant of the fcc crystal. In the first step, the two parameters (r_c, A) of HAP suggest a minimization of the structure dependent energy of the pure crystal and yield the relation $A = ze^2/r_c$ - (7)

The value of E_F^{1v} in Ryd (1 *Rydberg* = 13.605 *eV*) of equation (1) is computed using equation (7) for different values of parameter A of HAP [1 *Atomic Unit (AU)* = 0.0529177 *nm*] and the corresponding value of parameter r_c of HAP is calculated. The variation of E_F^{1v} with the parameter A is now plotted for nine different exchange and correlation functions (ECF) [17] for twenty different face-centered cubic (fcc) closed pack crystals, viz. (1) Aluminium (Al), (2) Calcium (Ca), (3) Scandium (Sc), (4) Iron (Fe), (5) Cobalt (Co), (6) Nickel (Ni), (7) Copper (Cu), (8) Strontium (Sr), (9) Rhodium (Rh), (10) Paladium (Pd), (11) Silver (Ag), (12) Lanthanum (La), (13) Cerium (Ce), (14) Prasudomium (Pr), (15) Ytterbium (Yb), (16) Iridium (Ir), (17) Platinum (Pt), (18) Gold (Au), (19) Lead (Pb) and (20) Thorium (Th) (arranged according to increasing atomic number).

4. Results and discussions

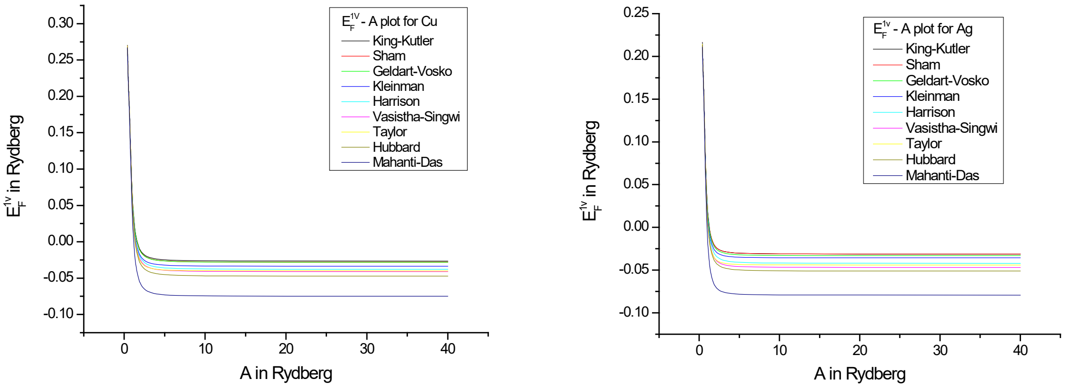

Figure 1 : $E_F^{1v} - A$ plot for copper (Cu) and silver (Ag)

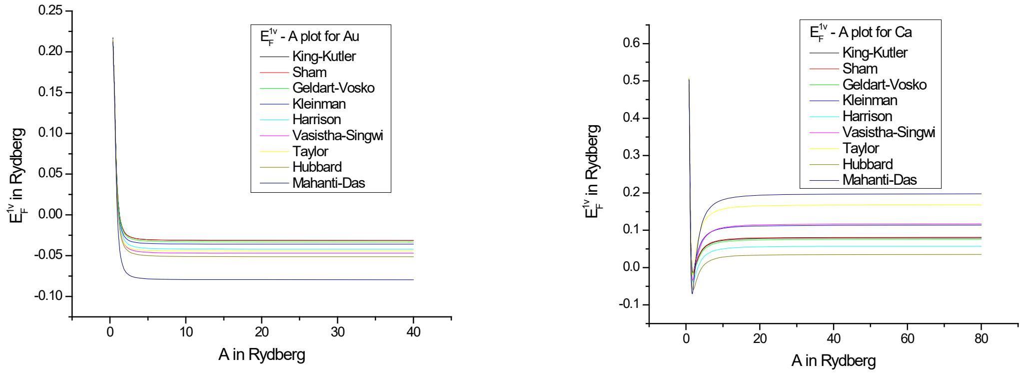

Figure 2 : $E_F^{1v} - A$ plot for gold (Au) and calcium (Ca)

