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Calculation of parameter of Ashcroft's potential using vacancy formation energy for bcc metals like Cr, Mo, W, V, Nb, Ta, Tl, Eu and Zr

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Abstract

Variation of vacancy formation energy with the parameter of Ashcroft's model for nine different exchange and correlation functions show almost similar nature for the bcc metals like Cr, Mo, W, V, Nb, Ta, Tl, Eu and Zr. The mean value of this parameter for these bcc metals are respectively 1.173, 1.383, 1.458, 1.263, 1.478, 1.489, 1.802, 2.222 atomic unit.

Keywords

Point defect, vacancy, interstitial, bcc metal, pseudopotential.

1. Introduction

Point defects (vacancies and interstitials) directly affect the kinetics and thermodynamics of metals and alloys and it is thus very important to develop a good understanding of their properties, in particular their energetics. This research work is devoted to get the best computed value of the parameter (r_c) of Ashcroft's empty core model potential (here after will be called AECMP) [1] necessary for the calculation of vacancy formation energy in some bcc metals where different calculations have been presented [2-3]. This is of immense importance for a broad scientific community interested in diffusion and transport phenomena.

Recently AECMP together with nine different exchange and correlation functions (called ECF), viz. (i) Hubbard [4], (ii) Sham [5], (iii) Harrison [6], (iv) Geldert and Vosko [7], (v) King and Kutler [8], (vi) Kleinmann [9], (vii) Mahanti and Das [10], (viii) Vashishta and Singwi [11] and (ix) Taylor [12], has been utilized successfully to fcc metals [13] and also in case of body centered cubic (bcc) metals [14-15]. So it is now applied to some other bcc metals. ECF of Hubbard and Sham are the oldest while Vashishta and Singwi's ECF explains metallic properties of simple metals. Mahanti and Das's ECF, the modified form of Geldart and Vosko uses exchange core polarization effect and exchange enhancement of the susceptibility due to electron-electron interaction and is best suitable for alkali metals.

2. Formulations

In Harrison's pseudopotential approach [6] the total energy of any crystal is given by

$$E_T = z[\frac{3\hbar^2 k_F^2}{10m} + <\vec{k} \mid W(r) \mid \vec{k}>] + [E_{bs} + E_{es}] \qquad (1)$$

Here z is the valency, k_F the Fermi wavenumber, m the electronic mass, and $W(r)$ the pseudopotential. The first square bracketed term is structure independent and the last square bracketed term is structure dependent. The structure dependent energy depends on ion-ion, ion-electron and electron-electron interactions and is also dependent on the modified lattice wave numbers. The modifications in the lattice wave numbers from their perfect lattice value are necessary to maintain the lattice volume and the number of lattice ions constant. The ion-ion interaction is determined from the electrostatic energy E_{es} for a lattice containing N number of atoms at N lattice sites with position vector for ith ion or atom being $\vec{r}_i$. The total pair interaction on ith ion due to all jth ions will be

$$V(r_i) = \Sigma_{j=1}^{N} v(\mid \vec{r}_i - \vec{r}_j \mid) - v(\mid \vec{r}_i - \vec{r}_i \mid) \qquad (2)$$

The electrostatic energy term for the pure lattice will be half of average of all pair interactions since we have counted each pair twice twice, i.e. $E_{es} = \frac{1}{2N}\sum_{i=1}^{N} V(r_i)$ and here we use the fact

that $$v(r) = \Sigma_q^{'} \frac{1}{N} v(q) e^{i\vec{q}\cdot\vec{r}} \qquad (3)$$

So $$E_{es} = \frac{1}{2N}\Sigma_{i=1}^{N} V(r_i) = \frac{1}{2N}\Sigma_{i=1}^{N}[\Sigma_{j=1}^{N} v(\mid \vec{r}_i - \vec{r}_j \mid) - v(\mid \vec{r}_i - \vec{r}_i \mid)]$$

$$= \frac{1}{2}[\Sigma_q^{'} \mid S(q) \mid^2 \underset{\eta\to\propto}{Lt} \frac{4\pi e^2 z^2}{\Omega q^2} e^{-\frac{q^2}{4\eta}} - \underset{\eta\to\propto}{Lt} \frac{2e^2 z^2 \sqrt{\eta}}{\sqrt{\pi}}] \qquad (4)$$

Here η is the convergence factor, e the electronic charge, Ω the atomic volume and $\vec{q}$ the wave number. The structure factor $S(q)$ for the lattice is defined as

