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Nature of boron solution and diffusion in α-iron

Dan H. R. Fors and Göran Wahnström
Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

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By using the density functional theory, we show that in contrast to carbon, boron predominantly enters as substitutional solute atoms in α-iron. However, at elevated temperatures, interstitial occupancy is not negligible and the diffusion of boron in α-iron is found to be governed by the interstitial mechanism. This mixed occupancy explains various apparently contradictory experimental results and will have important bearings on our ability to model the thermodynamic properties and the kinetics of boron containing steels.

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There are two main mechanisms by which solute atoms can diffuse through a crystalline solid, and the operative mechanism depends on the type of site occupied in the lattice. Substitutional atoms usually diffuse by a vacancy mechanism, whereas interstitial atoms migrate by finding their way between the surrounding atoms, i.e., interstitially. Diffusion of atoms is one of the most important elementary processes in materials, and a basic understanding of this is of crucial importance, e.g., for the understanding of the microstructural evolution in metallic alloys.

The most important and widely used group of metallic alloys is steels.[1] They are alloys of the element iron with carbon and usually several other elements. The stable structure for pure iron below 1185 K is bcc, which is often denoted as α-Fe or ferrite. At low concentrations, carbon forms an interstitial solution in ferrite, while other elements such as Cr, Ni, Mn, Mo, W, Si, and V form substitutional solutions. The elements B, C, N, and O are all shown to form interstitial solutions.[2] This observation for C,[3] N,[4] and O (Ref. 5) is also theoretically found by using *ab initio* calculations based on the density functional theory (DFT). However, the picture is not as clear for B. This is quite surprising. To our knowledge, there are no available results from *ab initio* calculations for B in ferrite, and a close inspection of the literature reveals a quite inconsistent picture based on various experimental studies. Despite the importance of boron in ferrite,[6,7] the type of solution and the diffusion mechanism are not settled.[8,9]

Substitutional occupancy is supported by x-ray lattice parameter measurements.[10] It is also supported by early diffusion experiments[11] by using a spectroscopic method. An activation energy of 2.69 eV is obtained, which is consistent with a substitutional mechanism. However, the obtained prefactor is very large, i.e., $10^2\ \mathrm{m}^2/\mathrm{s}$. In order to explain the diffusion data in Ref. 11, the concept of dissociative diffusion has been put forward.[12] On the contrary, interstitial occupancy is supported by internal friction measurements.[13] Inconsistent internal friction data are often obtained, and it has been argued that it is a consequence of the fact that B-Fe alloys always contain some contaminating carbon.[10] More recent diffusion measurements that use particle tracking autoradiography imply an interstitial mechanism with an activation barrier of 0.92 eV and a prefactor of $1.5\times10^{-7}\ \mathrm{m}^2/\mathrm{s}$ in a Fe-3% Si-B alloy.[8] The authors discuss several reasons for the discrepancy with the earlier data in Ref. 11, and they conclude that their results support interstitial occupancy. The present lack of knowledge of the nature of a boron solution in α-iron has led to the use of both interstitial and substitutional models in the development of B-Fe and related phase diagrams.[9]

In the present Brief Report, by using DFT calculations, we will show that in contrast to C, N, and O, boron predominantly enters as substitutional solute atoms in ferrite. However, at elevated temperatures, the interstitial occupancy is not negligible, and the diffusion of B in ferrite is governed by the interstitial mechanism.

The DFT calculations are based on the plane-wave method and/or the pseudopotential method, as implemented in the Vienna *ab initio* simulation package (VASP).[14–16] The exchange-correlation functional is approximated within the spin-polarized generalized gradient approximation according to Perdew and Wang,[17] and the electron-ion interaction is described by the projector-augmented-wave formalism.[18] The standard Fe, B, and C potentials with eight, three, and four valence electrons, respectively, were used. The α-Fe matrix is represented by both a 54-atom and a 128-atom supercell with periodic boundary conditions. The fictitious temperature broadening is set to 0.1 eV within the first order Methfessel–Paxton scheme. The converged k-point samplings were chosen to be $4\times4\times4$ for the 128-atom supercell, and $6\times6\times6$ for the 54-atom supercell. A cutoff at 420 eV was found to be sufficient in order to produce reliable volume relaxations.