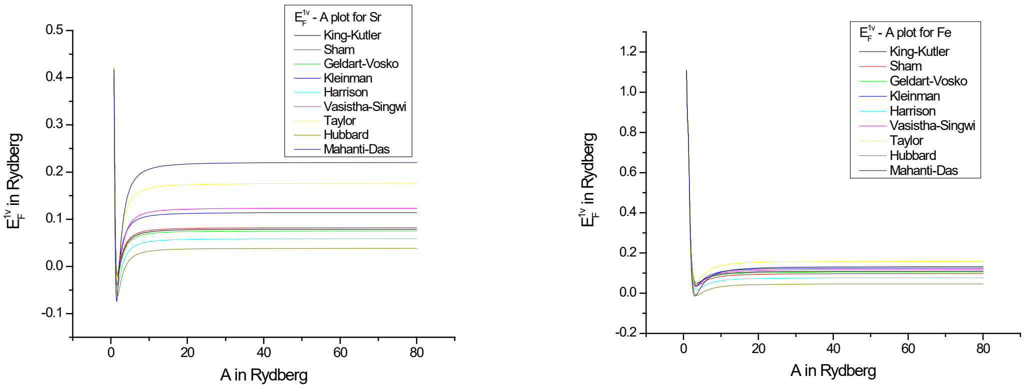

Figure 3 : $E_F^{1v} - A$ plot for strontium (Sr) and γ-iron (γ-Fe)

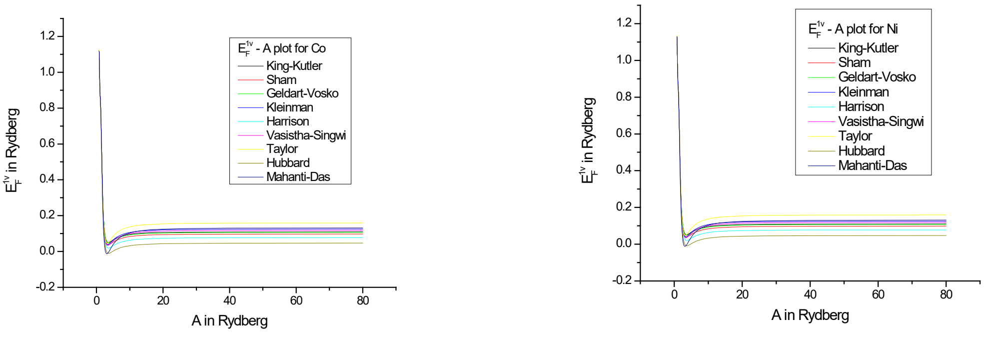

Figure 4 : $E_F^{1v} - A$ plot for β-cobalt (β-Co) and nickel (Ni)

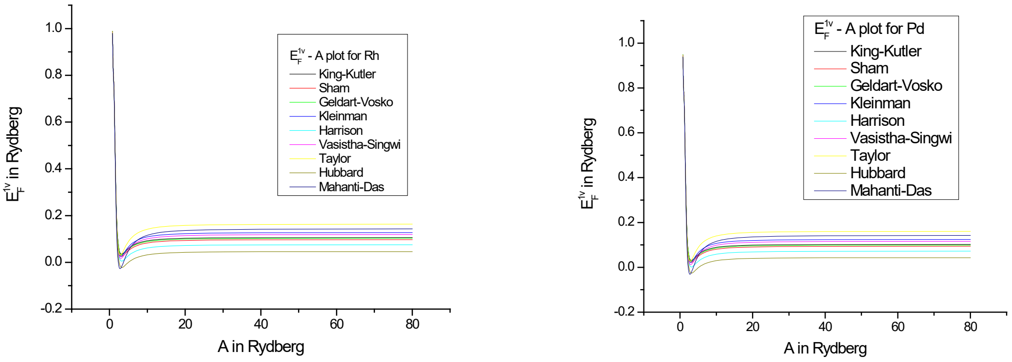

Figure 5 : $E_F^{1v} - A$ plot for rhodium (Rh) and paladium (Pd)

