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Strain field of interstitial hydrogen atom in body-centered cubic iron and its effect on hydrogen-dislocation interaction

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Abstract

Effect of hydrogen in body-centered cubic iron is explored by using the density function theory. Hydrogen atoms increase the concentration of free electrons in the simulation cell and have bonding interaction with Fe atom. Caused by anisotropic strain components of hydrogen atoms in the tetrahedral sites, elastic interaction for hydrogen with screw dislocation has been found. The dependence of hydrogen-screw dislocation interaction on hydrogen concentration is confirmed by repeated stress relaxation tests.

Keywords: density function theory; hydrogen embrittlement; iron alloys; stress relaxation

1 The strain field of H in iron is of crucial importance in understanding
2 the H-dislocation interactions. As a perfect screw dislocation only expresses
3 shear stress field, the interstitial atoms which have components of strain

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1 tensor equivalent in three axis of a rectangular coordinate ($\epsilon_{11} = \epsilon_{22} = \epsilon_{33}$)
 2 only interact with edge type dislocations. The assumption of such simple
 3 dilatation field has been applied to H atoms in many reports [1], in particular,
 4 in the theoretical framework of hydrogen enhanced plasticity model (HELP)
 5 [2] which now becomes one of the most accepted theories for understanding
 6 hydrogen embrittlement. The hydrogen-induced Snoek type internal friction
 7 peak has been observed in both BCC and FCC iron [3, 4], it was suggested
 8 that such Snoek type peak could be caused by unequal strain components,
 9 e.g. $\epsilon_{11} \neq \epsilon_{22}$ [1]. However, due to the low solubility and fast diffusion of H
 10 atoms, there is no direct measurement that can support the results for the
 11 bulk metal, and argument still exists.

12 This study introduces the analysis of electron structure of H-BCC iron
 13 system and the strain field of H atom based on density functional theory
 14 (DFT). For the first time, we combine the DFT calculation results with
 15 the classical calculation method developed by Cochardt et al. [5], which
 16 evaluates the interaction of interstitial atom with dislocation and has been
 17 proved to be in good agreement with experimental results for C interstitial
 18 atoms in BCC iron. The interaction of H with both edge type and screw
 19 type dislocations will be discussed. Hydrogen effects on dislocation motion
 20 will also be discussed based on repeated transients tests.

21 The grid-based real-space code GPAW [6] was used for DFT calculations.
 22 It is an implementation of the projector augmented wave (PAW) method
 23 of Blöchl [7], which is an all-electron full-potential method within the frozen
 24 core approximation. The Atomic Simulation Environment (ASE) [8] provided
 25 an interface to GPAW. The Perdew-Burke-Ernzerhof (PBE) parametrization

1 was used for the approximation of the exchanged-correlation (xc) function [9].
 2 Spin polarized calculation was performed with an initial magnetic moment
 3 of 2.20 for iron atoms. $(4 \times 4 \times 4)$ k points of the Brillouin zone sampling
 4 which uses the Monkhorst-Pack scheme was carried out [10, 11] with grid
 5 spacing of 0.18 Å and Fermi smearing of 0.1 eV.

6 Bulks of BCC iron with $(2 \times 2 \times 2)$ cell were created (Fe_{16}) and vacancy
 7 defect was imposed in some bulks (Fe_{15}). Periodic boundary conditions are
 8 considered for all calculations. H atoms were inserted initially into tetra-
 9 hedral positions of the cell, for the experimental evidence indicated such
 10 hydrogen occupancy for BCC Fe [1]. The variations of electron charge by
 11 adding hydrogen were analyzed by a fast and robust algorithm implemented
 12 by Tang et. al [12] based on the Bader partitioning scheme [13]. All calcu-
 13 lations were made for 0 K. The calculated lattice constant of Fe_{16} is 2.8369
 14 Å, bulk modulus is 162 GPa and magnetic moment is $2.17 \mu_B$, which are in
 15 good accordance with the results from experiment (2.8665 Å, 165 ± 5 GPa,
 16 $2.22 \mu_B$) and other calculations [14].

