Determination of the parameters of Heine and Abarenkov model potential in hcp crystals

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Abstract

Parameters of Heine and Abarenkov potential has been computed in this paper for twenty two hexagonal closed pack (hcp) crystals. From the minimization of structure dependent energy of the pure crystal the inter-relation between the two parameters of the potential is first determined. Calculation uses pseudopotential technique with nine different exchange and correlation functions and either only available experimental value of 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 parameter A of HAP and different exchange and correlation functions (ECF) show sharp fall in E_F^{1v} near very small value of A after which it shows constancy for all hcp crystals. Comparison is made with parameter of Ashcroft model also. For Aschroft this variation is almost flat showing averageness while for Heine and Abarenkov sharp variations are there from one hcp crystal to other.

Keywords

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

PACS Numbers

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1. Introduction

The general form of Heine and Abarenkov model pseudopotential (henceforth called HAP) [1,2] can be written as

$$\omega(r) = -A_l(E)P_l \quad \text{for} \quad r < r_c$$
$$= -\frac{ze^2}{r} \quad \text{for} \quad r \geq r_c \quad \text{- (1)}$$

The simplest form of it is obtained when $l = 0$, $P_l = P_0 = 1$ and $A_l = A_0 = A$ with its Fourier transform is

$$\omega(r) = \frac{4\pi A}{\Omega q^3}(qr_c \cos qr_c - \sin qr_c) - \frac{4\pi ze^2}{\Omega q^2}\cos qr_c \quad \text{- (2)}$$

Here z is the valency, Ω the atomic volume, e the electronic charge, and q the wave number. The values of its parameters (r_c, A) are calculated earlier using 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 vacancy formation energy (E_F^{1v}) will be used for the calculation of these two parameters.

The vacancy formation energy (E_F^{1v}) in the pseudopotential approach of Harrison [3-5] is

$$E_F^{1v} = \sum'_{q_0} \frac{q_0}{3} \frac{\partial U(q_0)}{\partial q_0} + \frac{\Omega}{2\pi^2} \int_0^\infty U(q)\, q^2 dq \qquad - (3)$$

Where
$$U(q) = \lim_{\eta \to \infty} \frac{4\pi z^2 e^2}{\Omega q^2} e^{-\frac{q^2}{4\eta}} + [\omega(q)]^2 \epsilon(q)\chi(q) \qquad - (4)$$

$$\epsilon(q) = 1 - \frac{8\pi e^2}{\Omega q^2}[1 - f(q)]\chi(q) \qquad - (5)$$

$$\chi(q) = -\frac{m k_F}{h^2}\left[1 + \frac{4k_F^2 - q^2}{4q k_F}\log\frac{2k_F + q}{2k_F - q}\right] \qquad - (6)$$

Here $\vec{q}_0$ and $\vec{q}$ are the lattice and quasi-continuous wave numbers respectively and m the electronic charge and mass respectively, η the convergence factor, $\omega(q)$ the pseudopotential, $\epsilon(q)$ the dielectric function, $\chi(q)$ the perturbation characteristics, k_F the Fermi wave number, and $f(q)$ the exchange and correlation function (ECF) whose nine chosen forms were cited elsewhere [3]. Out of several ECFs only nine such forms are chosen. Hubbard and Sham's ECFs are the old ones. Harrison and King and Kutler's ECFs are almost similar and modified forms of Hubbard's while Kleinmann's is the modified form of Sham. Geldart and Vosko's ECF, was modified by Mahanti and Das, and they use exchange core polarization effect and exchange enhancement of the susceptibility due to electron-electron interaction, and is best suitable for alkali metals. Vashishta and Singwi's ECF explains metallic properties of simple metals while Taylor's ECF was tested several times earlier.

2. 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

$$\int_0^\infty \to \int_0^1 \text{Gauss} - \text{Lagendre} + \int_1^\infty \text{Gauss} - \text{Laguerre} \qquad - (7)$$

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

$$\vec{a}_1 = \frac{\sqrt{3}a}{2}\hat{\imath} + \frac{a}{2}\hat{\jmath} \qquad \vec{a}_2 = -\frac{\sqrt{3}a}{2}\hat{\imath} + \frac{a}{2}\hat{\jmath} \qquad \vec{a}_3 = c\hat{k} \qquad - (8)$$

$$\vec{q}_1 = \frac{2\pi}{\sqrt{3}a}(\hat{\imath} + \sqrt{3}\hat{\jmath}) \qquad \vec{q}_2 = \frac{2\pi}{\sqrt{3}a}(-\hat{\imath} + \sqrt{3}\hat{\jmath}) \quad \vec{q}_3 = \frac{2\pi}{c}\hat{k} \qquad - (9)$$

With
$$\vec{q}_0 = \frac{m_1}{N_1}\vec{q}_1 + \frac{m_2}{N_2}\vec{q}_2 + \frac{m_3}{N_3}\vec{q}_3 \qquad - (10)$$

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 and c are lattice constants of hcp crystal. For simplicity, relaxation effect is not considered in these calculations as in the earlier cases [6-9].

