

# First-principles Calculation on the Interaction of an Interstitial Hydrogen Atom with a Screw Dislocation in BCC Iron

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The interaction of an interstitial hydrogen atom with a screw dislocation in BCC iron has been determined using the first principles calculation. The calculation was carried out for a pair of screw dislocations using the large-scale supercell containing 231 atoms and  $1 \times 1 \times 4$  k-point samplings. It is found that a hydrogen atom at an octahedral site near the screw dislocation attracts the dislocation core under the applied shear stress condition. However, the resultant stress-strain relation in the presence of a hydrogen atom is found to be almost the same with that of no hydrogen case. This indicates clearly that a significant enhancement of dislocation mobility, previously reported in Al, is not observed in BCC iron.

**Keywords:** first-principles calculation, screw dislocation, BCC iron, hydrogen atom, binding energy

## 1. INTRODUCTION

The presence of hydrogen atoms at interstitial sites causes a significant change in mechanical properties of solids. In particular, it is predicted that hydrogen atoms in metals enhance plasticity, which leads to an accelerated concentration of stress and fracture. The mechanism of this embrittlement due to hydrogen is not precisely known at present and is of much concern to the development of, for example, materials for hydrogen containment, high-tensile structural materials, and fusion and fission nuclear materials.

The fundamental question in deformation and fracture of metals is whether hydrogen atoms affect the motion of dislocations. In BCC metals, a screw dislocation controls the plastic behavior because it has a high stress barrier, the Peierls stress, to movement. Therefore, the understanding of the core structure and mobility of a screw dislocation in BCC metals is essential for predicting the mechanical properties, which requires atomistic level simulations. Moreover, the core structure and mobility of a screw dislocation in BCC iron are hard to understand because of the presence of magnetism. Since the development of empirical potential for BCC Fe and Fe-H system is retarded due to this difficulty, first principles calculations at the electronic scale are required to understand the bonding states of a dislocation core, particularly, in the presence of hydrogen.

In general, atomistic simulation of a dislocation core needs a large number of atoms because it has to take into account the effect of a long-range strain field. Numerous first-principles and empirical atomistic simulation studies have been carried out so far to determine the accurate core properties, however, the results of the core structure and Peierls stress differ depending on the simulation methods. Essentially, two core structures have been proposed for a screw dislocation in BCC molybdenum by various computational approaches [1][2][3][4][5]; the threefold structure is obtained using the empirical potential, while the symmetric structure is obtained by the tight-binding and the density functional theory (DFT) methods. Although the DFT method gives the most accurate energy among these methods, the sizes of its supercells are severely limited, and the effects of core overlapping and image stress can be significant. Woodward and Rao [2] proposed a boundary condition for the supercell containing one screw dislocation, in which atomic displacements due to a screw dislocation in the cell are allotted by the Green function method. Li *et al.* [4] introduced a pair of screw dislocations in the supercell and proposed a shape of the supercell in such a way as to cancel the strains among supercells. They evaluated the accuracy of the core energy by changing the size of the supercell, and concluded that the supercell containing 231 atoms is good

enough. We performed the most accurate DFT calculations using the supercell of this size by confirming the convergence on the number of k-point samplings, and concluded that the core of the  $a_0/2[111]$  screw dislocation in BCC molybdenum has a symmetric non-degenerate structure [6].

The core structure of a screw dislocation for BCC iron is predicted by starting with the threefold degenerate structure and relaxing the system. The result is found to be a symmetric non-degenerate structure with no preferential spreading along the  $(-1-12)$  directions [10], which is in agreement with the results of the previous calculations using equal to or less than 100 atoms [3][8]. It is probable that a symmetric non-degenerate core structure is obtained for a screw dislocation in BCC iron using the first principles calculations, however, the convergence of the k-point samplings must be critically checked for a final determination. Moreover, the Peierls stress for BCC iron is evaluated to be  $\tau_p \approx 1.1\text{GPa}$  by applying the shear strain to the system [10]. This result is the first direct determination of the Peierls stress of a screw dislocation in BCC iron.

With the determined core structure of a screw dislocation in BCC iron, the interaction of a hydrogen atom with a screw dislocation is studied to understand its effect on plastic behavior. The binding energy of a hydrogen atom at the tetrahedral and octahedral site to a screw dislocation in BCC iron is determined to be approximately  $-0.2\text{eV}$ [11], which is important in determining the hydrogen state near a dislocation core and the Peierls stress.

In this paper, we report the effect of the presence of a hydrogen atom on the Peierls stress of a screw dislocation core in BCC iron. The results will give us a clue to whether hydrogen-enhanced local plasticity exists in BCC iron, which was predicted in FCC aluminum [12].

## 2. COMPUTATIONAL METHOD

We have employed the VASP (Vienna *ab-initio* simulation package) code [9], which implements the density functional theory with the ultrasoft pseudopotential and the generalized gradient approximation (GGA) for the exchange correlation energy, for calculating accurately the total energy of the system. In order to exploit the vector processors on the ES system, we have tuned the code by using the one-dimensional FFT routine in the numerical library ASL/ES. For the problem with the supercell containing 231 atoms, the VASP code achieved 66.4% of the peak performance on the ES.

