

# Ab initio Simulation of Dissolution Energy and Bond Energy of Hydrogen with $3sp$ , $3d$ , and $4d$ Impurities in bcc Iron

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**Abstract**—The fundamental understanding of the localization of H atoms in steel is an important step to describe theoretically the mechanisms of hydrogen embrittlement at the atomic level. The influence of various substitutional impurities (Mg, Al, Si, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Pd, and Cd) on the energy of hydrogen dissolution in the bcc iron lattice is studied via ab initio calculations within the density functional theory (DFT). The electronic and elastic contributions of various impurities to the dissolution energy are found, and their influence on the bond energy of hydrogen and impurities is analyzed. There is a linear relationship between the energy of hydrogen dissolution and the magnitude of change in electron density inside a tetrahedral pore after the introduction of a hydrogen atom into it. The results obtained made it possible to formulate the key mechanisms of controlling the localization of hydrogen in the bcc iron by substitutional dopants.

**Keywords:** ab initio simulation, hydrogen, bcc iron, substitutional impurities, bond energy, dissolution energy

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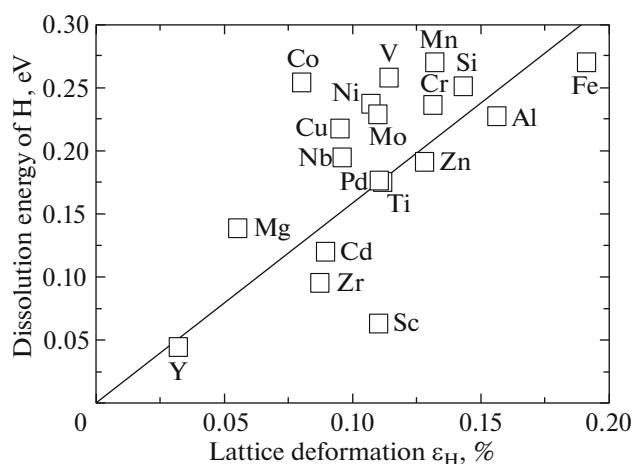
## 1. INTRODUCTION

The problem of hydrogen and metals and, in particular, the hydrogen brittleness of steels is both much old and new [1–4]. Its nature is due to the release of hydrogen gas captured by the melt from the atmosphere during the crystallization near lattice defects [5–8]. The hydrogen embrittlement was of interest to metallurgists and physicists for more than a hundred years. Several mechanisms of its occurrence were proposed, but it was not possible to formulate a complete theory of this phenomenon. Recent interest to this problem is due to the expansion of the network of main gas pipelines, through which hydrogen-containing mixtures are pumped. It is planned to pump a hydrogen-methane mixture in the future, when environmentally friendly hydrogen energy will be widespread [9].

A critical concentration of hydrogen must be reached in the crack initiation region regardless the steel embrittlement mechanism [4]. In addition, the transfer rate of hydrogen is required to be high enough to maintain this critical concentration. The volume and the rate of hydrogen transfer in a crystalline material, however, is controlled by its capture processes in the point and extended crystal defects, microvoids or dispersed precipitates [4, 10, 11]. The capture of hydrogen in traps introduced into the bulk of a metal,

therefore, may be used as an important method to avoid the embrittlement of steels. If the energy of hydrogen capture by various impurities observed often in steels is known, it is one of the important points to understand the embrittlement phenomenon and to avoid it in this regard.

The energy of hydrogen capture by impurities of  $3sp$ ,  $3d$ , and  $4d$  metals in a bcc iron matrix was simulated computationally within the density functional theory (WIEN-2k software) in our previous work [12]. We showed that hydrogen occupies only the tetrahedral pores in the lattice. When the electronic (chemical) and elastic contributions to the energy of dissolution and capture of hydrogen by impurities were considered, we showed that both contributions are comparable in magnitude and can compete with each other. The results [12] and ab initio simulation data [13], which are similar, appear to be a useful important information, whose physical explanation, however, has not been provided. The capture of hydrogen in iron by various impurities is analyzed more deeply in this work. We showed that the change in energy of hydrogen dissolution caused by any impurity is probably due to the perturbation of electron density of a matrix created by it.



**Fig. 1.** Relationship between dissolution energy of hydrogen in bcc iron alloys doped with impurities (their names are indicated in squares) and relative deformation of lattice of alloy during dissolution of hydrogen in it.