17 Large H concentrations were used in our DFT calculations ($C_H > 6\%$),
 18 but hydrogen has much lower solubility at experimental conditions [1]. To
 19 investigate strain field with C_H close to the experimental value, molecular
 20 dynamics (MD) calculation using embedded atom method (EAM) with the
 21 Potential B reported by Ramasubramaniam et al. [15] was carried out on
 22 a $\text{Fe}_{106561}\text{H}_1$ cell ($C_H < 10$ appm). LAMMPS code distributed by Sandia
 23 National Laboratories was used as MD simulator [16], and the relaxation of
 24 structure was performed by the conjugate gradient (CG) method.

25 The elastic interaction between H and dislocations was studied following

1 the classical method developed by Cochardt et al. [5]. In BCC iron the
 2 symmetry of both the octahedral site and tetrahedral site are expected to
 3 produce a strain field with local tetragonal symmetry. Since the exact atomic
 4 arrangement can be calculated using DFT method in this study, a strain
 5 tensor S_H of a unit cell containing one H atom can be obtained as $S_H =$
 6 $\{\epsilon_{11}, \epsilon_{22}, \epsilon_{33}\}$. If stress tensor $T_D = \sigma_{ij}^D$ of the dislocation field is expressed in
 7 the same coordinate system as the strain tensor S_H , the elastic interaction
 8 energy U_{DH} can be written as:

$$U_{DH} = -(T_D, S_H)a^3 = -\Sigma_{ij}\sigma_{ij}^D\epsilon_{ij}^H a^3 \quad (1)$$

9 where a is the lattice constant. For the strain tensor which are not in the same
 10 coordinate system with σ_{ij}^D , crystallographic relations is used for transforming
 11 the interstitial strain tensor into the same coordinate as the stress field of
 12 dislocations, for details can refer to the calculations focused on carbon atoms
 13 [5].

14 The repeated stress relaxation test developed by Spätig [17] has shown
 15 advantages in evaluating thermal activated behavior of dislocations, and such
 16 test was applied on hydrogen-charged iron specimens with purity better than
 17 99.996%, and grain size of $75 \pm 10 \mu\text{m}$. After cold rolling and punching,
 18 tensile specimen was annealed at 873 K in vacuum tube (1×10^{-4} Pa). The
 19 electrolyte for hydrogen charging is 0.5mol/l H_2SO_4 adding 50g/l Thiourea
 20 (promoter) and hydrogen charging was sustained in all relaxations. At 293
 21 K, the samples were initially strained with strain rate of $1 \times 10^{-4} \text{ s}^{-1}$ to 5%
 22 after the yield point. In each relaxation the tensile cross-head was stopped
 23 for 30 s and the strain is constant. Thermal activation analysis was based

1 on the obtained decreased stress ($\Delta\tau$) v.s. time (t) curves. The effective
 2 activation volume for dislocation motion yields [17]:

$$V_{eff} = kT \frac{\ln(\dot{\tau}_{i2}/\dot{\tau}_{i1})}{\Delta\tau} \quad (2)$$

3 where the numerator and denominator in the parentheses correspond to the
 4 stress rate at the onset of relaxation 2 and at the finish of stress relaxation 1,
 5 respectively. The quotient of the mobile dislocation density at a time $\rho_{m(t)}$
 6 and the mobile dislocation density at the onset of repeat relaxation $\rho_{m(0)}$
 7 yields:

$$\frac{\rho_{m(ij)}}{\rho_{m(0)}} = \frac{\dot{\tau}_{ij}}{\dot{\tau}_{i1}} (j = 1, 2, 3...) \quad (3)$$

8 The total density of states (DOS) at Fermi level for Fe₁₆ is 15.16 states/Ry
 9 atom (theoretical value: 15.37 [18]), and for Fe₁₅ is 15.64 states/Ry atom.
 10 The DOS at the Fermi level in the H-containing BCC iron is found to be
 11 reduced. This is different from FCC iron with H occupied at octahedral site,
 12 in which the DOS increases as reported by Gavriljuk's group [4].