The type of solution can be deduced by considering the solution energy E_A. Besides the substitutional site ($A=S$), we consider two interstitial sites, i.e., the octahedral ($A=O$) and the tetrahedral ($A=T$) sites. The solution energy is determined as the computed difference in energy between the lattice with defect and the sum of energy for the perfect α-Fe lattice with the same number of Fe atoms and an isolated B(C) atom. The calculations are performed for both constant volume conditions (constant V) and constant pressure ($P=0$) conditions (constant P). In the former case, all atomic positions are allowed to relax, with the constraint that the volume and shape of the supercell are kept fixed. On the other hand, in the latter case, the volume and shape of the supercell are allowed to relax. For a finite system, these two cases will differ. For large systems, however, they will approach the same value, provided that they are large enough to reach the asymptotic behavior.[19] By extrapolating $E_A(N)$ as a function of $1/N$ to infinite size ($N\rightarrow\infty$), the correct solution energy can be obtained.[19]

TABLE I. Solution energies (in eV) for a single impurity in α-Fe. The calculations are performed under constant volume (constant *V*) and constant pressure (constant *P*) boundary conditions by using a 128-atom supercell.

	Constant *V*		Constant *P*	
Configuration	B	C	B	C
S site	−5.57	−4.82	−5.59	−4.82
O site	−5.44	−7.08	−5.53	−7.16
T site	−4.77	−6.23	−4.84	−6.31

The calculated solution energies for boron and carbon atoms in α-Fe are presented in Table I. The substitutionally occupied systems retain their cubic structure under a constant *P* relaxation but are associated with a volume contraction, while the interstitially occupied sites force the cubic supercell to deform into a tetragonal supercell with the ratio $c/a=1.01$ (for the 128-atom supercell) together with a volume expansion.

As expected, we find that the carbon atom is located as an interstitial at the *O* site. The energy difference with substitutional occupancy is large, i.e., more than 2 eV. In contrast, the substitutional site is favored in the boron case. The energy difference with the *O* site is quite small, i.e., about 0.1 eV. We can obtain a more accurate estimate by extrapolating the constant *V* and constant *P* results to an infinite size. In Fig. 1, the extrapolation is shown by using two different supercell sizes. We expect the lines to better converge to the same value if larger supercells had been used. By taking the mean value in the extrapolation limit, we obtain the energy difference $E_O-E_S=86$ meV between the *O* and *S* sites for boron.

The atomic sizes of C and B are sufficiently small to allow for interstitial occupancy but are large enough to make lattice distortion important. In α-Fe, the nominal size of the *T* site is larger compared to that of the *O* site, and the commonly accepted explanation for the *O*-site occupancy of C is that at the *O* site—with only two nearest-neighbor Fe atoms—the strain relief is more favorable compared to that at the *T* site—with four nearest-neighbor Fe atoms.[1,3] The covalent radii for C and B are 0.77 and 0.82 Å, respectively,[20] and the size effect is more pronounced in the boron case. The displacement of the nearest-neighbor Fe atoms for boron are found to be +19% of the initial distance for the *T* site and +28% for the *O* site. The corresponding values for the carbon case are +15% and +25%, respectively. This implies substantial effects from the strain in both systems. For substitutional occupancy, the displacements are small.