For $q = q_0$ $S(q_0) = 1$
And for $q \neq q_0$ $S(q) = 0$ (5)

The lattice wave number $\vec{q}_0$ is defined as

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

With m_1 / N_1, m_2 / N_2 and m_3 / N_3 are the integers including zero and $\vec{q}_1$, $\vec{q}_2$ and $\vec{q}_3$ are the primitive wave vectors. The ion-electron and electron-electron interactions are included in the band structure energy term E_{bs}, which is calculated using second order perturbation theory incorporating pseudopotential model form. We write the ith ionic pseudopotential with its matrix element and band structure energy as

$$W(r_i) = \sum_{j=1}^{N} w(|\vec{r}_i - \vec{r}_j|) \tag{7}$$

Or,
$$W(q) = S(q) < \vec{k} + \vec{q} \,|\, w(r) \,|\, \vec{k} >= S(q) w(q) \tag{8}$$

Thus
$$E_{bs} = \sum_q{}^{'} \frac{2\Omega}{8\pi^3} \int \frac{d\vec{k}\, |< \vec{k} + \vec{q} \,|\, W(r_i) \,|\, \vec{k} >|^2}{\frac{\hbar^2}{2m}(k^2 - |\vec{k} + \vec{q}|^2)} = \sum_q{}^{'} |S(q) w(q)|^2 \, \varepsilon(q) \chi(q) \tag{9}$$

With
$$w(q) = -\frac{4\pi e^2 z \cos q r_c}{\Omega q^2} \tag{10}$$

$$\varepsilon(q) = 1 - \frac{8\pi e^2}{\Omega q^2}[1 - f(q)]\chi(q) \tag{11}$$

$$\chi(q) = -\frac{m k_F \Omega}{4\pi^2 \hbar^2}[1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \frac{|2k_F + q|}{|2k_F - q|}] \tag{12}$$

Here $w(q)$ is the one parameter (r_c) AECMP, $\varepsilon(q)$ the dielectric function, $\chi(q)$ the perturbation characteristics and $f(q)$ the ECF. From literature survey it is found that there are several forms of ECF and here nine different $f(q)$ are used which are given by

Table 1
Input parameters for different bcc metals [1 eV = 13.605 Rydberg and 1 Atomic Unit (AU) = 5.29177×10^{-2} nm]

Metal	Valency Z	Lattice constant a in nm [17]	Volume AU^3	k_F AU^{-1}	E_F Ryd.	Melting point T_m in K [17]
Cr	2	0.288	80.60	3.49	12.20	2133.0
Mo	2	0.315	105.46	3.60	12.95	2895.0
W	2	0.316	106.47	3.60	12.98	3695.0
V	3	0.303	93.86	3.10	9.63	2202.0
Nb	3	0.33	121.26	3.19	10.20	2750.0
Ta	3	0.33	121.26	3.19	10.20	3293.0
Tl	3	0.387	195.57	3.37	11.34	577.0
Eu	3	0.458	324.16	3.56	12.69	1091.0
Zr	4	0.361	158.74	2.99	8.94	2128.0

Hubbard [4]:
$$f(q) = \frac{q^2}{2(q^2 + k_F^2)} \tag{13}$$

Sham [5]:
$$f(q) = \frac{q^2}{2(q^2 + k_F^2 + \frac{2k_F}{\pi a_0})} \tag{14}$$

Harrison [6]:
$$f(q) = \frac{q^2}{2(q^2 + k_F^2 + \frac{k_F^2}{3})} \tag{15}$$

Geldert & Vosko [7]:
$$f(q) = \frac{q^2}{2[q^2 + \frac{2k_F^2}{1 + \frac{0.026 m'}{m}(\frac{3\Omega}{4\pi Z a_0^3})^{1/3}}]} \tag{16}$$

King & Kutler [8]: $$f(q)=\frac{q^2}{2(2k_F^2+q^2)} \tag{17}$$

Kleinmam [9]: $$f(q)=\frac{1}{4}[\frac{q^2}{k_F^2+\frac{2k_F}{\pi a_0}}+\frac{q^2}{q^2+k_F^2+\frac{2k_F}{\pi a_0}}] \tag{18}$$