13 As shown in Fig. 1, there is a strong peak for projected DOS (PDOS) at
 14 -8.62 eV ($E - E_F$) on the nearest neighbor Fe atom of interstitial H (Fe_{nn}).
 15 The -8.62 eV peaks in all Fe orbitals correspond to the H-1s states which
 16 indicate strong bonding interaction between Fe and H.

17 The total charge of H, individual iron atom (with no neighbor H atoms,
 18 Fe_{in}) and the Fe_{nn} atom resulted from the Bader analysis are shown in Table
 19 1. The total charge of Fe_{in} remains the same as in the hydrogen free bulk.
 20 Charge variation of +0.40e⁻ occurs on the H atom, and -0.07e⁻ occurs on

1 the nearest neighbor Fe atom. It has been reported that charge transference
 2 of $-0.31e^-$ appears from Fe_{nn} atom near an edge dislocation of BCC iron [19].

3 With a grid refinement number of 4, the distributions of all-electron den-
 4 sity (in a unit of Bohr^{-3}) for Fe_{nn} , H and vacancy are calculated and charac-
 5 terized by plotting contour surfaces with different isovalues in Fig. 2. Fe_{nn}
 6 atom expresses bonding behavior with H atom in Fig. 2a, and the distance of
 7 Fe_{nn} -H bond is less than the Fe_{nn} - Fe_{in} bond as shown in Table 1. Hydrogen
 8 atoms increase the electron charges in tetrahedral sites of the bulk (Fig. 2b)
 9 and also in the vacancy (Fig. 2c and Fig. 2d).

10 Although the H-induced variations in DOS at Fermi level for BCC iron
 11 are in opposite tendency with FCC iron, the result that hydrogen decreases
 12 electron density of Fe atom is in accordance with the FCC iron system [4].
 13 Unlike the carbon atom enhances local electron density of iron atoms and
 14 assists the covalent character of inter-atomic bonds [20], hydrogen increases
 15 the concentration of electrons in lattice and promotes the metallic character
 16 of atom interactions. Compared with covalent bonds, the metallic character
 17 could increase the local plasticity of metal and the mobility of dislocations.

18 After relaxation via DFT calculations, H atoms are stable in the tetrahe-
 19 dral sites of the lattice. The atomic forces in three axis for both H and
 20 Fe atoms are lower than $0.008 \text{ eV/\AA}$. The strain field of an interstitial
 21 atom is calculated from the displacement of Fe_{nn} atoms after relaxation,
 22 $\epsilon_{ii} = (L_i - a)/a$, where L_i is length in the i axis of one cell after intro-
 23 ducing H. By our DFT method, the strain tensor of C in octahedral sites
 24 of iron is calculated to be $\{\epsilon_{11}, \epsilon_{22}, \epsilon_{33}\} = \{0.21, -0.018, -0.018\}$, which is
 25 comparable to experiment value $\{0.38, -0.026, -0.026\}$ used in Cocharadt's

1 calculation [5]. The strain field of one H atom in Fe_{16}H_1 is calculated
 2 to be $\{0.014, 0.041, 0.041\}$. The MD calculation in large scale results of
 3 $\{0.015, 0.059, 0.059\}$, and shows good agreement with the DFT calculation.
 4 The three components were considered to be identically equaled in none-DFT
 5 calculations for supporting HELP theory [2, 21]. However, using the same
 6 parameter as BCC calculation in a FCC ($2 \times 2 \times 2$) cell (Fe_{32}H_1) the strain ten-
 7 sor of H atom at octahedral site is calculated to be $\{0.0327, 0.0327, 0.0327\}$,
 8 which is isotropic.