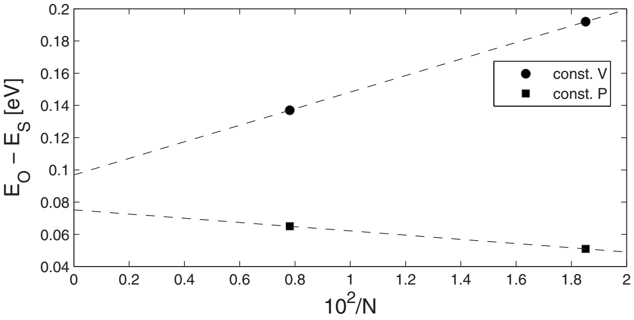

FIG. 1. Difference in solution energy between the *O* site and the *S* site in the α-Fe system as a function of system size. The linear interpolations with respect to $1/N$ for constant volume and constant pressure relaxations, are also shown.

To quantify the size effect, we separate the solution energy into two contributions, the mechanical and the chemical.[6] The mechanical part is defined by computing the energy release during the relaxation of the distorted α-Fe lattice after the removal of the impurity. The chemical part is then denoted by the chemical contribution. Our results are presented in Table II. We first notice that by only considering the chemical part of the solution energy, the *O* site also becomes the stable site for boron. It is the large mechanical contribution for the *O*-site occupancy (1.4 eV) that makes boron substitutional. The energy difference between the two different interstitial sites is also substantially increased by adding the mechanical contribution. For carbon, we notice that the mechanical contribution is indeed larger at the *T* site than at the *O* site, but the difference is quite small, i.e., only 0.2 eV. It is not the main explanation for the *O*-site occupancy of carbon. By considering only the chemical part of the solution energy, the *O* site is clearly favored by 0.6 eV. This is not in line with the commonly accepted explanation for the *O*-site occupancy of carbon in ferrite.[1]

An investigation in terms of projected density of states (PDOS) provides an explanation for the difference in the nature of boron and carbon. Figure 2 shows the projected states (spin up+spin down) on the first nearest Fe neighbor in the *O*-site configuration with (solid line) and without (dotted line) the solute atom. In Fig. 2 (lower parts), the projected states on the solute atom B(C) are also shown. In the carbon system, we see a pronounced increase at around −6 eV, a hybridization with main contributions from Fe 3*d*

TABLE II. Same as in Table I for the chemical part of the solution energies. The mechanical part values are in parentheses.

	Constant *V*		Constant *P*	
Configuration	B	C	B	C
S site	−5.61 (0.04)	−4.85 (0.03)	−5.64 (0.05)	−4.86 (0.04)
O site	−6.88 (1.44)	−8.19 (1.11)	−6.95 (1.42)	−8.25 (1.09)
T site	−6.68 (1.91)	−7.54 (1.31)	−6.74 (1.90)	−7.62 (1.31)

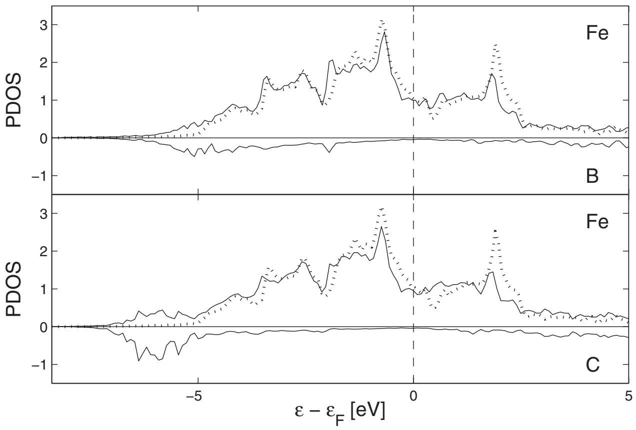

FIG. 2. Projected density (spin up+spin down) of $p+d$ states for the O-site occupancy. Upper panel: B and the first nearest Fe neighbor with (solid line) and without (dotted line) B. Lower panel: Same for C.

and C $2p$ states. The T site (not shown) also shows a similar—although weaker—bond formation, while the S site shows no bond formation at all. The boron system shows a similar—but much weaker—hybridization at around −5 eV at the O site. For the T site (not shown), the effect is even weaker and absent for the S site. This explains the large energy difference between the substitutional (S) and interstitial (T and O) sites for the carbon system and the corresponding smaller energy difference in the boron system.