Using the configuration of the symmetric non-degenerate core structure obtained by the previous work as an initial condition, we place one hydrogen atom at the octahedral site near the core of a screw dislocation and the whole system is relaxed to a minimum energy state by the conjugate gradient or the quasi Newton algorithm. Using the supercell consisting of 231 atoms with various k-point samplings, this proce-

dures requires considerable amounts of calculation time, which invalidates the original implementation of parallel coding on the VASP code. To overcome this situation, we have re-parallelized the code in terms of k-point samplings. The result shows that the parallel code achieves almost linear speedup. Analyzing the detailed profile data of the code, we found that the k-point parallelization has almost no influence on the average vector length. We have obtained the average vector length of 229.3 with 8 processors (1 node) and 229.1 with 80 processors (10 nodes), and the vectorization ratio of 99.3% and 99.1%, respectively. In the case of iron, spin polarization must be taken into consideration, and the convergence of the iterative electronic structure calculation is found to be degraded compared to the molybdenum case. The number of iterations for the iron case requires approximately five times more than that for the molybdenum case. Therefore, the numerical condition for the supercell containing 231 iron atoms with the  $1 \times 1 \times 4$  k-point samplings is adopted as a first trial numerical simulation.

## 3. RESULTS AND DISCUSSION

The effect of the presence of one hydrogen atom on the motion of a screw dislocation in BCC iron is surveyed by the molecular dynamics method before the detailed calculations by the first principles method. The molecular dynamics is carried out by placing a hydrogen atom at various octahedral sites near the dislocation core, where the newly-developed empirical potential of Fe-H interaction based on the Fe of Mendeleev et al. [7] is employed. The results boil down to two typical configurations, as shown in Fig. 1 (a) and (b). We have found that the hydrogen at the nearest octahedral site in Fig. 1 (a) has the effect of pinning the dislocation, while the configuration in Fig. 1 (b) induces a motion of the dislocation. Thus, we have employed the latter configuration as the initial condition for measuring the Peierls stress.

A pair of screw dislocations with different signs has been introduced into a system containing 231 BCC iron atoms, where one hydrogen atom is placed at the octahedral site of the type Fig. 1 (b) near one of the dislocations. The total system is relaxed under no external stress, and the core structure is shown in Fig. 3. In this figure, a new representation of the core structure of a screw dislocation is devised in stead of the conventional Vitek diagram using arrows in Fig. 2 (a). In this representation, an arrow connecting the atoms is replaced by the colored block as shown in Fig. 2 (b), where the six different colors are used corresponding to the length of an arrow as shown in Fig. 2 (c). For example, the maximum length of an arrow, which is one-third of the Burgers vector, is represented by yellow. This representation shows clearly a change of a dislocation core structure compared with the representation by arrows. The results in Fig. 3 show that the core of the dislocation on the left is attracted to a

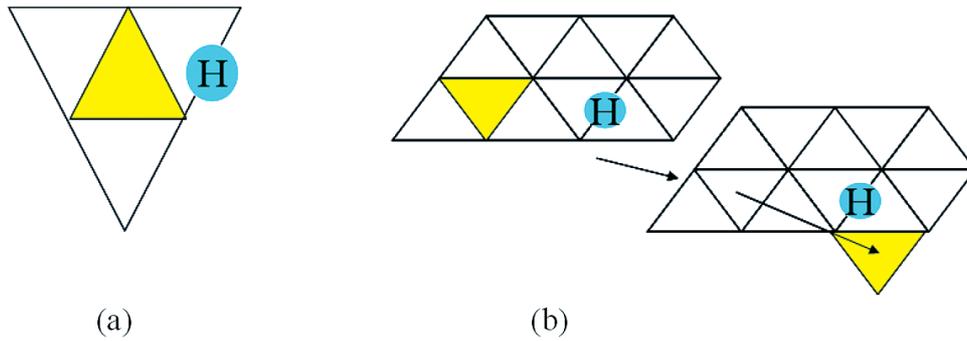


Fig. 1 A hydrogen atom at the octahedral site near the core of a screw dislocation. (a) a hydrogen site that pins the dislocation, (b) a hydrogen site that induces a motion of the dislocation.

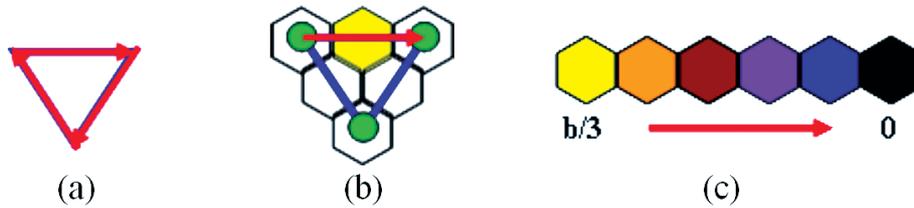


Fig. 2 Representations of atomic displacement differences for a screw dislocation with Burgers vector of  $[111]/2$  on the BCC  $\{111\}$  surface : (a) The Vitek diagram; a full length arrow between atoms represents an atomic displacement of one-third of the length of the Burgers vector in the  $[111]$  direction. (b) A color representation of the core of a screw dislocation; the arrow is replaced by a color block depending on the length of the arrow, as shown in (c).