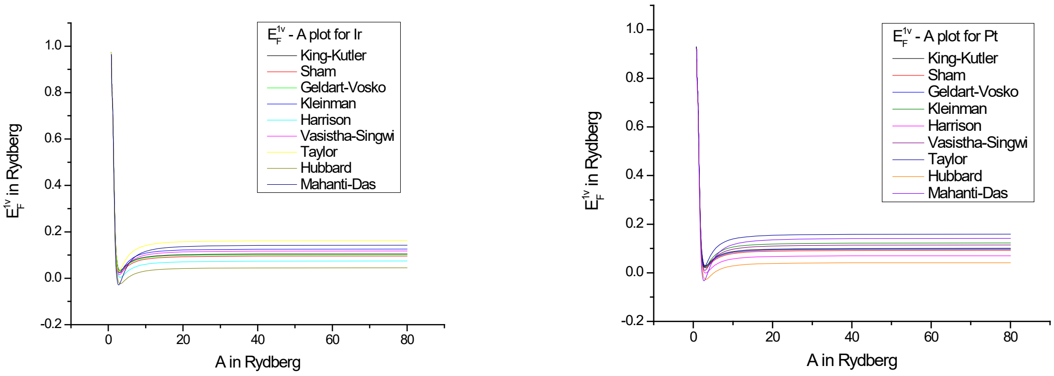

Figure 6 : $E_F^{1v} - A$ plot for iridium (Ir) and platinum (Pt)

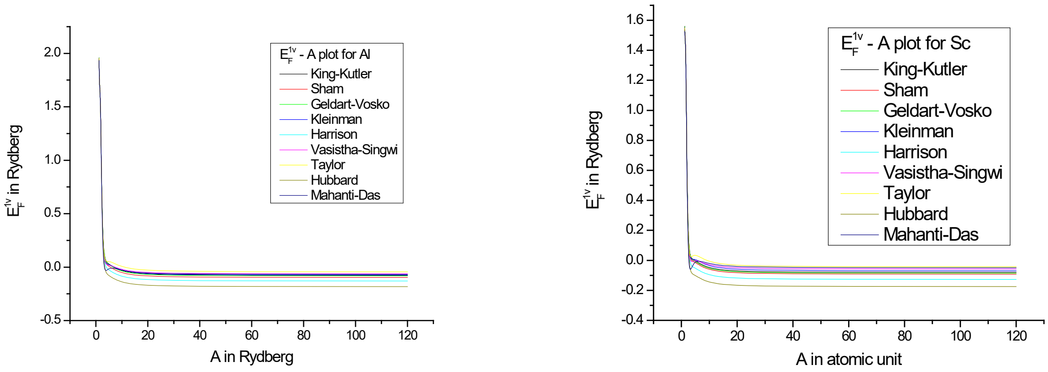

Figure 7 : $E_F^{1v} - A$ plot for aluminium (Al) and scirmium (Sc)

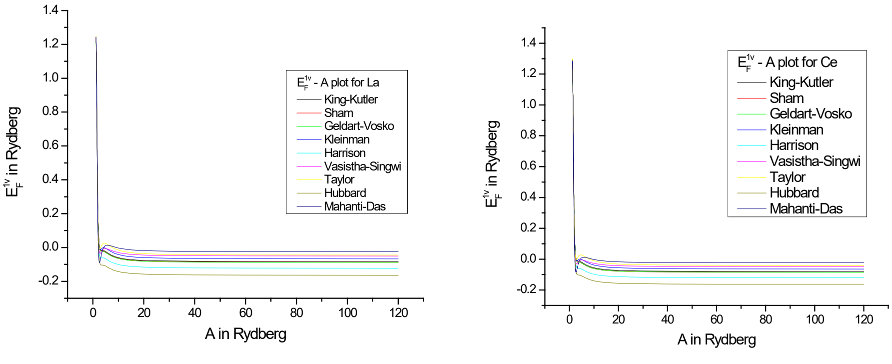

Figure 8 : $E_F^{1v} - A$ plot for and lanthanum (La) and cerium (Ce)

