Investigation of S diffusion in bulk Fe – a DFT study

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Abstract. The diffusion of Sulphur (S) in bulk Iron (Fe) was investigated by means of Density Functional Theory (DFT) using the QUANTUM Espresso code. The ground state properties of Fe was accurately described by the PW91 pseudopotential, delivering a lattice parameter of 2.852 Å, a bulk modulus of 154.4 GPa and a magnetic moment of 2.47 µB . The vacancy formation energy and binding energy of Fe was calculated as -2.658 eV and -4.878 eV respectively. Binding energies for the interstitial and substitutional positions of S in Fe were calculated as -1.660 eV and -3.605 eV respectively. The minimum energy path and migration energy of S was calculated using the Climbing Image Nudged Elastic Band (CI-NEB) method. The larger substitutional binding energy of S indicates a substitutional or interstitial-substitutional dissociative mechanism of diffusion. It was found that S prefers the strongly coordination sites in the Fe lattice and will diffuse via a interstitial-substitutional dissociative diffusion mechanism which provides the necessary coordination sites for S. The migration energy and activation energy for the diffusion of S in bcc Fe was calculated as - 1.003 eV and -3.661 eV respectively.

1. Introduction

The valuable properties offered by Fe have made it a popular metal in industry. The biggest problem faced when working with Fe is the impurities (P and S) in the metal, which causes a weakening of both mechanical and catalytic properties. Fe exposed to high temperatures, results in the segregation of these impurities to the surface and grain boundaries. S and P cause a decrease in the mechanical strength of Fe by occupying positions in the grain boundaries of the metal, leading to grain boundary embrittlement. The presence of S in Fe catalyst causes the catalyst to deactivate, as the S occupies positions on the surface. The Fe-S system has received a vast amount of attention, in order to determine the diffusion properties of the system. Theoretical studies have been performed by Hong *et al* [1] and Tsuru *et al.* [2] to determine the segregation properties of S in Bulk Fe. The question of the diffusion mechanism remains unclear, with some authors claiming a interstitial and others a substitutional diffusion mechanism. The study presented here will investigate the possibility of a interstitial, substitutional and a interstitial-substitutional dissociative diffusion mechanism. Properties of interest such as the binding energies, vacancy formation energy and the migration energies are calculated.

2. Theory

The Nudged Elastic Band Method (NEB) [3] is used to determine the minimum energy path (MEP), for a transition from one stable state to the next. A number of images are chosen along a path, from the initial to the final state, usually a linear initial path is chosen. The atom then moves along the path according to the coordinates given by the images and is optimized with respect to the NEB force given by equation 1.

$$\overline{F}_i^{NEB} = \overline{F}_i^{\perp} + \overline{F}_i^{S||} \tag{1}$$

where $F_i^{\perp}$ is the force projected perpendicular to the elastic band between two images, and is called the true force. This is the force experienced by the atom as a result of the potential energy surface in which it is located and is given by.

$$\overline{F}_i^{\perp} = -\nabla\overline{R}_i + \nabla\overline{R}_i \bullet \hat{\tau}_i \hat{\tau}_i \tag{2}$$

The force $\overline{F}_i^{S||}$ is the spring force parallel to the elastic band, experienced by the images as a result of the elastic band. Equation 3 gives the expression for the parallel spring force.

$$\overline{F}_i^{S||} = k\left(\left|\overline{R}_{i+1} - \overline{R}_i\right| - \left|\overline{R}_i - \overline{R}_{i-1}\right|\right)\hat{\tau}_i \tag{3}$$

where $\hat{\tau}_i$ is the tangent along the direction, $\overline{R}$, of the path from one image to a neighbouring image of higher energy and *k* is the elastic constant.

The elastic band is optimized in order to obtain the minimum energy path for the transition, this is done by minimizing the total force given by equation 1. The CI-NEB method [4] used in the calculation done here, is further modified by allowing the image of highest energy, *l*, to climb up the saddle point via a reflection in the force along the tangent $\hat{\tau}_l$. The force experienced by atom l is given by.

$$\overline{F}_l^{CI} = \overline{F}_l - 2\overline{F}_l \bullet \hat{\tau}_l \hat{\tau}_l \tag{4}$$

This image does not experience any spring forces and can climb freely along the saddle point. The CI-NEB method as implemented in the QUANTUM Espresso code was used in all calculations to calculate the migration energy of diffusion.