In the first step, the two parameters (r_c, A) of HAP suggests a minimization of structure dependent energy of the pure crystal and yields a relation $\qquad A = \frac{ze^2}{r_c} \qquad - (11)$

The value of E_F^{1v} in *Ryd* (1 *Rydberg*=13.605 *eV*) of equation (3) is computed using equation (7) for different values of parameter A of HAP [1 *Atomic Unit (AU)*=0.0529177 *nm*] and 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 ECFs and for twenty two different hexagonal closed pack (hcp) crystals, viz. (1) Beryllium (Be), (2) Magnesium (Mg), (3) Scandium (Sc), (4) Titanium (Ti), (5) Cobalt (Co), (6) Zinc (Zn), (7) Yttrium (Y), (8) Zirconium (Zr), (9) Technetium (Tc), (10) Ruthenium (Ru), (11) Cadmium (Cd), (12) Gadolinium (Gd), (13) Terbium (Tb), (14) Dysprosium (Dy), (15) Holmium (Ho), (16) Erbium (Er), (17) Thullium (Tm), (18) Lutetium (Lu), (19) Hafnium (Hf), (20) Rhenium (Re), (21) Osmium (Os) and (22) Thallium (Tl) (arranged according to increasing atomic number).

Table 1
Input parameters for hexagonal closed pack (hcp) crystals

Element	Atomic no	Valency z	a in nm[a]	c in nm[a]	V-S parameters		T_m in K[a]	E_{coh} in eV[a]	Q_0 in eV	Range of $(E_F^{1v})_{theo}$ in eV	Other $(E_F^{1v})_{theo}$ in eV[b]	$(E_F^{1v})_{expt}$ in eV
					A in AU	B in AU						
Beryllium (Be)	4	1	0.227	0.359	0.8079	0.3435	1562	3.32		1.00-1.30	1.04	0.75[e]
Magnesium	12	2	0.321	0.521	0.9009	0.3211	922	1.51	1.30[b]	0.45-0.77	0.78	0.80[d]
Scandium (Sc)	21	3	0.331	0.521	0.9096	0.3257	1814	3.9		1.17-1.51	1.87	0.96[d]
Titanium (Ti)	22	3	0.295	0.468	0.8769	0.3264	1946	4.85	3.14[c]	1.73-1.46	2.06	
Cobalt (Co)	27	3	0.251	0.407	0.8338	0.3368	1770	4.39		1.32-1.48	1.67, 1.93	
Zinc (Zn)	30	2	0.266	0.495	0.8496	0.3326	692.7	1.35	1.00[b]	0.41-0.58	0.47	0.54[d]
Yttrium (Y)	39	3	0.365	0.573	0.9409	0.3193	1801	4.37		1.31-1.50	1.87	
Zirconium (Zr)	40	4	0.323	0.515	0.9026	0.3264	2128	6.25	3.17[c]	1.74-1.88	2.03	
Technetium	43	2	0.274	0.44	0.8579	0.3305	2477	6.85		2.05-2.06	0.25	
Ruthenium	44	3	0.271	0.428	0.8554	0.3311	2527	6.74		2.02-2.11	2.68	
Cadmium (Cd)	48	2	0.298	0.562	0.8799	0.3326	594.3	1.16	0.86[b]	0.35-0.49	0.25	0.46[d]
Gadolinium	64	3	0.363	0.578	0.9390	0.3122	1587	4.14		1.24-1.32		
Terbium (Tb)	65	3	0.36	0.57	0.9360	0.3130	1632	4.05		1.22-1.36		
Dysprosium	66	3	0.359	0.565	0.9352	0.3137	1684	3.04		0.91-1.40		
Holmium (Ho)	67	3	0.358	0.562	0.9343	0.3139	1745	3.14		0.94-1.45		
Erbium (Er)	68	3	0.356	0.559	0.9324	0.3138	1797	3.29		0.99-1.50		
Thullium (Tm)	69	3	0.354	0.556	0.9306	0.3147	1820	2.42		0.73-1.52		
Lutetium (Lu)	71	3	0.35	0.555	0.9270	0.3155	1938	4.43		1.33-1.62		
Hafnium (Hf)	72	4	0.319	0.505	0.8991	0.3214	2504	6.44	3.35[c]	1.74-2.09	2.26	2.45[c]
Rhenium (Re)	75	4	0.276	0.446	0.8597	0.3302	3459	8.03		2.41-2.88	3.42	
Osmium (Os)	76	3	0.274	0.432	0.8579	0.3306	3306	8.17		2.45-2.76	3.03	
Thallium (Tl)	81	3	0.346	0.552	0.9234	0.3103	577	1.88	1.04[b]	0.48-0.57	0.40	0.46[d]

[a] ref. [8]; [b] ref. [9]; [c] ref. [10]; [d] ref. [11]; [e] ref. [12].

