

Vacancy formation energy of simple metals using reliable model and *ab initio* pseudopotentials

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Abstract

We present a self-consistent calculation of the mono vacancy formation energy for seven simple metals Li, Na, K, Rb, Cs (all bcc), Al (fcc) and Mg (hcp) using both model and *ab initio* pseudopotential used in earlier unified studies. The local model pseudopotential calculations show small variations with respect to different exchange-correlation functions and the results are in fair agreement with other similar calculations and the available experimental data. The comparisons show that reliable model (pseudo) potential for simple metals can indeed be obtained for explaining a host of properties. Also, considering the importance of third order term in *ab initio* calculations, the results of our second order calculation appear fairly reasonable and are comparable with other first principle calculations. The perturbation series being an oscillating one, we hope to improve the calculational results using suitable series convergence acceleration method in the next part of our study.

Keywords: Point defects, vacancy formation energy, pseudopotential perturbation theory, *ab initio* pseudopotential, linear dielectric screening, exchange and correlation function.

1. Introduction

Departure from perfect lattice structure, affects the kinetics and thermodynamics of metals and alloys and it is very important to develop a good understanding of their properties, in particular their energetics. The simplest kind of imperfection is point defects (vacancies and interstitials) and the relevant vacancy formation energy is very important for diffusion and transport phenomena.

The pseudopotential method has been very successful in the determination of stable crystal structure and other atomic properties of perfect simple metals. Moreover, the pseudopotential approach can account for even more complex problem like defects in a simple manner since perfectly ordered arrays of ions are not required [1]. The pseudopotential, representing the bare electron-ion interactions, together with the self-consistent linear screening theory offers a powerful tool for the study of defects in metals and in fact, the vacancy formation energy has previously been derived by Harrison [2].

Even for the simple metals, there exist very few calculations in the literature using either first principle/*ab initio* (without any adjustable parameter) or reliable model pseudopotentials which give a fair account for a number of other metallic properties. In this paper we present a self-consistent calculation of the vacancy formation energy for seven simple metals Li, Na, K, Rb, Cs (bcc), Al (fcc) and Mg (hcp) using both model and *ab initio* pseudopotentials (AP), used in earlier unified studies. Effect of different exchange and correlation functions (ECF) or the local-field correction factor (f_q) to the dielectric function representing linear screening due to the electron-electron interaction of metallic solids are also studied.

Local Heine-Abarenkov (HA) model pseudopotential [3] calculations up to second order in perturbation theory using two different (Taylor [4] and Vashishta-Singwi [5]) exchange and correlation functions, with model parameters determined from earlier unified studies of lattice mechanical (both dynamic and static) and transport properties [6] for the simple metals are presented. The results are compared with earlier important studies of Ho [7] and Popovic *et al* [8] and others and also with the experimental results.

A (semi-)local version [9] of the 'norm-conserving' *ab initio* pseudopotential, derived earlier by Bachelet *et al* [10], was found to provide a reasonable account for a host of lattice mechanical properties



of simple metals. We have also calculated the vacancy formation energy for the seven simple metals using this version of AP with five different exchange-correlation functions (Geldart-Vosko [11], Sham [12] and Sarkar *et al* [13] in addition to the other two) in second order (perturbation) approximation.

2. Theory

The structure-dependent parts of the total energy per ion of a simple metal, arising from three interaction potentials (ion-ion, ion-electron and electron-electron) are given by the band-structure and electrostatic terms. Any deformation in crystal structure changes these two terms only. For a pure lattice, they are given by [2]:

$$E_{str} = E_{es} + E_{bs} = \sum_q |S_q|^2 U_q - U_0 \quad (1)$$

with,

$$U_q = \lim_{\eta \rightarrow \infty} \frac{2\pi z^2 e^2}{\Omega q^2} \exp\left(\frac{-q^2}{4\eta}\right) + |w_q|^2 \chi_q \epsilon_q \quad \text{and} \quad U_0 = \lim_{\eta \rightarrow \infty} \frac{z^2 e^2 \sqrt{\eta}}{\sqrt{\pi}}$$

where $\epsilon_q = 1 - \frac{4\pi e^2}{q^2} (1 - f_q) \chi_q$ is the static dielectric function,