The probability of occupancy of the various sites is given by

$$P_A = \frac{1}{Z} g_A \exp(-E_A/k_BT), \tag{1}$$

where the degeneracies are $g_A=1$, 3, and 6 for the S, O, and T sites, respectively, and Z is the partition function, or the normalization factor. In Fig. 3, we show the result for the O-site occupancy as a function of temperature. Only the S and O sites are local minima and henceforth we will consider only these sites. In general, the energy E_A in Eq. (1) should be replaced by the free energy F_A. In the harmonic approximation, the contribution of the vibrational modes ω_A^i is given by $F_A=E_A+\Sigma_i[\hbar\omega_A^i/2+k_BT\ln(1-\exp(-\hbar\omega_A^i/k_BT))]$. This is particularly important for the modes associated with the motion of the boron atom. These strongly depend on the occupancy. By using a simple Einstein model, we have determined the dynamical matrix for the motion of the boron atom in a frozen surrounding Fe lattice. We find the normal frequencies 108 and 67 meV (twofold degenerate) at the O site, which are both localized well above the Fe phonon band (<40 meV). For the S site, we obtain the frequency of 23 meV (threefold degenerate), which is then located within the Fe phonon band. The frequencies are determined at constant V conditions. For the constant P calculations, they are changed by only a few percent. By using these frequencies in the expression for the free energy, the O-site occupancy is substantially reduced by 1 to 2 orders of magnitude (see Fig. 3). The dashed-dotted line in Fig. 3 shows the result if the classical limit for the free energy expression is used. The corresponding entropy difference is $\Delta S_{cl}=3.6k_B$.

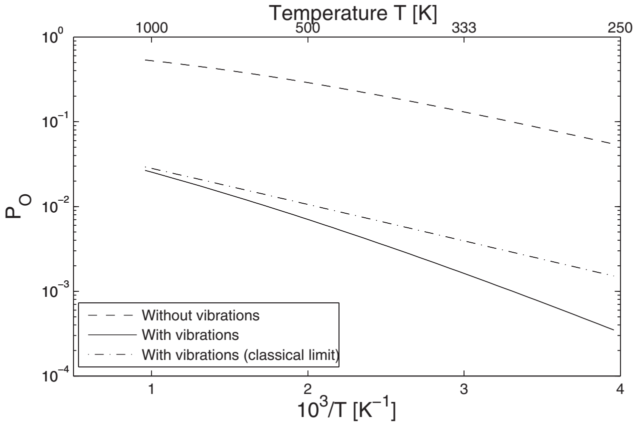

FIG. 3. The probability for a boron atom to occupy an O site with respect to the total number of boron atoms in the α-Fe matrix. The dashed line shows the result if the vibrational degrees of freedom are neglected.

Next, we consider the diffusion of boron. We assume that there is an equilibrium for the occupancy and that the substitutional and interstitial boron atoms diffuse independently. The effective diffusion coefficient can then be written as

$$D = P_O D_O + P_S D_S. \tag{2}$$

For the interstitials, we assume jumps between nearest-neighbor O sites and write the diffusion coefficient as $D_O=\frac{1}{6}n_O r_O^2 \nu_O \exp(-E_{i,m}/k_BT)$, where $n_O=4$ is the number of nearest-neighbor sites and $r_O=a/2=1.42$ Å ($a=2.831$ Å) is the jump distance. The migration energy $E_{i,m}$ is equal to the energy difference between the T and O sites, $E_{i,m}=E_T-E_O=0.67$ eV, and the prefactor ν_O is determined by using the harmonic quantum transition state theory.[21] In that calculation, we include three frequencies (108, 67, and 67 meV) at the O site and two frequencies (86 and 86 meV) at the T site. At $T=500$ K (1000 K), we then obtain the value $\nu_O=8.0$ THz (11.0 THz) for the prefactor.