9 Following the Cochardt's model, the interaction energy of hydrogen atoms
 10 at position $r = b$ and an edge dislocation laying in $\langle 211 \rangle$ with b in the
 11 direction $\langle \bar{1}11 \rangle$ is calculated. Since H atom may cause the less dilatation
 12 of 0.014 along axes 1, 2 or 3, there are three sets of constant in Eq. (1).
 13 The interaction energies are plotted in Fig. 3a, where angle ψ is the angle
 14 between $\langle \bar{1}11 \rangle$ and the radius vector from the dislocation to the considered
 15 elementary cell. It is shown that the lowest interaction energy locates at
 16 $\psi = 270$ degrees, and thus H atoms prefer to stay below the extra half plane
 17 of edge dislocations. The lowest energy comes from H atom with strain field
 18 of $\{0.014, 0.041, 0.041\}$, and the minimum $U_{DH}^E = -0.24$ eV.

19 The interaction for a screw dislocation in $[111]$ -direction and H atoms at
 20 position $r = b$ is calculated and shown in Fig. 3b, where φ is angle between
 21 $[2\bar{1}1]$ -axis and the normal direction of plane containing $\mathbf{r}$ and $\mathbf{b}$. Because of
 22 the trigonal symmetry of $\langle 111 \rangle$ axis, there is a phase difference of ± 120
 23 degrees for H atom in different positions. The angular dependence of U_{DH}^S
 24 characterized in Fig. 3b indicates that there are three equivalent positions of
 25 lowest energy at $\varphi = 0, 120$ and 240 degrees with minimum $U_{DH}^S = -0.051$

1 eV.

2 The interactions of H with edge dislocation and screw dislocation have
3 been calculated in considerable quantity of DFT and MD calculations, and
4 most of the works agree that hydrogen can be trapped by both edge and
5 screw dislocation cores [15, 22]. However, the trap energy reported in those
6 works are strongly depending on the position of H atom which is hard to be
7 predicted during energy minimization, and the trapping behavior of screw
8 dislocation is generally considered to be the influence of core structure[23].
9 The method used in this study shows the elastic energy and position rela-
10 tionship for both edge and screw dislocation. Due to the elastic interaction,
11 it indicates that H atom can be trapped by screw dislocation even away from
12 the dislocation core area.

13 During plastic deformation, the cross slip of perfect screw dislocation is
14 more important than the behavior of edge dislocations, for the unrecoverable
15 jogs it forms. As the group of Chateau pointed out [21], hydrogen atom
16 influence the cross slip of perfect screw dislocation in FCC mainly by screen-
17 ing interaction of two edge partials, but this theory can not be applied to
18 BCC metal directly due to there is no partial dislocations. By comparing
19 the accumulation of H around a screw and an edge dislocation, one can find
20 that the segregation of H atom takes place only below the glide plane of an
21 edge dislocation but all around a screw dislocation, roughly the screw can
22 bind twice as many H atoms as an edge dislocation. Although the elastic
23 interaction energy away from the screw dislocation core is much less than the
24 case of edge dislocation, increase of local H concentration could magnify the
25 H-screw interactions and influence the mechanical property of BCC metals.

1 As shown in Fig. 4a, at low cathodic current density, the yield stress in-
2 creases 5 MPa at most and the effective activation volume is almost constant,
3 which indicates dislocation motion is impeded when the H concentration is
4 low. As the interaction energy for H-edge is almost 5 times more than H-
5 screw interaction, at low H concentration the H-edge interaction could be
6 stronger than the H-screw one. Moreover, the hydrogen shielding in this
7 case may have less effect on enhancing dislocation mobility, as the flow stress
8 increases during tensile test, the deformation process is possibly controlled
9 by the H solute drag effect.

10 The mobile dislocation density decreases rapidly in hydrogen-free iron
11 after even one cycle in Fig. 4b. At higher H concentration, the dislocation
12 density decreases with a slower speed, and it can still maintain at a stable
13 value after 5 cycles. This and the steep decrease of effective activation vol-
14 ume in Fig. 4a together signify that hydrogen could increase the mobility
15 of dislocations in BCC iron at higher cathodic current densities more than
16 25 mA/cm². The elastic interactions of H-edge and H-screw dislocation is
17 proportional to the H concentration. At high H concentrations, the screw
18 dislocation is able to trap more hydrogen atoms than the edge one and the
19 interaction of H and screw dislocation is much more important in this condi-
20 tion. The enhanced cross slip and jog formation caused by H shielding effect
21 as reported by Chateau et. al [21] could be the main reason for the steep
22 reduction of yield stress and effective activation volume after 25 mA/cm².