S_q , f_q , and χ_q being the structure factor, the ECF and the Lindhard response function (static) respectively; screened pseudopotential formfactor w_q is the plane wave matrix elements of bare ion-electron pseudopotential divided by ϵ_q and Ω is the ionic volume. Here the band structure energy (E_{bs}) is derived using second order perturbation formalism using pseudopotential and the bare ion formfactor w_q^0 for the usual two parameter HA pseudopotential is given by:

$$w_q^0 = -\frac{4\pi z e^2}{\Omega q^2} \left\{ (1+u) \cos qr_c - \frac{u}{qr_c} \sin qr_c \right\} \quad (2)$$

On the other hand, the full nonlocal *ab initio* pseudopotential is formally written as:

$$\hat{w} = w(r) + \sum_l w_l(r) \hat{P}_l$$

where \hat{P}_l is the projection operator on angular momentum l . The analytical forms for $w(r)$ and $w_l(r)$ together with the tabulated parameters are given in [10]. The Fourier transform of the local part $w(r)$ plus the matrix element of the purely nonlocal part \hat{w}^{nl} between the initial $|\vec{k}_i\rangle$ and the final $|\vec{k}_f\rangle$ plane-wave states comprise the generalized formfactor. The contribution of the nonlocal part is given by

$$\begin{aligned} \langle \vec{k}_f | \hat{w}^{nl} | \vec{k}_i \rangle &= \frac{4\pi}{\Omega} \sum_l (2l+1) P_l(\cos \theta) \\ &\times \int w_l(r) j_l(|\vec{k}_i|r) j_l(|\vec{k}_f|r) r^2 dr \end{aligned} \quad (3)$$

where, spherical symmetry of the ionic pseudopotential is assumed and P_l and j_l are Legendre polynomials and spherical Bessel functions respectively, with

$$\cos \theta = \frac{\vec{k}_i \cdot \vec{k}_f}{(|\vec{k}_i| |\vec{k}_f|)}$$

The formfactors are determined using a semilocal approximation beyond the ‘on-Fermi-sphere’ approximation by considering scattering in all possible directions (on and off the Fermi sphere) [9]. The usual local approximation retains only the on-Fermi-sphere (OFS) back scattering terms in eqn.(3) which gives formfactors that result in a large value of resistivity (almost double) for simple metals such as Na, Mg and Al. The formfactors w_q^0 of AP so determined are considerably short ranged, smooth with fewer oscillations and smaller amplitude [9] (more than 25% reduction of the formfactor at the first maximum near $1.9k_f$ for Al compared to the OFS value) and appears to retain some essential nonlocal features as indicated by Heine and Weaire [14]. It should be also noted that, the approximation saves a lot of computation compared to the nonperturbative nonlocal calculation and yet produces reasonable agreement

with experimental values which suggests fair degree of reliability of the semilocal formfactors.

Finally, the single vacancy (or monovacancy) formation energy up to 2nd order perturbation is given by [1]

$$E_f^{1v} = \sum_{q_0} \frac{q_0}{3} \frac{\partial U_{q_0}}{\partial q_0} + \frac{\Omega}{2\pi^2} \int_0^\infty U_q q^2 dq, \quad (4)$$

where q_0 and q represent the discrete and quasi-continuous wave numbers respectively.