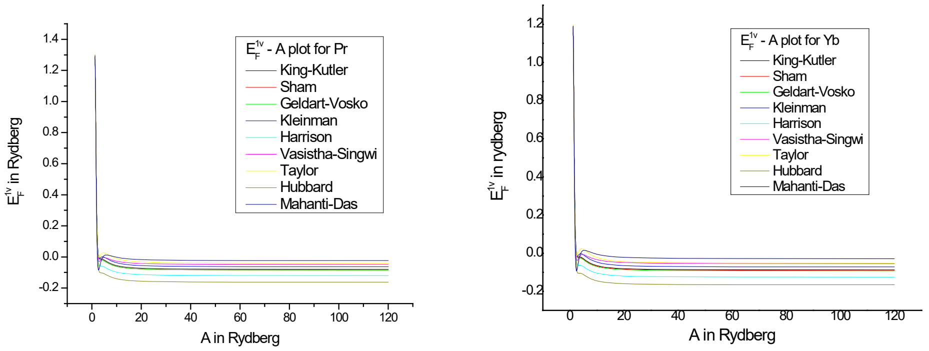

Figure 9 : $E_F^{1v} - A$ plot for praseodymium (Pr) and ytterbium (Yb)

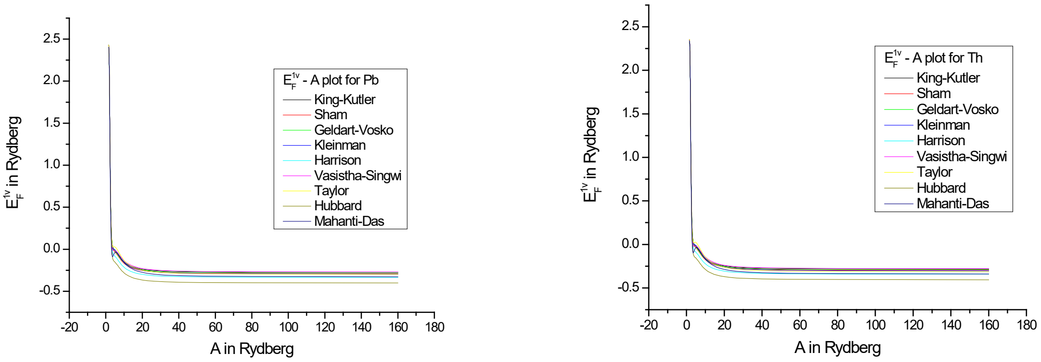

Figure 10 : $E_F^{1v} - A$ plot for lead (Pb) and thorium (Th)

There is a sharp fall in E_F^{1v} near very a small value of A in the $E_F^{1v} - A$ plot and with increase in A, E_F^{1v} shows constancy for all fcc crystals as shown in figure 1 to figure 10. The values of A and hence r_c are determined from fitting to all the experimental values of $(E_F^{1v})_{expt}$ or the theoretical mean value of $(E_F^{1v})_{theo}$ near this bend. The necessity of $(E_F^{1v})_{theo}$ is due to the fact that in most of the cases the experimental value of E_F^{1v} is not available and so $(E_F^{1v})_{theo}$ is determined from an empirical relation between the melting temperature (T_m), the cohesive energy (E_{coh}) and the activation energy for self diffusion (Q_0) [17]. Thus a plot of $E_F^{1v} - r_c$ with fixed value of A shows definite convergence. The theoretical estimation using the empirical relation is also very close to *ab initio* calculations by Angsten et. al. [18]. This is shown in the table 1.

