

Non-split interstitial formation in Cu, Ag, Au and Pb based systems

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Abstract : Expressions for formation energies (E_{FH}'') for different non-split interstitials considering relaxation effect and their changes for impurity interstitial ($\Delta E_F'$) are formulated here using the framework of pseudopotential formalism. Calculations of these energy terms in four fcc metals, viz. copper, silver, gold and lead are discussed here using Heine-Abarenkov model potential with Taylor's exchange and correlation for octahedral, tetrahedral and crowdion type of interstitial.

Keywords : fcc metals, non-split interstitials, pseudopotential formalism

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1. Introduction

Studies on interstitials are interesting due to their complicated nature of formation and motion through different solid substances [1], [2]. In Harrison's approach [3] the perturbation in the conduction electron distribution caused by the creation of a defect is sufficiently weak to be treated in a simple linear response formalism. Any defect in the lattice changes the structure dependent lattice energy and so an algebraic difference between the energy after defect creation and that before will yield the defect formation energy when considered for the whole lattice. This structure dependent total energy depends on ion-ion, ion-electron and electron-electron interactions and is also dependent on the modified lattice wave numbers. The modification in the lattice wave numbers from its perfect lattice value is necessary to maintain the lattice volume and the number of lattice ions constant [4]. In this paper formulations for formation energies and their change in presence of impurities of different non-split interstitials, viz. octahedral, tetrahedral and crowdion, in very dilute binary alloys of copper, silver, gold and lead are derived and the results are discussed.

2. Formulations

Let us consider a lattice consisting of I number of substitutional impurities and a total of N ions. The impurities are distributed throughout the lattice so that the interactions among

impurity ions are almost negligible ($I \ll N$). The total structure dependent energy of this lattice is given by [3], [5], [6]

$$E = \sum_q \left[|S(q)|^2 U(q) + \sum_{i=1}^I \left\{ S(q) e^{i\mathbf{q} \cdot \mathbf{r}_i} + S^*(q) e^{-i\mathbf{q} \cdot \mathbf{r}_i} \right\} \Delta U(q) + \left| \sum_{i=1}^I e^{i\mathbf{q} \cdot \mathbf{r}_i} \right|^2 \Delta^2 U(q) \right] - \lim_{\eta \rightarrow \infty} \frac{(N-I) Z_H^2 + I Z_I^2}{N} e^2 \sqrt{\frac{\eta}{\pi}}, \quad (1)$$

where

$$U(q) = \lim_{\eta \rightarrow \infty} \frac{2\pi Z_H^2 e^2}{\Omega_H q^2} e^{-q^2/4\eta} + [\omega_H(q)]^2 \varepsilon_H(q) \chi_H(q), \quad (2)$$

$$\Delta U(q) = \lim_{\eta \rightarrow \infty} \frac{2\pi(Z_I - Z_H)Z_H e^2}{\Omega_H q^2} e^{-q^2/4\eta} + [\omega_I(q) - \omega_H(q)] \omega_H(q) \varepsilon_H(q) \chi_H(q). \quad (3)$$

$$\Delta^2 U(q) = \lim_{\eta \rightarrow \infty} \frac{2\pi(Z_I - Z_H)^2 e^2}{\Omega_H q^2} e^{-q^2/4\eta} + [\omega_I(q) - \omega_H(q)]^2 \varepsilon_H(q) \chi_H(q) \quad (4)$$

and

$$S(q) = \sum_{i=1}^N \exp(-i\mathbf{q} \cdot \mathbf{r}_i) / N. \quad (5)$$

The subscripts H and I are for host and impurity respectively, Z the valency, Ω_H the atomic volume, e the electronic charge, η the convergence factor, \mathbf{q} the wave number, $S(q)$ the structure factor, \mathbf{r}_i the position vector for the i th ion in the lattice, $\omega_H(q)$ the pseudopotential for the host, $\varepsilon_H(q)$ the dielectric function and $\chi_H(q)$ the perturbation characteristics. The expressions for $\varepsilon_H(q)$, $\chi_H(q)$ and $\omega_I(q)$ are given by [7, 8]

$$\varepsilon_H(q) = 1 - \frac{8\pi e^2}{\Omega_H q^2} [1 - f_H(q)] \chi_H(q), \quad (6)$$

$$\chi_H(q) = -\frac{3Z_H}{4\varepsilon_{FH}} \left[(1/2) + \frac{4k_{FH}^2 - q^2}{8qk_{FH}} \ln \left| \frac{2k_{FH} + q}{2k_{FH} - q} \right| \right] \quad (7)$$

and

$$\omega_I(q) = \frac{\Omega_I \varepsilon_I(q)}{\Omega_H \varepsilon_H(q)} \omega_I^0(q). \quad (8)$$