3. Results

The results of our calculations with model pseudopotentials are presented and compared with other similar calculations in Table-II. The pseudopotential parameters are adjusted to satisfy the extrapolated ‘harmonic’ equilibrium condition exactly and an overall agreement of different lattice mechanical properties [6]. The ‘harmonic’ equilibrium lattice constants and the model parameters of the seven simple metals are given in Table-I. For Al and Mg, an arbitrary exponential cut-off factor $\exp(-\frac{\zeta q^2}{4k_F^2})$ is applied to the formfactor of eqn.(2) for better convergence. Our model pseudopotential calculations of vacancy formation energy show small variations with respect to different exchange-correlation functions and the results are in fair agreement with the experimental data. The comparison shows that reliable model (pseudo)potential for number of simple metals can indeed be obtained for explaining a host of properties.

Table-I : The ‘harmonic’ equilibrium lattice constants and HA model parameters for both Taylor (T) and Vashishta-Singwi (VS) ECFs (taken from earlier unified studies [6].)

Metals	Lattice Constant ‘a’ (harmonic values) in au	Model HA + T			Model HA + VS		
		r_c in au	u	ζ	r_c in au	u	ζ
Li	6.5621	1.4850	-0.1990	0	1.4958	-0.254	0
Na	7.9403	2.2985	-0.6177	0	2.3540	-0.675	0
K	9.8624	3.1550	-0.6545	0	3.2780	-0.738	0
Rb	10.5338	3.5835	-0.7384	0	3.7210	-0.808	0
Cs	11.4226	3.9596	-0.7341	0	-	-	-
Al	7.5811	1.2745	-0.3438	0.05	1.2586	-0.3418	0.05
Mg	6.01564 c/a = 1.6231	1.68	-0.568	0.10	-	-	-

Table-II : Results of the present calculation of vacancy formation energy in Ryd. using HA local model pseudopotentials, compared with other model calculations and experimental data.

Metals	Ho	Chulkov		Popovic et al*	Present calculation		Expt.	
		GV	VS		HA+T	HA+VS		
Li	0.027			0.021 (0.028)	0.032	0.030	0.0294 ^a	0.0250 ^b 0.0353 ^c
Na	0.029			0.030 (0.035)	0.027	0.026	0.0287 ^a	0.0309 ^d 0.0265 ^e
K	0.026			0.026 (0.031)	0.031	0.027	0.0287 ^a	
Rb	0.026			0.023 (0.032)	0.028	0.026	0.0198 ^f	
Cs	0.024			0.021 (0.030)	0.029	-	0.0206 ^g	
Al				0.063 (0.065)	0.064	0.059	0.056 ^h	
Mg		0.066	0.045		0.047	-	0.043 ⁱ	0.059 ^j

* Results given within parenthesis are of calculations with present formulation using model potential parameters and local-field correction factors of Popovic *et al* calculations [8].

^a Ref.[15], ^b Ref.[16], ^c Ref.[17], ^d Ref.[18], ^e Ref.[19], ^f Ref.[20], ^g Ref.[21], ^h Ref.[22], ⁱ Ref.[23], ^j Ref.[24].

The formulation of vacancy formation by Popovic *et al* [8] is based on the previous work of Ho [7], but with some modifications. They have maintained vacancy formation as a bulk phenomenon while

Ho's derivation involves surfaces. According to the authors, "The differences are not numerically very significant in the alkalis but are critical in Al for which we obtain satisfactory results" compared to those from Ho's theory.

There is also a minor difference with the energy expression of our formulation. In Popovic *et al* formulation, one atom is taken out to keep the lattice volume fixed and a relaxation term is considered. The relaxation energy term, although can be formulated in this constant volume condition, is usually very small as pointed out by Ho [7]. The vacancy relaxation in alkali metals is less than 4% and for Al, it is about 2% of the radial distance for the nearest neighbours. The relaxation energy is only about 10 – 15% of the vacancy formation energy and is, however, not a determining factor for calculating formation energy [25-27]. Popovic and Carbotte [28] have also formulated the lattice statics method for hcp metals and their calculated relaxation energy indicates that in Mg, as is the case in Al, the relaxation contribution to the vacancy formation energy is small. Chulkov [29] has studied the vacancy formation energy of hcp metals Be and Mg along with other polyvalent metals without taking into account lattice relaxation energy. In his extensive second order perturbation calculations with four different local-field correction factors including those of Geldart-Vosko (GV) and Vashishta-Singwi (VS), he used Krasko and Gurskii model pseudopotential. For Mg, the calculation gives reasonable results which are compared in Table-II.

