Research Article

Defect Studies in bcc and fcc Iron

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Variation of vacancy formation energy (E_F^{lv}) with r_c of Ashcroft's empty core model potential (AECMP) model for different exchange and correlation functions (ECFs) show almost independent nature but slight variation with ECF for both bcc α iron and fcc γ iron.

1. Introduction

Recently in some papers, defect structures in α -Fe were discussed using Monte Carlo (MC) technique [1, 2], *ab initio* density functional (PP) model [3–5], and molecular dynamics (MD) simulation [6]. Iron exists in different phases, namely α -Fe (room temperature to 768°C, bcc structure, lattice constant $a = 5.48$ AU, and ferromagnetic), β -Fe (768°C to 910°C, bcc structure, $a = 5.48$ AU, and nonmagnetic), γ -Fe (910°C to 1400°C, fcc structure, $a = 6.73$ AU, and paramagnetic), and δ -Fe (1400°C to 1535°C, bcc structure again). Korhonen et al. [7] predicted that the stability of a self-interstitial in bcc-Fe depends on the range of potential but not on the type, while Osetsky et al. [8] predicted significant larger values of vacancy formation energy than the experimental ones in cases of bcc V and Cr using LDA.

Söderlind et al. [9] incorporated the results of above two groups of researchers using a full-potential, linear muffin-tin-orbital (FP-LMTO) method in conjunction with both the local-density approximation (LDA) and the generalized-gradient approximation (GGA) in bcc metals. A complementary *ab initio* pseudopotential (PP) method has also been used. They predicted FP-LMTO-LDA and PP-LDA formation energies are nearly identical within or close to experimental error bars for all bcc metals except Cr, and the overall agreement with experiment is better for the 4d and 5d metals than the 3d metals. GGA and LDA formation energies

are very similar for the 4d and 5d metals but for the 3d metals, and especially Fe, GGA performs better. The dominant structural effects are an approximate 5% inward relaxation of the first near-neighbor shell for group V metals and a corresponding 1% inward relaxation for group VI metals, with the exception of Mo, for which the second-shell atoms also relax inward by about 1%. Thus it will be interesting to use in this paper the one parameter (r_c) Ashcroft's empty core model potential (called here after AECMP) [10] to study the variation of monovacancy formation energy (E_F^{lv}) in iron with the help of nine different types of exchange and correlation functions (called ECF) [11–20].

2. Formulations

The structure-dependent energy of a crystal 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 electrostatic energy and the last two interactions are included in the band structure energy, which is calculated using the second-order perturbation theory incorporating pseudopotential model form [16]. When a vacancy is created the Brillouin zone volume has to be scaled up in order to keep the lattice volume constant and so the lattice wave numbers are modified. Finally,

TABLE 1: Different forms of ECF $f(q)$ and corresponding fitted value of parameter r_c of AECMP in atomic unit (AU).

	Different forms of $f(q)$	bcc α -Fe	fcc γ -Fe
King and Cutler [11, 12]	$\frac{q^2}{2(q^2 + 2k_F^2)}$	1.1017	1.0028
Sham [13]	$\frac{q^2}{2(q^2 + k_F^2 + 2k_F/\pi a_0)}$	1.1176	1.0204
Geldert and Vosko [14]	$\frac{q^2}{2[q^2 + 2k_F^2/(1 + (0.026m'/m)(3\Omega/4\pi za_0^3)^{1/3})]}$	1.1069	1.0083
Kleinman [15]	$\frac{1}{4} \left[\frac{q^2}{k_F^2 + 2k_F/\pi a_0} + \frac{q^2}{q^2 + k_F^2 + 2k_F/\pi a_0} \right]$	1.1536	1.0496
Harrison [16]	$\frac{q^2}{2(q^2 + k_F^2 + k_F^2/3)}$	1.1432	1.0478
Vashishta and Singwi [17]	$A(1 - e^{-Bq^2/k_F^2})$	1.1539	1.0501
Taylor [18]	$\frac{q^2}{4k_F^2} \left(1 + \frac{0.1534}{\pi k_F} \right)$	1.1687	1.0566
Hubbard [19]	$\frac{q^2}{2(q^2 + k_F^2)}$	1.1723	1.0789
Mahanti and Das [20]	$\frac{q^2}{k_F^2[1 + (2/(1 + (0.026m'/m)(3\Omega/4\pi za_0^3)^{1/3}))^2]} + \frac{q^2}{q^2 + k_F^2[1 + (2/(1 + (0.026m'/m)(3\Omega/4\pi za_0^3)^{1/3}))^2]}$	1.2334	1.1282

one gets the expressions for vacancy formation energy E_F^{1v} considering relaxation energy associated with these defect formations as

