BCC Fe surface and cluster magnetism using a magnetic potential

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Abstract

A semi-empirical potential for ferromagnetic bcc iron that also models the co-linear magnetic moment of each atom, has been applied to clusters and surfaces. Surface energies of low index facets, surface relaxation and magnetic moment are calculated and compared to various other empirical potentials, recent density functional theory (DFT) results and experimental data. Quantitatively the resulting surface magnetic moments enhancements are underestimated, however qualitatively the general behavior of the magnetic moment as a function of surface or cluster layer is comparable to that predicted by DFT calculations.
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1. Introduction

The recent development of an empirical potential for bcc Fe [1–3] that explicitly takes into account the contribution of itinerant ferromagnetism to atomic cohesion, opens a new path for large scale atomistic simulations in which the co-linear magnetic structure of atomic configurations can be investigated. The need for such a potential was demonstrated by density functional theory (DFT) calculations demonstrating that the local magnetic moment of single self-interstitial defects in bcc Fe is significantly altered at and around the defects due to the large local deformations [4,5]. As a result, the lowest self-interstitial defect structure for bcc Fe is the 1 1 0 dumbbell instead of the 1 1 1 crowdion as it is for the group V and VI non-magnetic bcc transition metals [6]. The interstitial cluster kinetics for Fe being unique amongst the bcc metals [7], it can be expected that defect kinetics have to be reconsidered especially for materials developed for extreme environments in terms of temperature, pressure and irradiation. Since modelling plays an

important role in this research field, it is necessary to be able to perform multi-million magnetic-atomistic simulations with a computational efficiency equal to that of any other empirical potential model – a regime traditional density functional theory (DFT) methods cannot address. For example, large dislocation loop structures can now be routinely modelled where the elastic strain fields surrounding the defect perturb the bulk magnetic moment [2,3] – the so-called magneto-elastic effect [8].

The only property used in the fitting of the magnetic potential for under coordinated environments was the vacancy formation energy, and no application of the method to more complex cases with reduced coordination environments have thus far been considered. Surface magnetism constitutes an important domain of application of the magnetic potential since accurate quantum mechanical results and experimental data are readily available for comparison. For example, DFT calculations have shown that surfaces are characterised by a higher magnetic moment in comparison to the bulk [9]. This, together with detailed information on surface relaxation structures obtained using low energy electron surface diffraction [11–13], form an interesting test case for application of the magnetic potential. Similarly, moment enhancements have been

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observed for nano-sized clusters using Stern-Gerlach deflection spectrometry [10]. Measurements have also been performed on polycrystalline materials yielding an average surface energy for bcc Fe [14].

In the present work the co-linear magnetic structure of low Miller index bcc surfaces and of bcc clusters is calculated using the approach outlined in Refs. [1–3]. The paper is organised as follows. Section 2 presents the theoretical framework of the magnetic moment calculation using the magnetic potential. Section 3.1 discusses the surface relaxation structures for low index 100, 110 and 111 bcc Fe using the magnetic potential, and compares the results with other non-magnetic empirical potentials, DFT data and experiments. The surface co-linear magnetic moment predicted by the potential are compared to DFT results. Section 3.2 presents a similar analysis for small bcc clusters for which data from quantum mechanical calculations and experiments are available. In terms of surface energy, the magnetic potential produces the correct 100, 110 and 111 surface energy density ordering. For the surface and cluster co-linear magnetic moment predictions the magnetic potential generally underestimates the moment enhancement. For the 110 and 111 ideal surfaces the magnetic moment predictions are in qualitative agreement with DFT. The magnetic potential performs most unsatisfactorily for the 100 surface where the outward surface relaxation predicted by DFT calculations and observed in experiment is not predicted. The origin of this failure is discussed in Section 4 and concluded to be due to a strong 100 surface state close to the Fermi energy as is seen in both DFT calculations and experiment.