23 In summary, H in BCC iron can increase the electron densities at tetrahe-
24 dral sites and vacancy, and that the hydrogen-enhanced metallic character of
25 inter-atomic bonds can increase the mobility of dislocations and contribute

1 to the HELP theory. Two components of strain tensor for H interstitial atom
2 are calculated to be unequal, which is expected to cause elastic interaction of
3 H with screw dislocations, as it does with edge dislocations. For the angular
4 dependence of H-edge dislocations interaction, H atoms prefer to stay under
5 extra atomic plane, while for screw dislocation there are more positions for
6 the lowest interaction energy and high local H concentration is possible. The
7 repeated transients tests for H-charged α -iron indicate that significant hydro-
8 gen enhanced plasticity can be observed with relative high H concentrations,
9 and in those cases, the H-screw interaction should be considered, and it is
10 possible to lead for a new understanding of hydrogen embrittlement in BCC
11 iron.

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Figure Captions

- 1 1. Fig. 1 Projected density of states over iron and H atoms.
- 2 2. Fig. 2 Contour surfaces of electron density in Fe-H system by Bader
3 analysis. (a) Fe_{nn} atom, with isovalue of 0.08 Bohr^{-3} . (b) Interstitial
4 H atom at tetrahedral site of iron lattice, with isovalue of 0.08 Bohr^{-3} .
5 (c) Hydrogen-free vacancy, with isovalue of 0.02 Bohr^{-3} . (d) Vacancy
6 binding with H atom, with isovalue of 0.02 Bohr^{-3} .
- 7 3. Fig. 3 Elastic interactions of Hydrogen and different kinds of disloca-
8 tion. (a) Edge dislocation laying in $\langle 211 \rangle$, $b = \langle \bar{1}11 \rangle$. (b) Screw
9 dislocation in $[111]$ -direction.
- 10 4. Fig. 4 Thermal activation analysis of dislocation motion in hydrogen
11 charged BCC iron. (a) Variation of effective activation volume (left
12 axis) and yield stress (right axis) at different H concentrations. (b)
13 Evolution of mobile dislocation density with and without H.

Table Captions

- 1

1. Table [1](#) Variation of charges and bonding behavior in BCC iron con-
- 2

 taining H.

Table 1: Variation of charges and bonding behavior in BCC iron containing H.

Atom	Bader charge	Bond	Distance ($\text{\AA}$)
Fe_{in}	25.9437	$\text{Fe}_{in}\text{-Fe}_{nn}$	2.392
Fe_{nn}	25.8713	$\text{Fe}_{nn}\text{-H}$	1.681
H	1.4024		