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

where

$$U(q) = \frac{Lt}{\eta - \infty} \frac{2\pi e^2 z^2}{\Omega q^2} e^{-q^2/4\eta} + [w(q)]^2 \varepsilon(q) \chi(q), \quad (2)$$

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

$$\varepsilon(q) = 1 - \frac{8\pi e^2}{\Omega q^2} [1 - f(q)] \chi(q), \quad (4)$$

$$\chi(q) = -\frac{3z}{8E_F} \left[1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right]. \quad (5)$$

Here q_0 and q are the lattice and quasi-continuous wave numbers, respectively, Ω is the atomic volume, e the electronic charge, z the valency, η the convergence factor, k_F the Fermi wavenumber, E_F the Fermi energy, $w(q)$ the AECMP with parameter r_c , $\varepsilon(q)$ the dielectric function or screening factor, $\chi(q)$ the perturbation characteristics, and $f(q)$ the ECF whose nine different forms have been shown in Table 1.

3. Discussions

The calculation of (1) needs integration over quasi-continuous wavenumbers by quadrature technique and the discrete sum over lattice wave numbers. The input and output parameters for this purpose for fcc iron (γ -Fe) and bcc iron (α -Fe) are shown in Table 2. In the first step the variation of E_F^{1v} with parameter r_c of AECMP is plotted for nine different ECF from 0 to 5 AU as shown in Figure 1 for fcc iron (γ -Fe) and Figure 2 for bcc iron (α -Fe). The two graphs have positive peaks and they look almost similar due to $\cos^2 q r_c$ term of AECMP for all exchange and correlations but there is a slight variation. 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 $a_0 \leq r_c < 2\pi/k_F$, where a_0 is the Bohr radius.

It is observed that the experimental value of E_F^{1v} , obtained from positron annihilation technique, lies within the range of the theoretical value of it obtained from the empirical relation [23–25]:

$$T_m(K) = 1200E_F^{1v} = 660Q_0 = 360E_{\text{coh}}. \quad (6)$$

Here T_m is the melting temperature, Q_0 the activation energy, and E_{coh} the cohesive energy of the metal. From the experimental value of E_F^{1v} we note that the fitted value of r_c is within the first peak value of 2 AU and we note from Table 2 that r_c values lie close to Bohr radius ($a_0 = 1$ AU). ECF's of Kleinman [15], Harrison [16], Vashishta and Singwi [17],

TABLE 2: Input and output parameters for fcc and bcc iron (1 eV = 13.605 Rydberg and 1 atomic unit (AU) = 5.29177×10^{-2} nm).

	fcc γ -Fe	bcc α -Fe
Valency z	2	2
Lattice constant a AU	6.727	5.424
Volume AU ³	76.118	79.765
k_F AU ⁻¹	0.920	0.905
E_F Ryd.	0.846	0.820
Melting temperature T_m (K)	1536	1811
Cohesive energy E_{coh} eV	4.28	4.28
Activation energy for self-diffusion Q_0 eV	2.943	2.658
Vashishta-Singwi parameters		
A	0.929633	0.938470
B	0.309178	0.312208
E_F^{1v} (theo) in eV ¹	1.284–1.619	1.284–1.509
E_F^{1v} (expt) in eV ²	1.40	1.60
Range of r_c fitted to E_F^{1v} (expt) in AU	1.0028–1.1282	1.1017–1.2234
Mean r_c in AU	1.0492	1.1501

¹ Using (6) [21]; ² [22]. E_F^{1v} - r_c plot for fcc iron (γ -Fe)

— King-Kutler — Kleinman — Taylor
— Sham — Harrison — Hubbard
— Geldart-Vosko — Vashishta-Singwi — Mahanti-Das

FIGURE 1: E_F^{1v} - r_c plot for fcc γ -iron (γ -Fe). E_F^{1v} - r_c plot for bcc iron (α -Fe)

— King-Kutler — Kleinman — Taylor
— Sham — Harrison — Hubbard
— Geldart-Vosko — Vashishta-Singwi — Mahanti-Das

FIGURE 2: E_F^{1v} - r_c plot for bcc α -iron (α -Fe).

and Taylor [18] give reasonably close values of r_c while others give the range over of r_c .

In conclusion, it should be noted that the inherent simplicity of AECMP makes it difficult to have a universal r_c parameter for all types of atomic property calculations and we have to use different ECFs of which Taylor, Harrison, Kleinmann, Vashishta and Singwi type of ECF give better results in this case.

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