Our calculated vacancy formation energies appear to be slightly higher compared with others' calculations, where a relaxation term appears. Also, Popovic *et al* have used high temperature lattice constant and bulk modulus as inputs to determine the model potential parameters and pointed out that vacancy formation energy decreases with increasing temperature. This might be one reason for difference in the results. Yoshioki and Mori [30] and So and Woo [31] have extended their studies for simple metals (Na, K, Al and Mg) to third-order, using local and nonlocal model pseudopotentials respectively. The significance of these studies will be discussed in the next section.

It is also appropriate to note here that, the formation energy measurements are generally much less precise and reproducible. The theoretical procedure employed to extract formation energies from experiments is based on a theorem proven in the harmonic approximation only and the assumption regarding the similarity of the effect of anharmonicity on both the vacancy formation and lattice expansion warrants further scrutiny.

Bachelet *et al* have developed a consistent set of 'norm-conserving' *ab initio* pseudopotentials for almost all elements across the entire periodic table to reproduce the results of all-electron calculations for the self-consistent electronic structure of atoms and with optimum transferability to various systems. However, the calculations with this nonlocal potential require huge computation which restricts the scope of extensive theoretical studies. In an earlier work, one of the authors of the present paper has determined the formfactors using a semilocal approximation beyond the on-Fermi-sphere approximation. The pseudopotential formfactors together with the linear dielectric screening provides encouraging results for various lattice mechanical and transport properties of simple metals in a perturbative calculation beyond second order. In Table-III, the results of our calculations of simple metal vacancy formation energies using this *ab initio* pseudopotential are compared with the experimental data.

Table-III : Simple metal vacancy formation energies in Ryd. using *ab initio* pseudopotential (up to second order) with five different dielectric functions.

Metals	Sham	Geldart -Vosko	Vashissta -Singwi	Taylor	Sarkar
Li	0.051	0.050	0.043	0.045	0.046
Na	0.035	0.035	0.035	0.029	0.030
K	0.056	0.054	0.053	0.055	0.059
Rb	0.064	0.062	0.064	0.067	0.071
Cs	0.079	0.078	0.083	0.091	0.095
Al	0.070	0.083	0.038	0.033	0.069
Mg	0.087	0.087	0.063	0.060	0.081

Except for Na and Al, the results of our second order *ab initio* calculations differ appreciably from the available experimental data for the other simple metals. This is expected considering the importance of the higher order perturbation contribution. Several studies [26,32-37] on defect properties of metals using *ab initio* pseudopotential have been reported in the literature. However, the studies are in most

cases made for only one or two metals in isolation. In the next section we discuss our result and compare it with other *ab initio* calculations.

4. Discussions

DuCharme and Weaver have earlier observed [1] that the model potentials which best fit the phonon dispersion curves produce the most reasonable values of activation energy. The model pseudopotentials of our earlier unified studies, give satisfactory description of the phonon dispersion curves of the simple metals under study. From our present calculations it appears that second-order perturbation theory with Heine-Abarenkov local model pseudopotential give fairly good account of the properties of the simple metals under investigation.

In both Yoshioki-Mori calculations using local model pseudopotential and So-Woo calculations with two nonlocal model pseudopotentials for simple metals, comparison shows that the maximum third-order perturbation contribution is only about 7% of the corresponding second-order contribution. This means that the perturbation series do converge reasonably well in all these cases. The calculated third-order vacancy formation energies for Na and K agree fairly with corresponding experimental values. But, since the vacancy formation energies in the second order is a small difference of two large quantities, for multivalent Mg and Al, both the convergence and as well as the agreement of the overall results with the experimental values get worsened with the inclusion of the third-order terms [31]. However, we have found that since the order-wise sums of the perturbation series make an oscillating series, the results can be improved to reasonable values using series convergence acceleration procedures.