Here, $f_H(q)$ is the exchange and correlation, ε_{FH} and k_{FH} are the Fermi energy and wavenumber respectively and $\omega_I^0(q)$ is the form factor for the impurity in its pure state. The structure factor for the perfect lattice $S(q)$ is defined as

$$\begin{aligned}
 S(q) &= 1 \text{ for } q = q_0 \\
 &= 0 \text{ for } q \neq q_0,
 \end{aligned} \tag{9}$$

q_0 the lattice wave number is defined as

$$q_0 = (m_1 / N_1)q_1 + (m_2 / N_2)q_2 + (m_3 / N_3)q_3 \tag{10}$$

with $m_1 / N_1, m_2 / N_2$ and m_3 / N_3 are integers including zero and q_1, q_2 and q_3 are the primitive wave numbers.

Let us consider a single defect in an otherwise pure lattice (*i.e.* $l = 0$). If the point defect is a non-split interstitial then the Brillouin zone volume has to be scaled down by a factor of $(N - 1)/N$ in order to keep the lattice volume constant, *i.e.* the lattice wave numbers are modified to $\mu_l q_0$ with $\mu_l \approx (1 - 1/3N)$. In presence of non-split interstitial the surrounding neighbours around it relax producing relaxation energy. Finally, one gets the expression for non-split formation energy (E_{FH}^l) using eq. (1), as

$$\begin{aligned}
 E_{FH}^l &= \sum_{q_0} \left[2(\cos q_0 \cdot r_i - 1)U(q_0) - \frac{q_0}{3} \frac{\partial U(q_0)}{\partial q_0} + \sum_{i=1}^{n_i} 2(\cos q_0 \cdot r_i' - \cos q_0 \cdot r_i)U(q_0) \right] \\
 &+ \frac{\Omega_H}{2\pi^2} \int_0^\infty \left[1 + \sum_{i=1}^{n_i} 2 \left(\frac{\sin q |r_i - r_i|}{q |r_i - r_i|} - \frac{\sin q |r_i - r_i'|}{q |r_i - r_i'|} \right) \right. \\
 &\left. + \sum_{i=1}^{n_i} \sum_{j=1}^{n_j} \left(\frac{\sin q |r_i - r_j|}{q |r_i - r_j|} - 2 \frac{\sin q |r_i - r_j'|}{q |r_i - r_j'|} + \frac{\sin q |r_i' - r_j'|}{q |r_i' - r_j'|} \right) \right] U(q) q^2 dq, \tag{11}
 \end{aligned}$$

where n_i is the number of relaxed neighbours around the non-split interstitial, r_i' the relaxed position of the *i*th neighbour with original position vector r_i and r_i the interstitial position.

When the impurity is at an interstice it changes the interstitial formation energy. The change in this case of formation energy is given by

$$\begin{aligned}
 \Delta E_F^l &= \sum_{q_0} 2(\cos q_0 \cdot r_i - 1) \Delta U(q_0) \\
 &+ \frac{\Omega_H}{\pi^2} \int_0^\infty \left[1 + \sum_{i=1}^{n_i} \left[\frac{\sin q |r_i - r_i|}{q |r_i - r_i|} - \frac{\sin q |r_i - r_i'|}{q |r_i - r_i'|} \right] \Delta U(q) q^2 dq \right]. \tag{12}
 \end{aligned}$$

So we have two expressions for defect formation energy and its change in presence of impurity ion. Several other formulations can be deduced using equation (1) viz. (i) host interstitial formation energy in presence of substitutional impurity at an adjacent lattice site, (ii) split interstitial formation energy with one or two impurities, etc.