2. The magnetic potential model and the calculation of the local moment

Within the magnetic potential model [1–3], the total cohesive energy of N atoms may be written within the usual embedded atom method (EAM) formalism [15]:

$$E_{\text{tot}} = \sum_{i=1}^{N} F[\rho_i] + \frac{1}{2} \sum_{ij, i \neq j}^{N} V(r_{ij}), \qquad (1)$$

where the local electron density ρ_i is evaluated via

$$\rho_i = \rho_c \sum_{j, i \neq j} f(r_{ij}). \qquad (2)$$

Within the Finnis–Sinclair (FS) formalism [16,17], Eq. (2) represents the second moment of the local electronic density of states rather than a local electronic density, with the non-magnetic embedding energy given by the band term, $F[\rho] = -A\sqrt{\rho}$. For the magnetic potential, the embedding energy is given by

$$F[\rho] = -A\sqrt{\rho} - \frac{B}{\ln 2}\left(1 - \sqrt{\frac{\rho}{\rho_c}}\right)\ln\left(2 - \frac{\rho}{\rho_c}\right)\Theta(\rho_c - \rho), \qquad (3)$$

where the second term represents the magnetic energy contribution to the cohesive energy. The detailed derivation of Eq. (3) may be found in Refs. [1,3]. In the above formalism, the repulsive potential $V(r)$ and pair wise electronic density $f(r)$ are represented as knot functions that are fitted, along with A and B in Eq. (3), to a large database of physical properties derived from both DFT calculations and experiment [1]. Inspection of Eq. (3) reveals that when $\rho \rightarrow \rho_c$ from the positive side, where ρ_c is a critical local electronic density, the magnetic energy becomes zero, indicating that at some critical volume per atom the magnetic moment vanishes. This has been demonstrated in DFT calculations of the equation-of-state curves for ferromagnetic and non-magnetic bcc Fe, which converge at a critical volume of approximately 20% of the bulk bcc equilibrium value with a corresponding reduction to zero of the bcc ferromagnetic moment [18,19].

To develop an understanding of how the co-linear magnetic moment of each atom can be determined, one must return to the theoretical derivation of Eq. (3) as presented in Refs. [1,3], where the magnetic energy as a function of magnetic moment can be written within the Ginzburg-Landau approximation as

$$E_{\text{magnetic energy}} = \alpha\zeta^2 + \beta\zeta^4. \qquad (4)$$

Here the quadratic term, in which α can be either positive or negative, drives the Stoner instability to ferromagnetism and the positive quartic term provides for the final unsaturated finite magnetic moment per atom in bcc Fe. The parameters α and β depend on the local environment of the atom. In the above equation, the magnetic moment ζ is considered a free parameter. The equilibrium magnetic moment is given by the condition

$$\frac{\partial E_{\text{magnetic energy}}}{\partial \zeta} = 2\zeta(\alpha + 2\beta\zeta^2) = 0, \qquad (5)$$

the solutions of which are, $\zeta = 0$ (the non-magnetic solution), and

$$\zeta = \pm\sqrt{-\frac{\alpha}{2\beta}}. \qquad (6)$$

Eq. (6) constitutes the desired symmetry-broken ferromagnetic solutions which upon substitution into Eq. (4) gives the magnetic part of the embedding energy [1]. From Ref. [1] one can demonstrate that when $\rho \rightarrow \rho_c$ the leading order environmental dependence of Eq. (4) is via $\alpha \propto \sqrt{\rho} - \sqrt{\rho_c}$, resulting in the magnetic moment on each atom scaling as

$$\zeta \propto \pm\left(\sqrt{\rho_c} - \sqrt{\rho}\right)^{\frac{1}{2}}. \qquad (7)$$

In the equilibrium bulk bcc ferromagnetic regime ρ is non-negligibly greater than ρ_c leading to practical generalisations of Eqs. (4) and (7). In the former case this leads to an expression for the embedding energy as shown in Eq. (3), whereas for the magnetic moment, past work [3] has represented ζ more generally as