For the substitutional diffusion, the activation energy is given by the sum of the Fe vacancy formation energy E_v and the migration barrier $E_{s,m}$ to move the boron atom from one substitutional site to the vacant site. We neglect any dependence of the vacancy formation energy on the presence of the boron atom and write the diffusion coefficient as $D_S=\frac{1}{6}n_S r_S^2 f \nu_S \exp[-(E_v+E_{s,m})/k_BT]$,[22] where $n_S=8$ and $r_S=\sqrt{3}a/2=2.45$ Å. We obtain $E_v=2.16$ eV and $E_{s,m}=0.15$ eV, where $E_{s,m}$ is obtained by placing the boron atom at the halfway position. The large formation energy for vacancies makes the substitutional diffusion coefficient very small. The factor f is the correlation factor for impurity diffusion, and assuming that all relevant jump frequencies are equal, we have $f=0.7$.[23] For the prefactor, we simply use one of the S-site vibrational frequencies, i.e., $\nu_S=5.7$ THz.

Figure 4 shows the two contributions to the diffusion coefficient D. Due to the small number of Fe vacancies at equilibrium, the contribution from substitutional boron atoms is very small. The contribution from the interstitial boron atoms

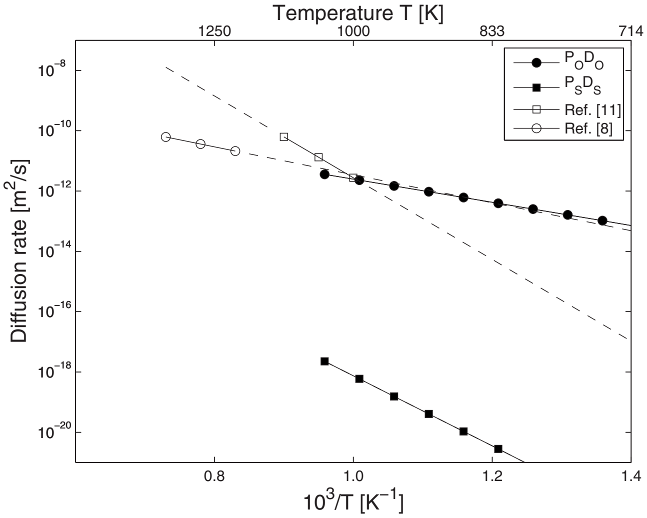

FIG. 4. Calculated diffusion rates (up to the Curie temperature of 1043 K) together with experimental data (Refs. 8 and 11). The dashed lines represent extrapolations outside the measured intervals.

(line with filled circles) dominates by several orders of magnitudes despite the minority population. If compared with the experimental data, our results would be consistent with those of Wang *et al.*[8] The activation energies and prefactors differ slightly, but one should bear in mind that the experiments are performed in an alloy with 3 wt % Si and above the Curie temperature. Our calculation of ν_O, in particular, can also be improved by a full phonon treatment, and the magnetic ordering effects can be treated in a more accurate way. However, our data are not consistent with the older experimental data in Ref. 11, but the precision of their experimental technique has been criticized.[8] We are also aware of one experimental study of boron diffusion in Fe presented in Ref. 24, but the aim of this study was not to accurately measure the diffusion coefficient; hence, we do not reproduce their data here.

In conclusion, we have shown that in contrast to carbon, boron forms a substitutional solution in ferrite at low temperatures. For carbon, the interstitial O site is stabilized by a quite pronounced hybridization between the Fe $3d$ state and the C $2p$ state. This hybridization is considerably less pronounced for boron occupying the same site. The energy cost to distort the lattice is also less for C compared to B at the O site. At elevated temperatures, the interstitial O-site occupancy of B cannot be neglected, and the diffusion of boron in ferrite is governed by the interstitial mechanism. This is consistent with available experimental results for the diffusion of boron in ferrite. These findings will have important bearings on our ability to thermodynamically model B-Fe systems,[9] and to describe and understand the microstructural evolution of boron containing steels.[25]

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