Mohanti & Das [10]: $$f(q)\frac{q^2}{k_F^2[1+(\frac{2}{1+\frac{0.026m'}{m}(\frac{3\Omega}{4\pi Za_0^3})^{1/3}})^2]}+\frac{q^2}{q^2+k_F^2[1+(\frac{2}{1+\frac{0.026m'}{m}(\frac{3\Omega}{4\pi Za_0^3})^{1/3}})^2]} \tag{19}$$

Vashishta & Singwi [11]: $$f_H(q)=A(1-e^{-\frac{Bq^2}{k_F^2}}) \tag{20}$$

Taylor [12]: $$f(q)=\frac{q^2}{4k_F^2}(1+\frac{0.1534}{\pi k_F}) \tag{21}$$

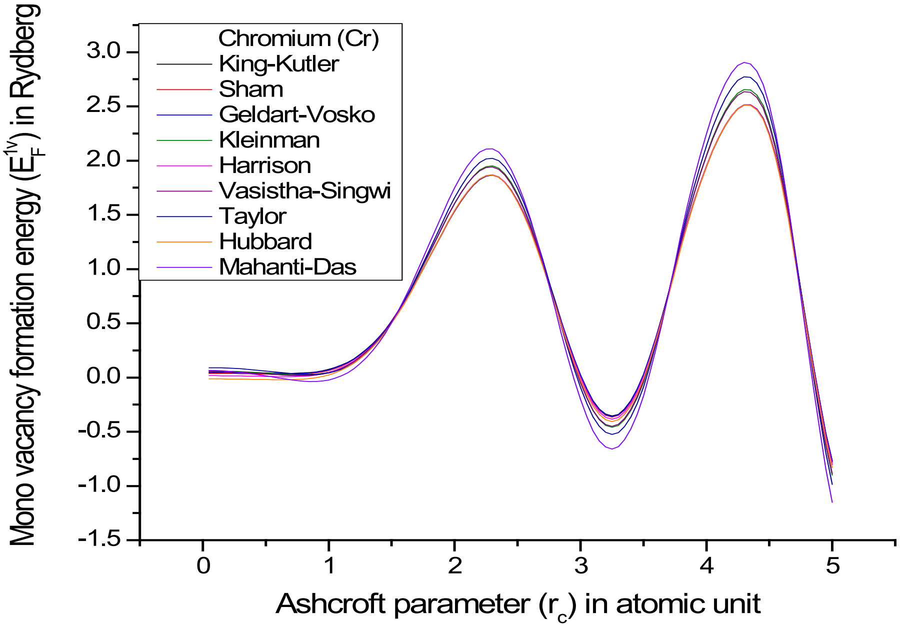

Figure 1 : $E_F^{1v}-r_c$ plot for chromium (Cr)

3. Monovacancy formation energy

Any defect in the crystal lattice changes the structure dependent energy and an algebraic difference between the energy after defect creation and that before will give us the defect formation energy when considered for the whole lattice. Let us consider a single vacancy in an otherwise perfect lattice. The Brillouin zone volume has to be scaled up by a factor of $(N+1)/N$ in order to keep the lattice volume constant, i.e. the lattice wave numbers are modified to μq_0 with $\mu\approx 1+1/3N$. Due to this structure factor $S(q)$ will also change and finally one gets the expression for monovacancy formation energy E_F^{1v} as

$$E_F^{1v}=N[(E_{es}^v+E_{bs}^v)-(E_{es}+E_{bs})]$$

Or, $$E_F^{1v}=\sum\nolimits_{q_0}' \frac{q_0}{3}\frac{\partial U(q_0)}{\partial q_0}+\frac{\Omega}{2\pi^2}\int_0^\infty U(q)q^2dq \tag{22}$$

With $$U(q) = Lt_{\eta\to\infty} \frac{2\pi e^2 z^2}{\Omega q^2} e^{-\frac{q^2}{4\eta}} + [w(q)]^2 \varepsilon(q)\chi(q) \qquad (23)$$