Several authors have studied the defect properties of metals using different first principle techniques including *ab initio* pseudopotential. Calculations of both the relaxed and unrelaxed constant volume formation energy and the formation volumes at constant pressure have been reported in the literature. Frank *et al* [32] in their investigation using ‘norm-conserving’ *ab initio* pseudopotential have noted that the vacancy migration energy for Li is appreciably small and the vacancy formation energy is very close to the experimental value of activation energy. Apart from this study, Benedek *et al* [33] and Pawellek *et al* [34] have also calculated the formation energy for Li using ‘norm-conserving’ pseudopotentials. Schott *et al* [35] and Jacucci and Taylor [26], however, have calculated the vacancy formation energies for the three alkali metals Li, Na and K.

The result of our second order formation energy calculation for Li compared well with the results 0.039 Ryd, 0.040 Ryd, 0.044 Ryd, 0.042 Ryd and 0.038 Ryd as obtained by Schott *et al* (using Kohn-Sham density functional approach), Frank *et al*, Pawellek *et al*, Benedek *et al* (all using ‘norm-conserving’ *ab initio* pseudopotentials) and Jacucci and Taylor (using *ab initio* DRT pair potential) respectively. Similarly, for Na and K our results are comparable with those obtained by Schott *et al*. Also, the first principle calculations by Polatoglu *et al* [36] and Gillan [37] for Al also comparable with our results.

For Li, Na, Al and Mg the contributions of nonlocal part are reasonably smaller compared to those from local part and for K, the two are comparable. But for heavier alkali metals Rb and Cs, nonlocal contributions are even greater than those from the local parts! This is, however, expected since nonlocality appears as a general characteristic of a single-particle description of a manybody system [38]. *Ab initio* pseudopotentials are derived from all-electron atomic reference states with the requirement that the pseudo and all-electron valence eigenstates and energy agree beyond a chosen core radius. This makes them nonlocal and larger the atom – stronger the nonlocality.

For K, Rb and Cs and also for the polyvalent metal Al and Mg, different exchange-correlation functions produce large variations in nonlocal contributions. For heavier alkali metals, there are considerable variations in the local contributions too. More importantly, for all the simple metals studied here, the nonlocal contributions are significant to the overall formation energy values. In general, the contributions of the successive l -terms in the nonlocal part are of decreasing importance. Beyond $l = 2$, the contributions are found insignificant for Rb and Cs and we have ignored presumably further insignificant S-O coupling terms in *ab initio* pseudopotential of Ref. [10] for these two metals.

The results of our *ab initio* second order calculation appear fairly reasonable considering the importance of third order term [9] and are comparable with other first principle calculations. The five different exchange-correlation functions used in our second order calculation show some variations among themselves. The variations are most prominent with Vashishta-Singwi and Taylor ECFs in the case of Al. For *ab initio* pseudopotentials higher order perturbation terms usually become important and can not be neglected.

The present study clearly indicates that, at least for the simple metals, reliable local model pseu-

dopotential may be constructed for second order perturbation calculation to provide a fair description of both the perfect and imperfect lattice properties. On the other hand, a microscopic study with *ab initio* pseudopotential requires beyond second order perturbation term(s). However, it appears that the semilocal approximation adopted here retains the essential nonlocality of Bachelet *et al's* AP in explaining the defect properties of the simple metals. We intend to extend the present study with the higher order perturbation terms of the semilocal *ab initio* pseudopotential. The perturbation series being an oscillating one [9], reasonable improvement of the calculational results are expected with the use of suitable series convergence acceleration procedures. Only then, a proper assessment of the different exchange-correlation functions would be possible.

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