3. Discussion

Here integration over quasi-continuous wave numbers is done by quadrature technique and the discrete sum is done over lattice wave numbers. Calculations are done using Heine-Abarenkov model potential and Taylor's exchange and correlation (hence forth called HAT). For simplicity, relaxation effect is not considered in these calculations [1]. Out of six kinds of interstitials calculations, only for non-split type, viz. octahedral, tetrahedral and crowdion, are discussed here in cases of noble metals (copper, silver and gold) and lead as both host and impurity. From the above formulation, it seems that the values of formation energy and its change (E_{FH}^{II} and $\Delta E_F'$) will be large in cases of heterovalent systems in comparison to homovalent systems due to valency, pseudopotential and exchange and correlation. Table 1 gives the input parameters utilised in the present calculations while Table 2 gives the calculated values of E_{FH}^{II} and $\Delta E_F'$. It is found that HAT combination yields slightly lower values of E_{FH}^{II} in comparison to the values calculated by [1]. They reported the values of E_{FH}^{II} for octahedral, tetrahedral and crowdion type in cases of copper, silver and gold as respectively (0.25, 0.34, 0.40), (0.22, 0.31, 0.36) and (0.21, 0.30, 0.35) Rydbergs. Other previous calculations were also shown in their work. Lower values in the present calculations arise due to the fact that relaxation effect is not considered. There is a systematic increase in the value of E_{FH}^{II} from octahedral to crowdion for each metal which most probably indicates that the crowdion type is more unstable. It has been pointed out by [2] that the stable interstitial configuration in noble metals is |100| split. In case of lead, E_{FH}^{II} is negative for the octahedral configuration and has large positive values in comparison to those of noble metals for the other two configurations. This perhaps indicates the lower probability of occurrence of these defects in lead where vacancy plays the dominant role [9]. Hence the present calculations agree fairly well with the earlier calculations.

Table 1. Parameters used for defect energy calculations and pseudopotential for pure metals

Metal	Z	a	Ω	k_{FH}	ϵ_{FH}	r_{m^*}	A *
		AU	AU	AU	Rydberg	AU	Rydberg
Cu	1.0	6 8219	79.370	0.7199	0.5182	2 407	0.8308
Ag	1.0	7.7101	114.582	0.6369	0.4057	2.716	0.7364
Au	1.0	7 6912	113.742	0 6385	0 4077	2 715	0.7366
Pb	4.0	9 3542	204.622	0.8334	0.6945	2.0109	3.1827

* taken from [6]

The computed values of the change in the impurity-interstitial formation energy over host interstitial ($\Delta E_F'$) are also shown in Table 2, and it is found that $\Delta E_F'$ gradually increases in magnitude from octahedral to crowdion and their orders of magnitude are in accordance with the earlier calculations [2]. Also every binary system of noble metals and its reverse (say Cu-Ag and Ag-Cu) shows complementary character. But it is not so in the case of lead based systems where Cu, Ag, and Au impurity crowdion formations show lower values than host interstitial formation. Thus they are more probable than host crowdion interstitial formation. At present, there are very few experimental data on point defect parameters. So it is difficult to say the last word about the calculated defect parameters.

Table 2. Evaluated defect formation energies and its change (in Rydbergs) for Cu, Ag, Au and Pb based binary systems.

Metal	$E_{FH}^{I/}$	$E_{FH}^{I/}$	$E_{FH}^{I/}$	system	$\Delta E_F^{I/}$	$\Delta E_F^{I/}$	$\Delta E_F^{I/}$
	Oct	tetra	crow		oct	tetra	crow
Cu	0.1738	0.2580	0.3201	Cu-Ag	0.0591	0.0577	0.0578
				Cu-Au	0.0590	0.0575	0.0577
				Cu-Pb	0.6498	0.9025	1.0872
Ag	0.1580	0.2326	0.2881	Ag-Cu	-0.0440	-0.0426	-0.0424
				Ag-Au	-0.0001	-0.0001	-0.0001
				Ag-Pb	0.4188	0.6489	0.8152
Au	0.1592	0.2339	0.2895	Au-Cu	-0.0440	-0.0425	-0.0423
				Au-Ag	0.0001	0.0001	0.0001
				Au-Pb	0.4253	0.6559	0.8225
Pb	-0.0444	0.8759	1.6859	Pb-Cu	0.8120	0.11930	-0.4915
				Pb-Ag	1.0040	0.3397	-0.2751
				Pb-Au	1.0040	0.3392	-0.2756

It has been mentioned earlier that a proper choice of a pseudopotential is very important and careful attention must be paid in achieving accuracy in numerical computation in order to arrive at a meaningful result. Hence, Heine-Abarenkov model with approximate overall explanation of all atomic properties is perhaps a good choice.

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