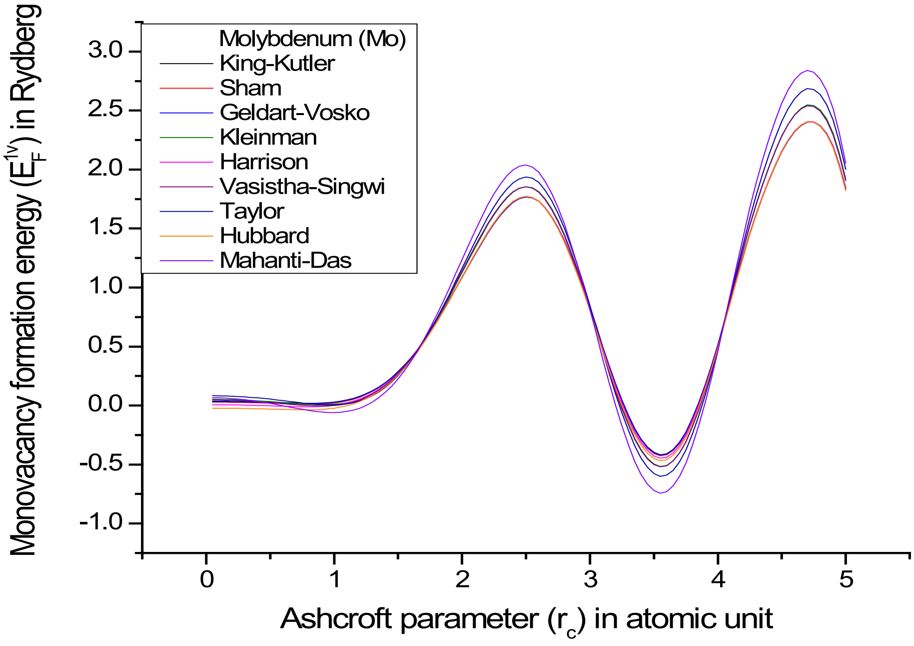

Figure 2 : $E_F^{1v} - r_c$ plot for molybdenum (Mo)

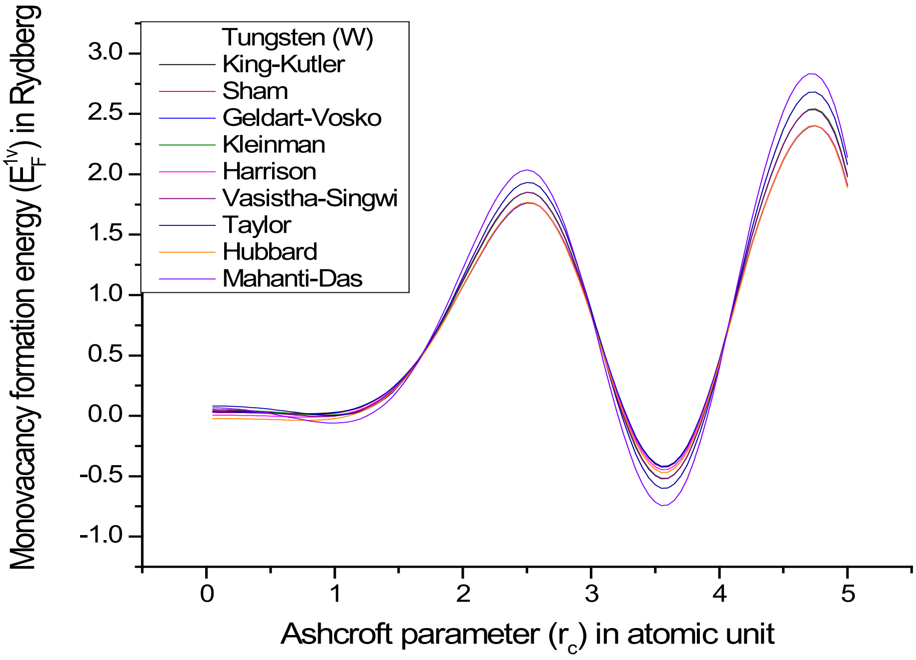

Figure 3 : $E_F^{1v} - r_c$ plot for tungsten (W)

4. Calculation procedure

For the calculation of monovacancy formation energy E_F^{1v} in equation (22) the discrete sum is done over lattice wave numbers $q = q_0$ shown in equation (6) with maximum value of $m_i / N_i = 14$, $i = 1,2,3$ and the lattice wave numbers are generated in the cubic Brillouin zone. The integration over quasi-continuous wave numbers $q \neq q_0$ is done by 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.

$$\int_0^\infty \rightarrow \int_0^1 Gauss - Lagendre + \int_1^\infty Gauss - Laguerre \tag{24}$$