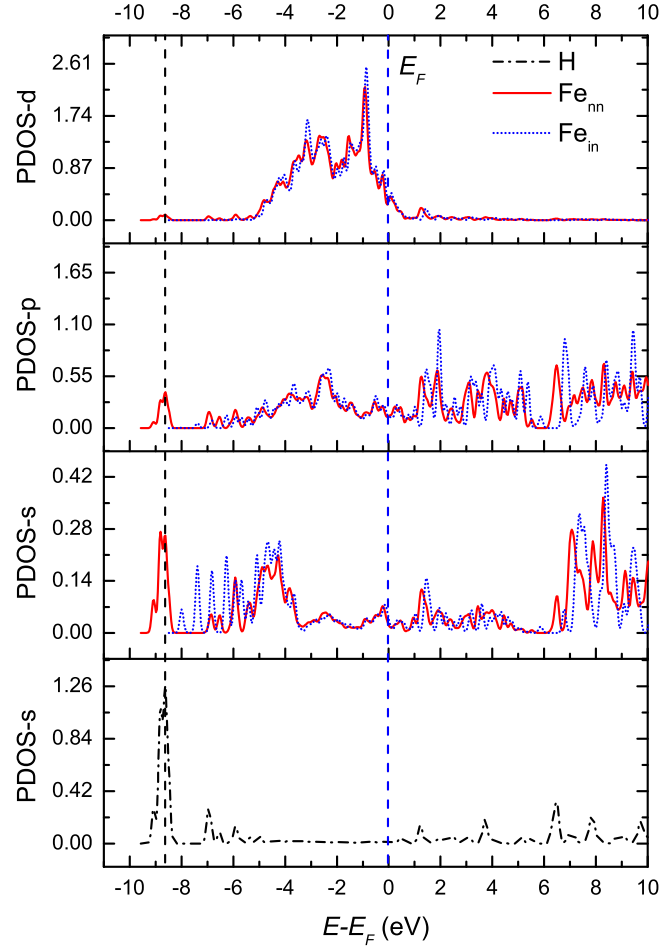


Figure 1: Projected density of states over iron and H atoms.

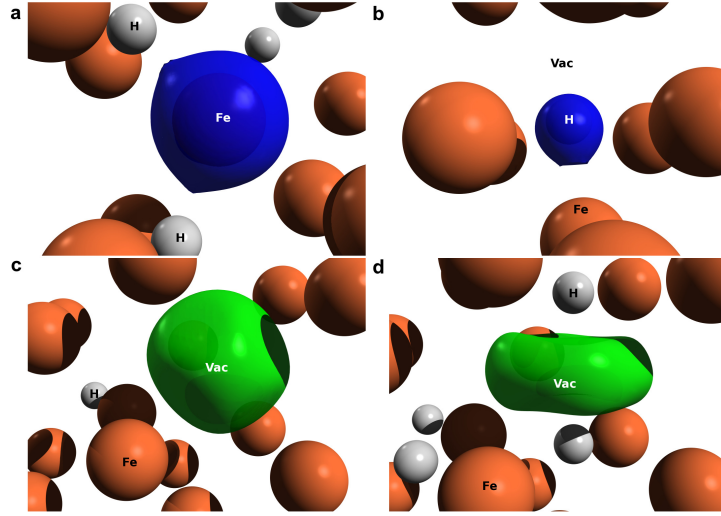


Figure 2: Contour surfaces of electron density in Fe-H system by Bader analysis. (a) Fe_{nn} atom, with isovalue of 0.08 Bohr^{-3} . (b) Interstitial H atom at tetrahedral site of iron lattice, with isovalue of 0.08 Bohr^{-3} . (c) Hydrogen-free vacancy, with isovalue of 0.02 Bohr^{-3} . (d) Vacancy binding with H atom, with isovalue of 0.02 Bohr^{-3} .