3. Computational Details

All calculations were performed using the QUANTUM Espresso code [5], which performs fully self-consistent DFT calculations to solve the Kohn–Sham equations [6] within the generalized-gradient spin approximation (GGSA), using the functional of Perdew and Wang (PW91) [7]. The electronic wavefunctions are expanded as linear combinations of plane waves, truncated to include only plane waves with kinetic energies below the energy cut-off, Ecut, of 28 Ry. Core electrons are replaced by ultrasoft pseudopotentials [8] to render the computations tractable as well as to enhance efficiency. k-Space sampling is performed using a Monkhorst-Pack mesh [9] of 8x8x8 for all single unit cell calculations and a mesh of 3x3x3 for all calculations on the 3x3x3 supercell, for surfaces in the z direction a 3x3x1 mesh was used. For metallic smearing, the scheme of Methfessel and Paxton [10] with a degauss value of 0.04 Ry was used. A starting value for the magnetization resulting in the lowest energy, 0.4 was used to include the effects of magnetism. To ensure that the calculations for the supercells are reliable, the bulk properties have been converged with respect to the computational parameter: Ecut, k-point sampling, smearing and degauss on a single unit cell.

For the CI-NEB calculations a 6 image initial path was chosen and atomic positions were relaxed according to the Broyden scheme along this path. The minimum and maximum values for the elastic constant, *k*, was chosen as 0.1542 a.u and 0.0366 a.u respectively. The convergence criteria for the CI-NEB calculations was chosen as 0.05 eV/Å.

4. Results and discussion

4.1. Fe bulk properties

Convergence with respect to the computational parameters stated above, resulted in the ground state properties of bcc Fe shown in column 1, column 2 is the values obtained from literature and column 3 contains the experimental values.

Table 1: Bulk properties of bcc Fe. The values in column 1 is that of the current work and column 2 and 3 is values calculated by other authors and experimental results respectively.

	Calculated in this work	**Literature [11]**	**Experimental [11]**
Lattice parameter (Å)	2.852	2.869	2.866
Bulk modulus (GPa)	154.4	140	168
Magnetic moment (μB)	2.47	2.37	2.22

4.2. Binding and Vacancy formation energy

For the 3x3x3 supercell of Fe, a binding energy of -4.878 eV was obtained, which is in good agreement with the literature value of -4.893 [13] and the experimental value of -4.28 [12]. The vacancy formation in Fe was simulated as the formation of a Schottky defect [14, 15] on a Fe(100) surface. The first 5 layers of the 3x3x3 supercell was allowed to relax while keeping the 2 bottom layers fixed. To eliminate interactions between one surface and the bulk of the next periodic cell, a vacuum spacing of 28 Bohr was used. The calculation resulted in a vacancy formation energy of -2.658 eV which is in good agreement with the values obtained from literature -1.7 – -2.33 eV [16, 17, 18, 19] and the experimental value of -2eV [3]. The binding energies for interstitial and substitutional S in bcc Fe was calculated as -1.660 eV and -3.605 eV respectively, which is in good agreement with the literature values. Tsuru *et al.* calculated a interstitial binding energy of -1.53 eV [2], while a substitutional binding energy of -3.10 eV was calculated by Hong *et al.*[1].

4.3. Migration and Activation energy

The large substitutional binding energy compared to the interstitial binding energy of S indicates a substitutional or interstitial substitutional diffusion mechanism. The substitutional diffusion of S in Fe, whereby a S atom will diffuse from a substitutional position to a nearest neighbour vacancy, was calculated as an unfavourable diffusion path. Instead of diffusing towards the vacancy, the S atom would diffuse in a direction were it can form a large number of bonds with the Fe lattice, thus S prefers a high coordination number with the Fe lattice.