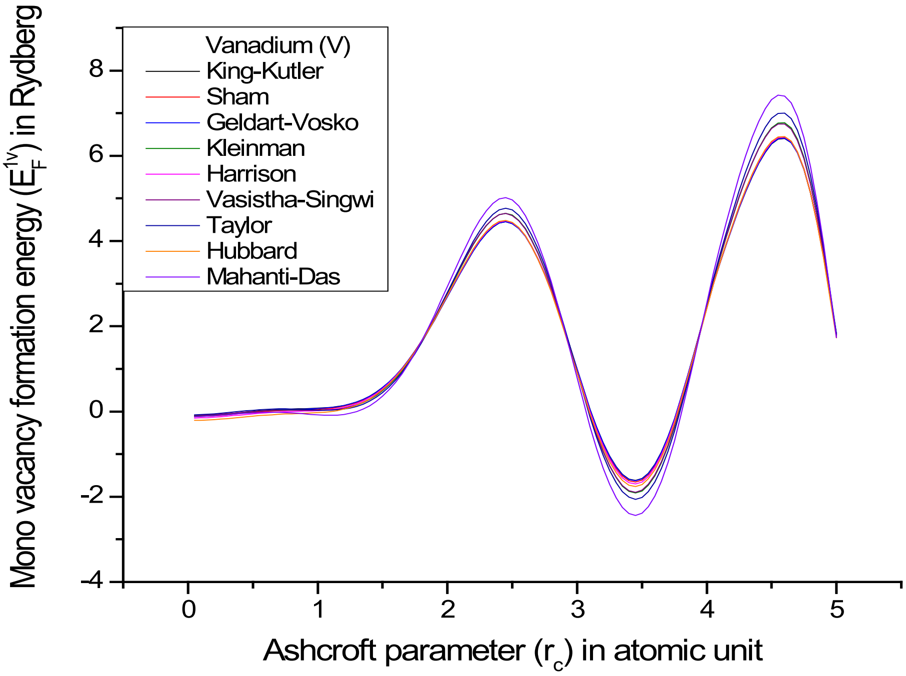

Figure 4 : $E_F^{1v} - r_c$ plot for vanadium (V)

The input parameters for the bcc metals like chromium (Cr), molybdenum (Mo), tungsten (W) (all divalent in active valence state), vanadium (V), niobium (Nb), tantalum (Ta), thallium (Tl), europium (Eu) (all trivalent) and zirconium (Zr) (tetravalent) are shown in Table 1.

5. Results

In the first step variation of E_F^{1v} with parameter r_c of AECMP in equation (10) is plotted for nine different exchange and correlation functions from 0 to 5 AU as shown in figures 1 to 9. Due to $\cos^2 qr_c$ term of AECMP the graph shows positive peaks, although almost similar for all exchange and correlations but there is a slight variation with valency, group, and period. It is observed that experimental value of E_F^{1v} lies near the nodal point corresponding to the condition $E_F^{1v} \rightarrow 0$ rather than that to the maxima. Fitted value of r_c has been chosen corresponding to the condition

$$a_0 < r_c < \frac{2\pi}{k_F} \tag{25}$$

Here a_0 is the Bohr radius and k_F the Fermi wave number.

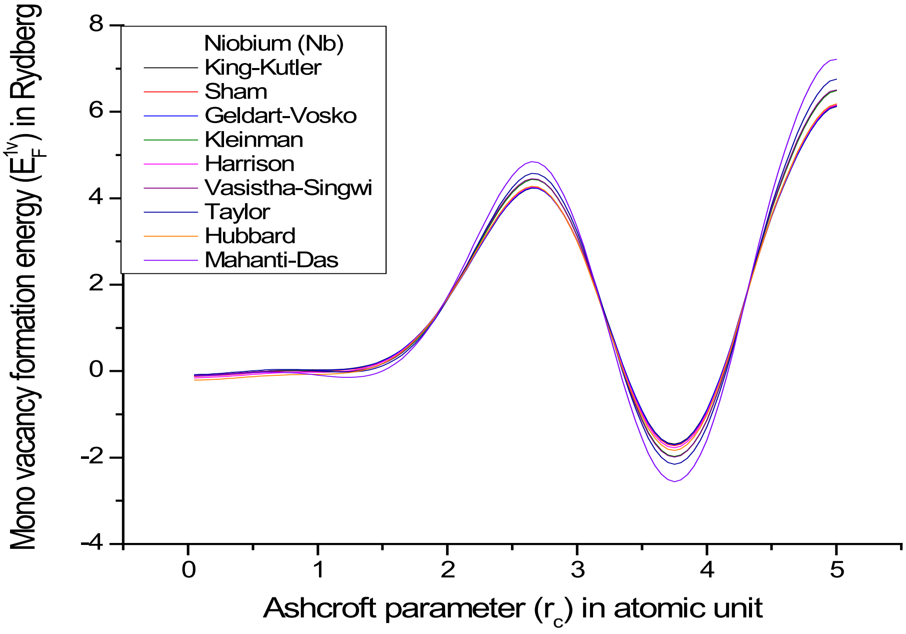

Figure 5 : $E_F^{1v} - r_c$ plot for niobium (Nb)