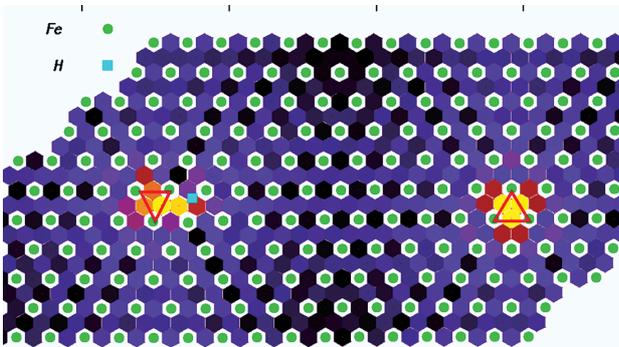


Fig. 3 A change in the core structure of screw dislocations in the presence one hydrogen atom at the octahedral site under the relaxed condition.

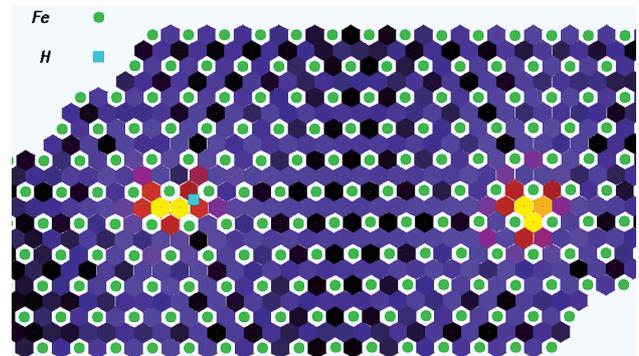


Fig. 4 A change in the core structure of screw dislocations in the presence one hydrogen atom at the octahedral site under the condition of the applied shear stress.

hydrogen atom, while the core of the dislocation on the right is almost a perfect screw dislocation. A stress-strain relation of this system is derived under the shear stress condition, and the results are shown in Fig. 4. A shear strain of a given value is applied to the parallelepiped region by displacing the atoms in the  $[111]$  direction. With this initial configuration, the whole system is relaxed to obtain a converged value of stress. The results in Fig. 4 show the stressed state of the core structure, in which the core is more attracted to the hydrogen atom. A stress-strain relation for this system is shown in Fig. 5. We show here that the presence of one hydrogen atom near the screw dislocation core in BCC iron

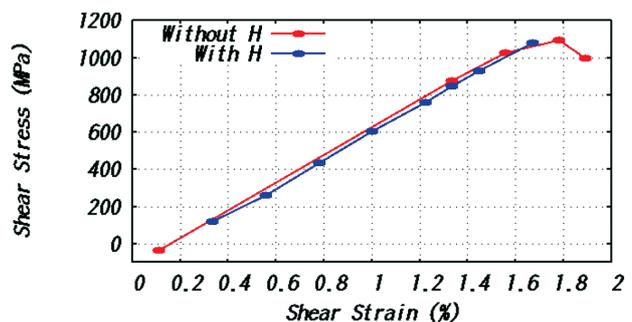


Fig. 5 A stress-strain relation for a system of BCC iron containing a pair of screw dislocations with and without the presence of one hydrogen atom.

does not affect significantly the stress-strain relation. In particular, a large reduction of the Peierls stress predicted in aluminum [12] is unlikely to occur in the BCC iron.

A further study for the effect of hydrogen atoms on the motion of a screw dislocation under the kink pair mechanism is needed to determine the plastic behavior of BCC iron. However, this will require larger computational resources.

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# 第一原理計算によるBCC鉄中らせん転位と格子間水素原子の相互作用の計算

プロジェクト責任者

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第一原理計算を用いてBCC鉄中の $a_0/2[111]$ のらせん転位と格子間水素原子間の相互作用を計算した。本計算は、2つのらせん転位を含む231個の原子からなる大規模なスーパーセルにおいて、 $1 \times 1 \times 4$ のk点サンプリングを用いて行った。転位芯近傍の正八面体格子間原子サイトに水素原子を置いて外部応力下で計算した結果、転位芯は水素原子の方へ引き寄せられていることが分かった。この時の応力-ひずみ関係を導出した結果、水素が存在する時としない時でほとんど差異が無いことが明らかになった。これより、BCC鉄においては水素の存在により転位の運動が促進される効果は小さいことが分かった。

キーワード: 第一原理計算, らせん転位, BCC鉄, 水素原子, 結合エネルギー