## 2. CALCULATIONS

Figure 1 shows a relationship between the energy of hydrogen dissolution in bcc iron doped with various impurities and the magnitude of lattice deformation that occurs when hydrogen atom is in a tetrahedral position near impurity atom [12]. The position was chosen based on the lowest total energy of the system. It is clear that the elastic energy arising during the incorporation of hydrogen atom is not the only factor that determines the energy of hydrogen dissolution.

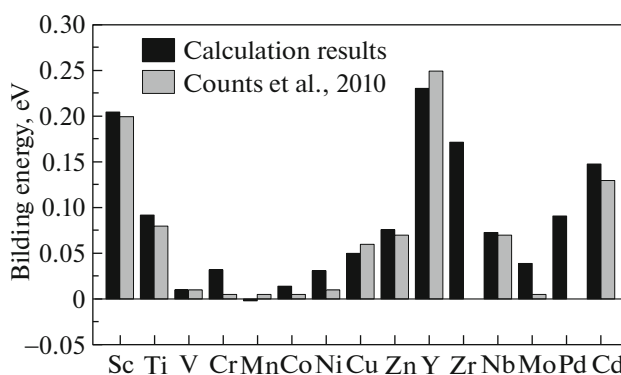
Figure 2 [12], which shows the energies of hydrogen capture by all the impurities, also confirms this fact. Indeed, the Y impurity, which has a large atomic radius, binds hydrogen well, whereas Mn and Co impurities with a radius similar to that of iron do not form a bond.

The capture energy or bond energy of hydrogen with an impurity was found from the following formula:

$$E_{\text{bind}}(\text{H-X}) = E(\text{Fe}_{54}\text{H}) - E(\text{Fe}_{53}\text{XH}), \quad (1)$$

where  $E_{\text{bind}}(\text{H-X})$  is the energy of bond between hydrogen and X impurity in bcc iron,  $E(\text{Fe}_{54}\text{H})$  the total energy of a supercell comprising of 54 iron atoms and a hydrogen one incorporated into the tetrapore, and  $E(\text{Fe}_{53}\text{XH})$  the energy of the supercell, but with an X impurity atom instead iron one.

The energy of hydrogen dissolution was calculated for various lattice parameters of a pure bcc Fe for clarification. The elastic stress resulting from the uniform deformation of a lattice was found as  $\sigma = 3K$ , where  $K$  is the bulk elasticity modulus for iron, whose experimental value was 162 GPa. The relationship between the energy of hydrogen dissolution and the voltage applied to the supercell simulated (Fig. 3) was con-

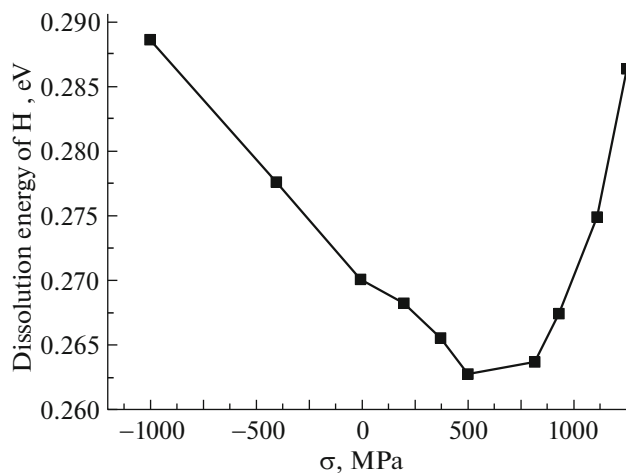


**Fig. 2.** Comparison of simulation results of bond energy of hydrogen atoms with substitutional impurities in bcc iron with data from [13].

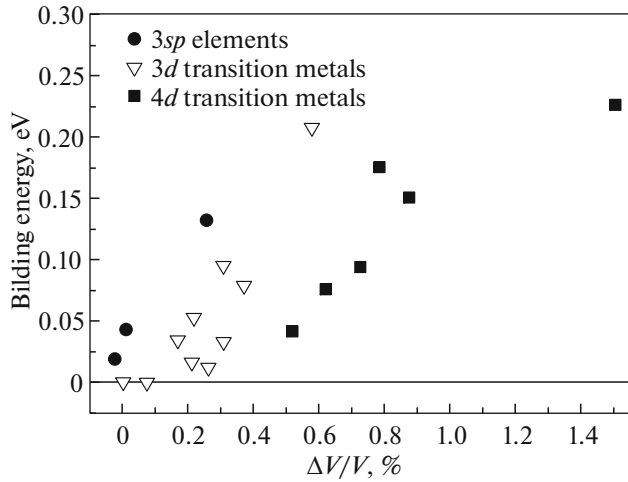
structed from these equations. This relationship consists of two clear parts. The descending section from  $-1000$  to  $+500$  GPa describes the well-known linear relationship between the energy of hydrogen dissolution and the hydrostatic deformation of the lattice [14]. The ascending section has a completely different pattern and is probably due to an increase in electron density  $n$  inside the tetrahedral pore. This hypothesis is confirmed by the semiempirical model of an effective medium [15], in which the energy of incorporation of hydrogen into a metal matrix with an electron gas density  $n$  increases sharply with an increase in this value.