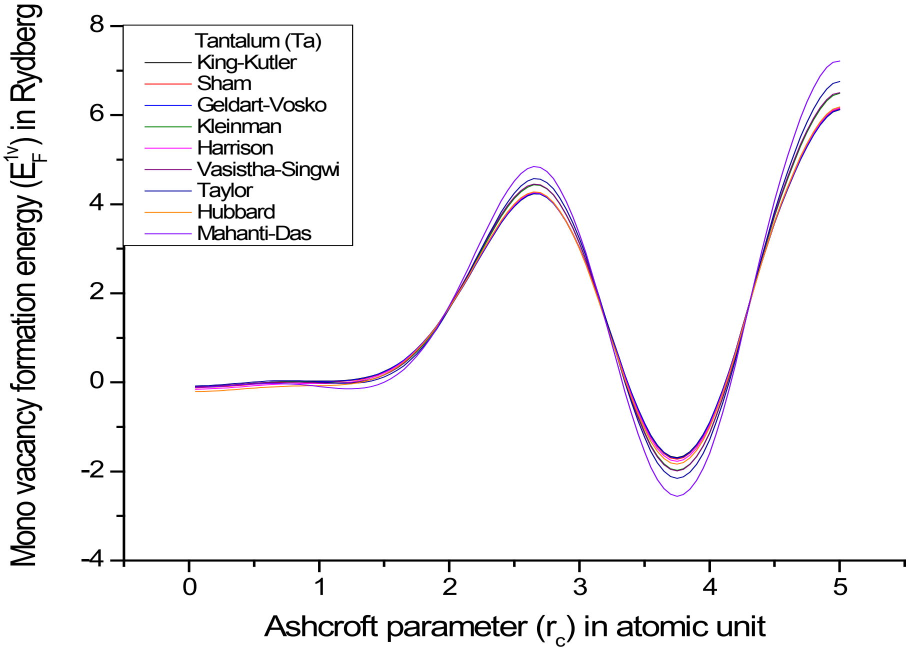

Figure 6 : $E_F^{1v} - r_c$ plot for tantalum (Ta)

Table 2

Vashistha – Singui parameters and vacancy formation energy values for different bcc metals [1 eV = 13.605 Rydberg and 1 Atomic Unit (AU) = 5.29177×10^{-2} nm]

Metal	Vas-Sing parameters [11]		Theoretical range of E_F^{1v}	Experimental values of E_F^{1v}
	A	B		
Cr	0.93937	0.31294	1.23 - 2.51	2.0, 2.27[1], 2.08[2]
Mo	0.97099	0.30512	2.046 - 2.413	3.0, 3.2[1]
W	0.97130	0.30548	2.670 - 3.34	4.0, 4.1, 3.6-4.0[1]
V	0.95586	0.30939	1.593 - 2.519	2.2 [1]
Nb	0.98576	0.30406	2.271 - 2.292	2.6, 2.7-3.0[1]
Ta	0.98576	0.30406	2.354 - 2.744	2.8, 2.9, 3.1[1]
Tl	1.04372	0.29327	0.48 - 3,651	
Eu	1.11056	0.28079	0.558 - 0.909	
Zr	1.01502	0.29717	0.468 - 1.875	

[1] reference [18], [2] reference [19]

In table 2 Vashistha – Singui parameters and available experimental values of vacancy formation energy are shown together with the range of theoretical value of E_F^{1v} obtained from the empirical relation

$$T_m = 1200E_F^{1v} = 660Q_0 = 360E_{coh} \tag{26}$$

Here T_m is the melting temperature, Q_0 the activation energy and E_{coh} the cohesive energy of the metal. Cr, Mo, W and V show two peaks within 5 AU while for the others like Nb, Ta, Tl, Eu and Zr, the second peak is outside of 5 AU clearly showing the dependence on valency, group and period. The average theoretical value of E_F^{1v} from table 2 is taken into account for the determination of r_c where there is no experimental value.