The interstitial-substitutional dissociative diffusion mechanism, whereby the substitutional bonded S atom diffuses along a interstitial path to a next nearest neighbour vacancy, has been shown to be the diffusion mechanism whereby S will diffuse. This reaction path ensures that a large number of coordination sites is available to the diffusing S atom. Also the S atom is small enough so that it can easily diffuse via an interstitial path, with only a small distortion in the surrounding lattice atoms. Using the CI-NEB method, a migration energy of -1.003 eV was calculated and taking the vacancy formation energy of -2.658 eV into account, a activation energy of -3.661 eV was calculated for the diffusion of S in bcc Fe. The migration energy of the S atom as a function of the reaction coordinates along with the crystal structures of each image is given in figure 1.

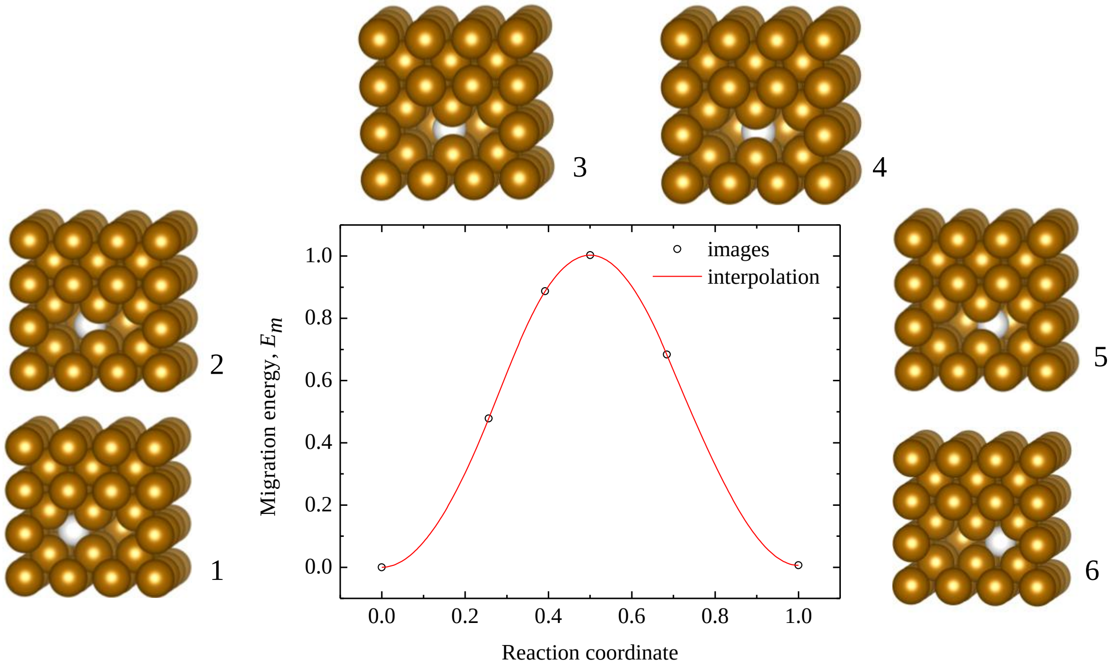

Figure 1: The migration energy as a function of the reaction coordinates for the interstitial-substitutional dissociative diffusion mechanism of S in bcc Fe. The crystal structures for each of the 6 images are also shown to illustrate the diffusion process.

5. Conclusion

The diffusion of S in bcc Bulk Fe has been investigated using the computational technique DFT. The strong binding energy of S (-3.605 eV) in a substitutional lattice site over the interstitial binding energy (-1.660 eV) indicated a higher probability of S diffusing via a substitutional or interstitial-substitutional mechanism. The diffusion of S via the substitutional mechanism was found to be energetically unfavourable, due to the lack of coordination sites for the S atom along a substitutional path. The interstitial-substitutional mechanism provides such a path, with a migration energy of -1.003 eV and taking the vacancy formation energy of -2.658 eV into account, a activation energy of -3.661 eV for the diffusion of S in Fe was obtained.

6. References

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