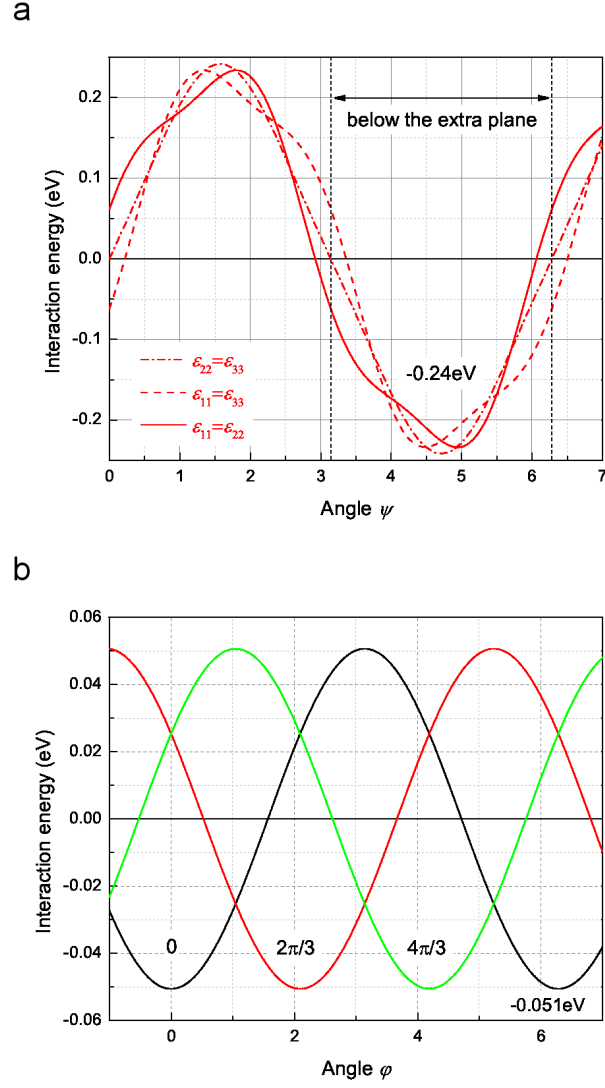


Figure 3: Elastic interactions of Hydrogen and different kinds of dislocation. (a) Edge dislocation laying in $\langle 211 \rangle$, $b = \langle \bar{1}11 \rangle$. (b) Screw dislocation in $[111]$ -direction.

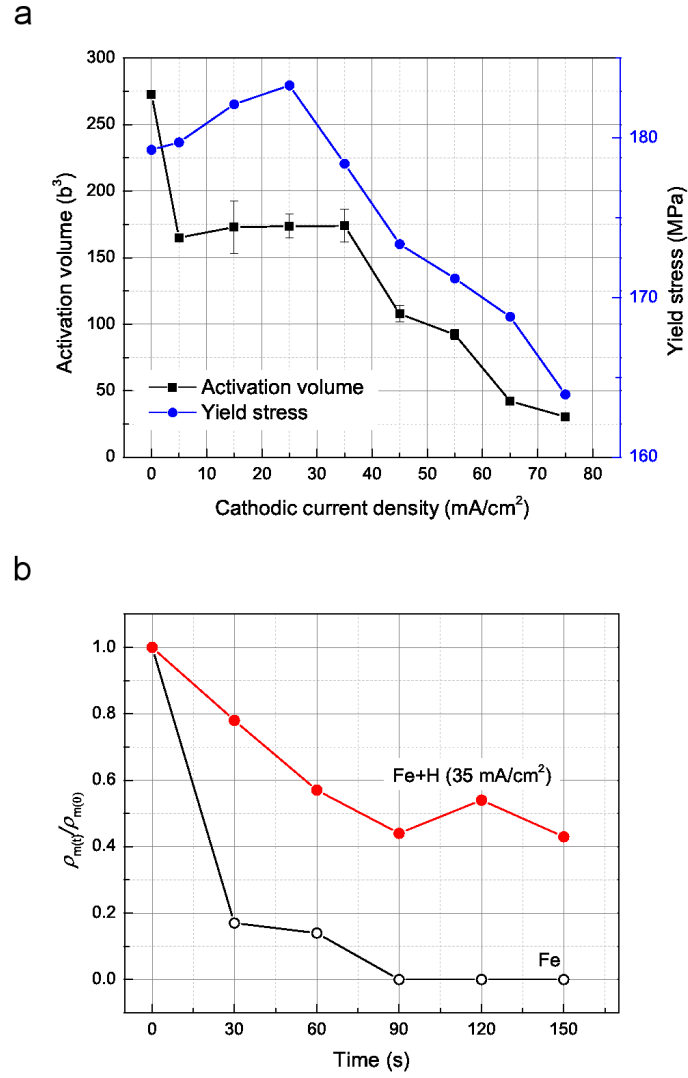


Figure 4: Thermal activation analysis of dislocation motion in hydrogen charged BCC iron. (a) Variation of effective activation volume (left axis) and yield stress (right axis) at different H concentrations. (b) Evolution of mobile dislocation density with and without H.