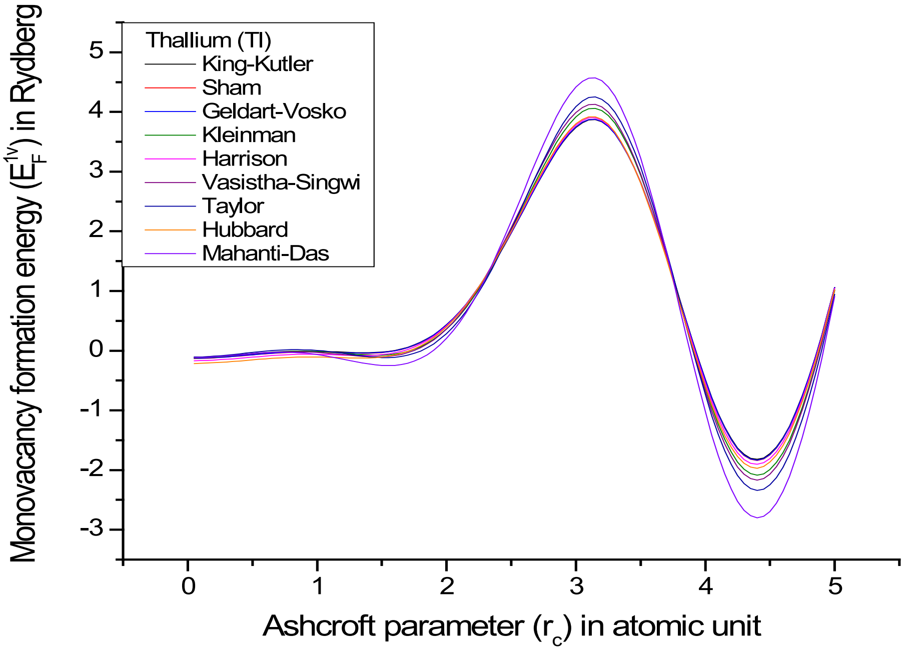

Figure 7 : $E_F^{1v} - r_c$ plot for thallium (Tl)

Table 3

Value of parameter r_c in atomic unit (AU) of AECMP for different bcc metals using different ECF

Metal	K-K	Sham	G-V	Kle	Harr	V-S	Tay	Hub	M-D	Mean r_c
Cr	1.138	1.152	1.143	1.184	1.174	1.183	1.200	1.201	1.256	1.173
Mo	1.358	1.364	1.361	1.390	1.382	1.391	1.409	1.402	1.449	1.383
W	1.440	1.445	1.442	1.464	1.458	1.462	1.477	1.472	1.504	1.458
V	1.198	1.227	1.205	1.294	1.259	1.288	1.321	1.296	1.403	1.263
Nb	1.430	1.446	1.435	1.501	1.467	1.501	1.535	1.493	1.596	1.478
Ta	1.445	1.458	1.451	1.511	1.479	1.511	1.545	1.504	1.603	1.489
Tl	1.749	1.757	1.755	1.824	1.784	1.837	1.886	1.809	1.948	1.802
Eu	2.164	2.164	2.169	2.242	2.196	2.269	2.334	2.218	2.396	2.222
Zr	1.392	1.445	1.414	1.543	1.505	1.567	1.597	1.559	1.730	1.506

K-K→King and Kutler [8]; Sham→[5]; G-V→Geldert and Vosko [7]; Kle→Kleinmann [9]; Harr→Harrison [6]; V-S→Vashishta and Singwi [11]; Tay→Taylor [12]; Hub→Hubbard [4]; M-D→Mohanti and Das [10].