Table 1

Vacancy formation energy $(E_F^{1v})_{expt}$ and Heine-Abarenkov parameters $(A, r_c)_{HA}$.

fcc crystal	$(E_F^{1v})_{expt}$ in eV	Range of $(E_F^{1v})_{theo}$ in e	Ashcroft $(r_c)_{Ash}$ in nm		Heine-Abarenkov $(A, r_c)_{HA}$ parameters			
			$(r_c)_{Ash}$[a]	$(r_c)_{Ash}$	$(r_c)_{HA}$ (nm)	Other $(r_c)_{HA}$ (nm)	$(A)_{HA}$ (eV)	Other $(A)_{HA}$ (eV)
Cu	1.13[a] 1.19[a] 1.282[a] 1.17[b]	1.047-1.13[c] 1.07[d]	0.0659 0.0667 0.068	0.065[e] 0.043[e] 0.093[f]	0.1161 0.1180 0.1207	0.066[g] 0.1274[h]	12.4053 12.2084 11.9318	26.536[g] 11.303[h]

Ag	1.02[a] 1.11[a] 1.01[b]	0.885-1.057[c] 0.68[d]	0.0764 0.0779	0.076[e] 0.055[e] 0.099[f]	0.1353 0.1386	0.079[g] 0.1437[h]	10.6492 10.3923	18.088[g] 10.019[h]
Au	0.89[a] 0.90[a] 0.93[a] 1.01[b]	0.994-1.143[c] 0.40[d]	0.074 0.0739 0.0746	0.075[e] 0.043[e] 0.108[f]	0.1304 0.1301 0.1315	0.084[g] 0.1437[h]	11.0467 11.0777 10.9528	11.886[g] 10.021[h]
Ca	1.10	0.552-0.926[c] 1.13[d]	0.1013		0.1680		17.1502	
Sr		0.516-0.868[c] 0.95[d]	0.1089		0.1787		16.1294	
Fe	1.40	1.284-1.619[c] 2.32[d]	0.0555		0.0906		31.8296	
Co	1.34	1.317-1.526[c] 1.84[d]	0.0546		0.0889		32.4434	
Ni	1.45[a] 1.55[a] 1.78[a] 1.79[a] 1.40[b]	1.332-1.603[c] 1.39[d]	0.0548 0.0554 0.0608 0.0567		0.0895 0.0908 0.0934 0.0935		32.2191 31.7642 30.8561 30.8256	
Rh		1.517-1.866[c] 1.57[d]	0.0631		0.1024		28.1652	
Pd	1.54, 1.7, 1.85	1.167-1.521[c] 1.16[d]	0.0642 0.0651 0.0659		0.1061 0.1079 0.1098		27.1754 26.7039 26.2370	
Ir		2.082-2.273[c] 1.55[d]	0.0662		0.1108		26.0145	
Pt	1.30[a] 1.32[a] 1.35[a] 1.70[b]	1.624-1.752[c] 0.61[d]	0.0637 0.0639 0.064		0.1047 0.1050 0.1054		27.5325 27.4496 27.3560	
Al	0.66[a] 0.79[b]	0.778-1.017[c] 0.61[d]	0.069	0.060[e] 0.059[f]	0.0861	0.073[g] 0.1058[h]	51.7000	12.617[g] 37.55[h]
La		0.994-1.341[c] 1.44[d]	0.1058		0.1499		28.8495	
Sc		1.17-1.51[c] 2.07[d]	0.0857		0.1207		35.8327	
Ce		0.84-1.296[c] 1.30[d]	0.1014		0.1439		30.0618	
Pr		1.007-1.011[c] 0.76[d]	0.101		0.1419		30.4764	
Yb		0.914-1.38[c]	0.1102		0.1559		27.7394	
Pb	0.50[a] 0.58[a] 0.53[b]	0.5-0.612[c] 0.45[d]	0.0997 0.0999	0.057[e] 0.059[f]	0.1233 0.1245	0.1064[i]	46.9068 46.4254	43.3[i]
Th	1.28[a]	1.686-1.86[c] 1.92[d]	0.105		0.1371		42.0696	

[a]reference [16]; [b]reference [19]; [c]reference [20,21]; [d]reference [18]; [e]reference [22]; [f]reference [14]; [g]reference [23]; [h]reference [15,24]; [i]reference [15].