3. Discussions

There is a sharp fall in E_F^{1v} near very small value of A in the $E_F^{1v} - A$ plot. With the increase in A, E_F^{1v} shows constant horizontal line for all hcp crystals as shown in figure 1a and figure 1b although values differ with ECF. Be, Mg, Co, Zn, Tc and Cd show smooth sharp fall while Sc, Ti, Y, Zr, Ru, Gd, Tb, Dy, Ho, Er, Tm, Lu, Hf, Re, Os and Tl show a kink before a

horizontal line. Due to this similar nature only two graphs are shown. It shows E_F^{1v} is independent of A. The value of A and hence r_c are determined from fitting to the theoretical mean value of $(E_F^{1v})_{theo}$. 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} or $(E_F^{1v})_{expt}$ is not available and so $(E_F^{1v})_{theo}$ 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) as

$$T_m(K) = 1200E_F^{1v}(eV) = 660Q_0(eV) = 360E_{coh}(eV) \qquad \text{- (12)}$$

Whenever there is kink in the $E_F^{1v} - A$ plot the fitting is considered at the lowest value of A to ensure the condition, $r_c \geq$ Bohr radius. All these are shown in table 1.
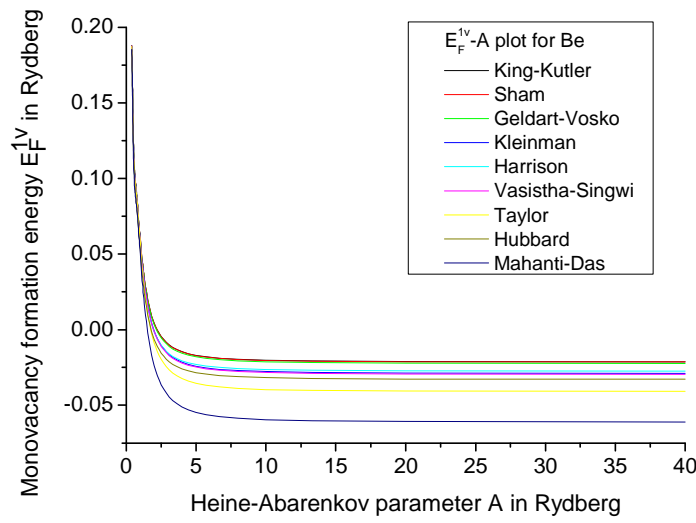

Figure 1a : $E_F^{1v} - r_c$ plot for beryllium (Be) and for scandium (Sc)
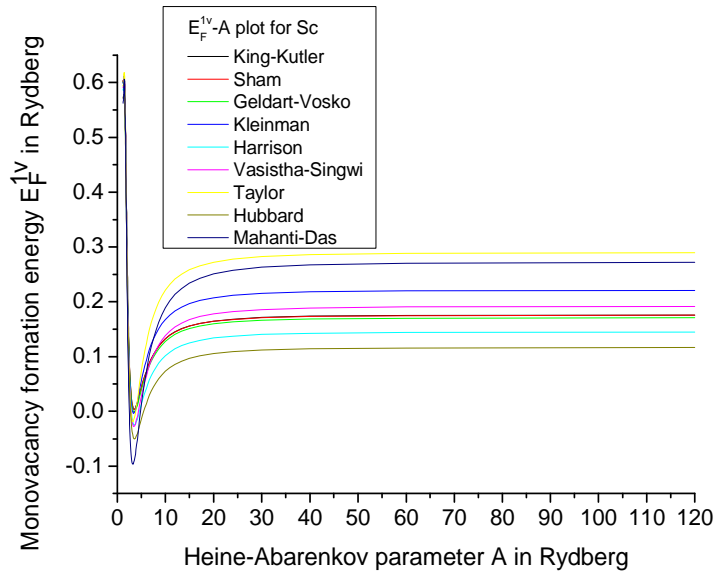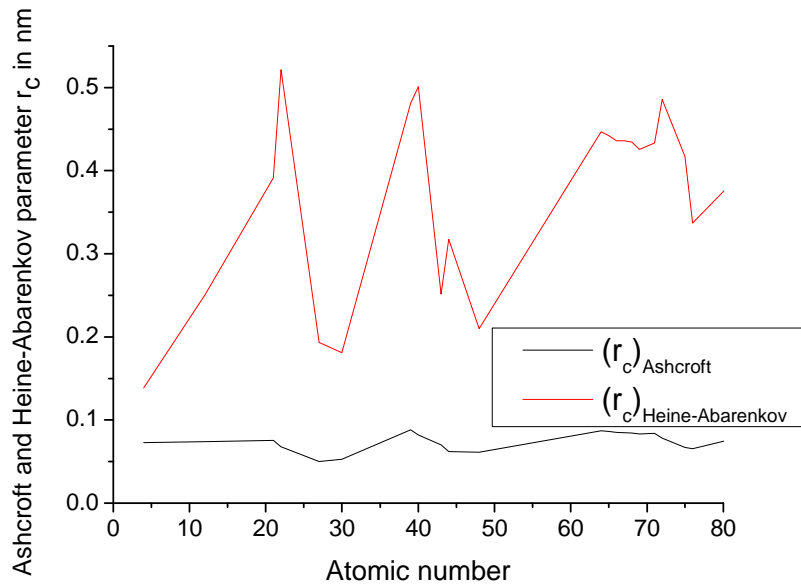