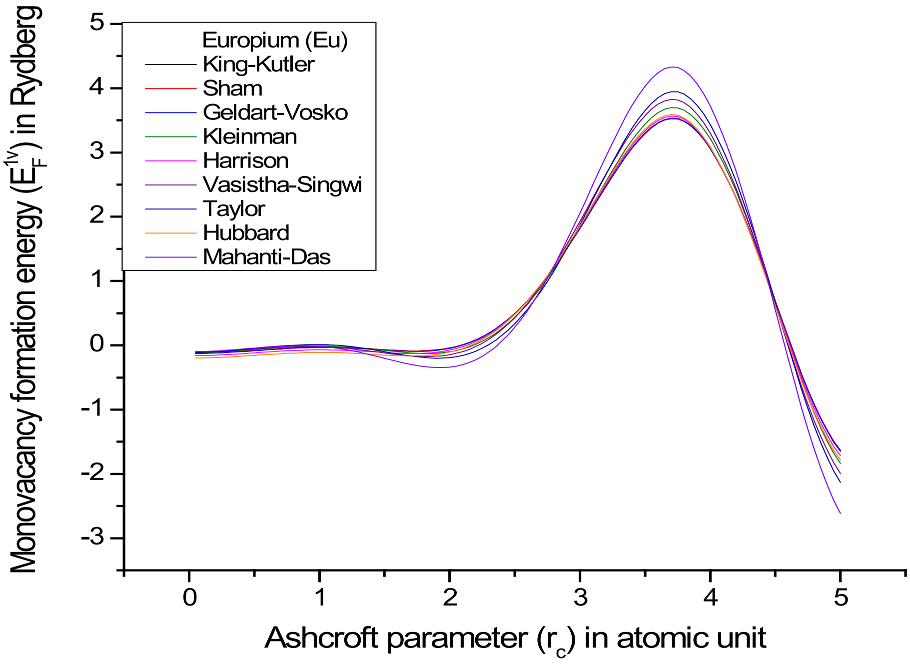

Figure 8 : $E_F^{1v} - r_c$ plot for europium (Eu)

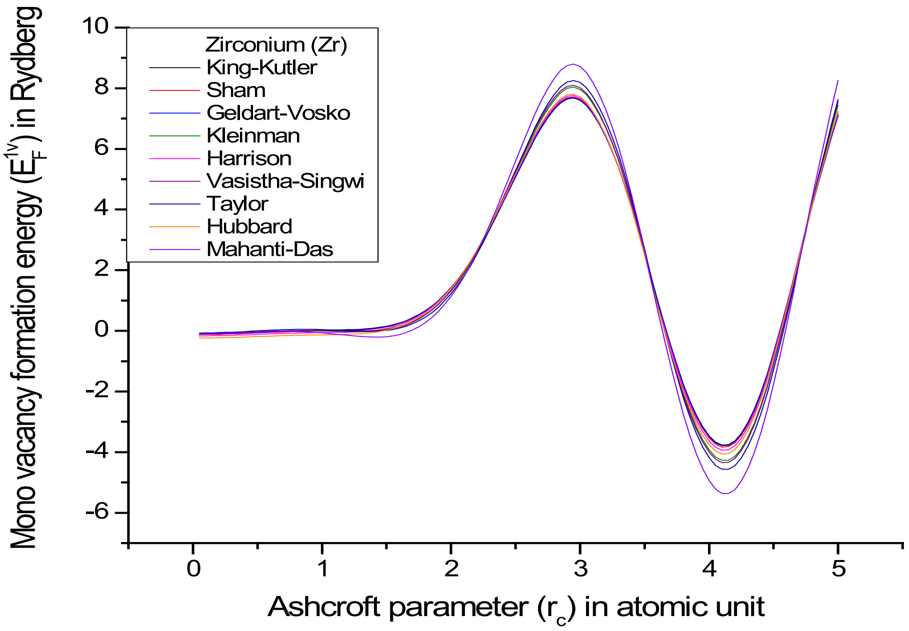

Figure 9 : $E_F^{1v} - r_c$ plot for zirconium (Zr)

6. DISCUSSIONS

Table 3 shows the values of parameter r_c in atomic unit (AU) of AECMP for different bcc metals using different ECFs. There is a systematic increase in the fitted value of r_c from one ECF to other as follows: K-K<Sham<G-V<Kle<Harr<V-S<Tay<Hub<M-D. K-K and M-D are the two extreme ends and others lie in between. Thus it is difficult to assign a particular value of r_c for all ECFs in these cases of bcc metals and a mean value is chosen which is also shown in the table 3. Harrison, Kleinmann, Vashishta and Singwi, and Taylor are almost similar, give moderate results, and may be trusted for better results.

The inherent simplicity of AECMP makes it difficult to have a universal r_c parameter for all types of atomic property calculations where electronic configurations, viz. sp hybridization, d-electron interaction etc. change differently. A proper choice of pseudopotential is very important and a careful attention must be paid in achieving accuracy in numerical computation in order to arrive at a meaningful result.

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