However, there is a systematic decrease in the fitted value of A for every fcc metal from one ECF to the other, so also there is an increase in the value of r_c from one ECF to the other. The mean difference for 1b group elements Cu, Ag, Au is $\Delta A = 0.005 eV$, $\Delta r_c = 0.014 nm$; for 2a group elements Ca, Sr is $\Delta A = 0.002 eV$, $\Delta r_c = 0.006 nm$; for 8 group elements Fe, Co, Ni, Rh, Pd, Ir, Pt is $\Delta A = 0.018 eV$, $\Delta r_c = 0.016 nm$; for 3b and 3a group elements Al, Sc, La, Ce, Pr, Yb is $\Delta A = 0.029 eV$, $\Delta r_c = 0.025 nm$; for 4 group elements Pb, Th is $\Delta A = 0.042 eV$, $\Delta r_c = 0.031 nm$. This difference increases from monovalent to tetravalent metals and clearly these are very small in comparison to the values in table 1.

In table 1, the values of r_c for both Ashcroft empty core potential [25] and HAP are shown for a comparison of the change in its value from one potential to the other for different available experimental values of E_F^{1v} depicted in reference [16]. Also, for different available experimental values of E_F^{1v}, the variations of HAP parameter A are shown in table 1. The variations of HAP parameters of A and r_c for all nine ECFs are not shown but only their mean for three experimental values have been given while fitting for a particular Taylor's ECF [15].

Figure 11 shows the variation of HAP parameters $(A, r_c)_{HA}$ with Ashcroft parameter $(r_c)_{Ash}$ and valency. $(r_c)_{HA}$ has increased in magnitude in comparison to $(r_c)_{Ash}$. As for the increase in valency, the parameter A of HAP increases and shows distinctly different curves.

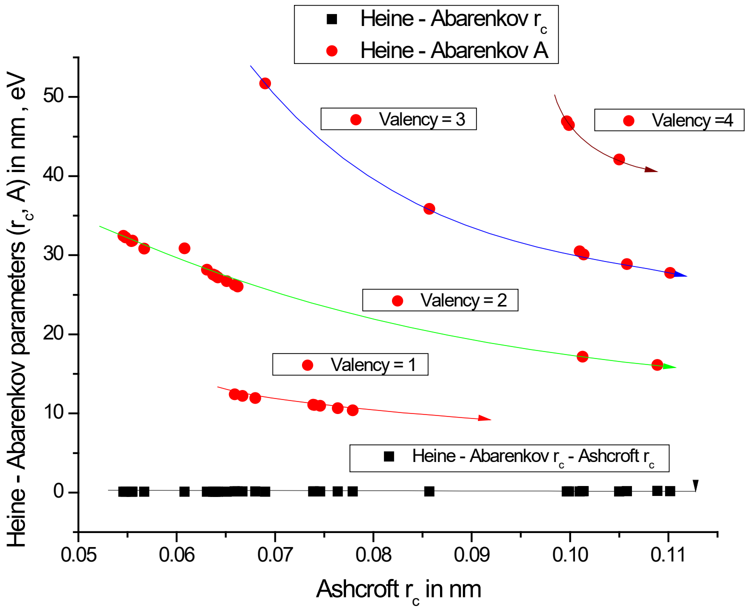

Figure 11 : HAP parameters $(A, r_c)_{HA}$ and Ashcroft parameter $(r_c)_{Ash}$ variation with valency

5. Conclusions

In conclusion, HAP parameters are compared with Ashcroft empty core potential parameter [25] and in all cases parameter r_c is greater than Bohr radius. It should be noted that Geldart and Vosko, Kleinmann, Harrison, Vashishta and Singwi and Taylor type of ECF [17] gives better results. It shows that E_F^{1v} is practically independent after about 10 *Rydberg* value of HAP parameter A.

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