Figure 1b : $E_F^{1v} - r_c$ plot for beryllium (Be) and for scandium (Sc)

Table 2

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

Metal	ΔA for different ECF of HAP in eV	Δr_c for different ECF in HAP in nm	Mean Ashcroft $(r_c)_{Ash}$[a] in *nm*	Mean Heine-Abarenkov parameters	
				$(r_c)_{HA}$ *nm*	$(A)_{HA}$ *eV*
Beryllium (Be)	1.201	1.1985	0.0725	0.1385	10.397
Magnesium (Mg)	2.709	2.1265	0.0739	0.2503	23.008
Scandium (Sc)	3.298	3.9293	0.0755	0.3911	33.132
Titanium (Ti)	1.733	7.4792	0.0677	0.5214	24.856
Cobalt (Co)	3.560	1.6180	0.0501	0.1931	29.828
Zinc (Zn)	5.853	0.9841	0.0528	0.1807	31.874
Yttrium (Y)	2.360	5.4921	0.0881	0.4807	26.960
Zirconium (Zr)	5.377	4.2850	0.0819	0.5008	46.003
Technetium (Tc)	1.258	4.5788	0.0701	0.2513	22.919
Ruthenium (Ru)	4.025	3.2195	0.0621	0.3172	40.853
Cadmium (Cd)	5.080	1.1339	0.0613	0.2098	27.459
Gadolinium (Gd)	2.762	4.6925	0.0871	0.4464	29.028
Terbium (Tb)	2.795	4.6357	0.0861	0.4422	29.309
Dysprosium (Dy)	2.977	4.3529	0.0850	0.4357	29.744
Holmium (Ho)	2.906	4.4598	0.0848	0.4358	29.735
Erbium (Er)	2.936	4.4145	0.0845	0.4341	29.850
Thullium (Tm)	3.127	4.1437	0.0831	0.4256	30.451
Lutetium (Lu)	2.619	4.9476	0.0841	0.4331	29.925
Hafnium (Hf)	6.369	3.6174	0.0782	0.4855	47.450
Rhenium (Re)	6.526	3.5304	0.0672	0.4171	55.232
Osmium (Os)	2.974	4.3570	0.0651	0.3368	38.473
Thallium (Tl)	5.208	2.4883	0.0767	0.3845	33.703

[a] ref [3].

Figure 2 : Variation of AP and HAP parameter r_c with atomic number

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In table 2 the mean over all ECFs of HAP parameters (r_c, A) are shown together with variation $(\Delta r_c, \Delta A)$ which is very small. Ashcroft parameter (r_c) is also tabulated for comparism [3]. At present there is almost no theoretical value of simple HAP parameter values and so they are tested in the plot of atomic number and parameter r_c. For AP this variation is almost flat showing its averageness while for HAP sharp variations are there from one hcp crystal to other.

4. Conclusion

In conclusion it should be noted that Geldart and Vosko, Kleinmann, Harrison, Vashishta and Singwi and Taylor type of ECF [3,7] give better results. It shows that E_F^{1v} is practically independent after about 10 *Rydberg* value of HAP parameter A. A computation of defect energy show that HAP is perhaps betttter choice in comparison to AP.

5. The bibliography

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