In addition, we constructed the relationship between the hydrogen capture energy and the change in volume of a bcc iron lattice during the introduction of a dopant into it (Fig. 4).

There is a clear and almost linear correlation between the energy of a hydrogen–impurity interac-



**Fig. 3.** Relationship between dissolution energy of hydrogen in bcc Fe and the applied elastic stress.



**Fig. 4.** Relationship between bond energy of hydrogen atom with a dopant and relative deformation of bcc iron lattice during dissolution of this impurity in it.

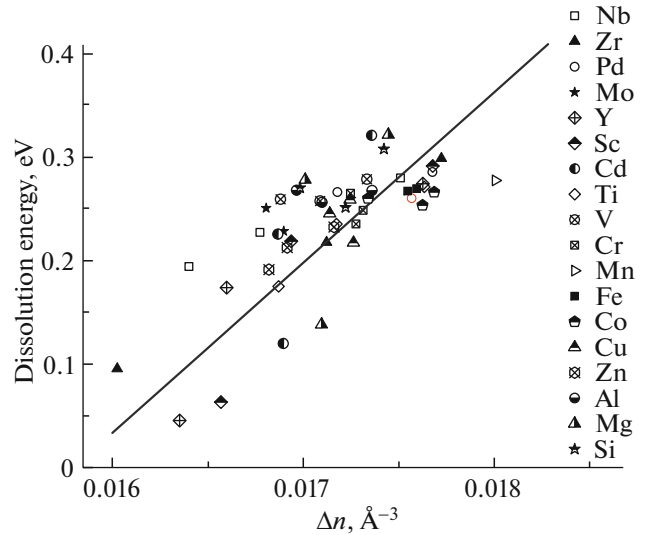
tion and the degree of expansion of the iron lattice by this impurity. At the same time, the linear dependences have slightly different slopes and are shifted relative to each other for 3d and 4d impurities and 3sp elements. This indicates that besides elastic energy, there is another factor that depends on the position of impurity in the Periodic Table or on the number of valence electrons of the impurity. The contribution of the lattice deformation field, therefore, can contain both the elastic and electronic contributions to the energy of hydrogen dissolution depending on a sign (tension or compression). The study of the contributions and the comparison of their relative values is still a great challenge despite the fact that such a hypothesis was formulated quite a long time ago [16].

It is quite clear, therefore, that the dissolution energy of hydrogen and its energy of binding with impurities depends on the local electron density and the energy of local deformation, and the latter can also depend on the electron density.

These relationships led to the problem to calculate the electron density in the iron–substitutional impurity system and in the iron–impurity–hydrogen system to assess the influence of electron density on the capture energy of hydrogen by impurity. For this purpose, we calculated the changes in density of valence electrons in the volume of a tetrapore after the incorporation of a hydrogen atom into them:

$$\Delta n = n_{\text{Fe}_{53}\text{X}} - n_{\text{Fe}_{54}} - n_{\text{H}}, \quad (2)$$

where  $n_{\text{Fe}_{53}\text{X}}$  is the charge density of valence electrons in the bcc iron supercell with one of the substitutional impurities  $\text{Fe}_{53}\text{X}$ ,  $n_{\text{Fe}_{54}}$  the charge density in a pure iron supercell, and  $n_{\text{H}}$  the charge density in a supercell containing a single hydrogen atom. A supercell with a constant geometry was used in all cases, and the charge



**Fig. 5.** Dissolution energy of hydrogen near various impurities in iron matrix and the change in electron density inside corresponding tetrahedral pore after incorporation of hydrogen atom into it.

density was calculated for the volume of a tetrapore of the bcc iron lattice.

### 3. RESULTS AND DISCUSSION

We calculated the changes in electron density of valence electrons caused by the incorporation of a hydrogen atom into the tetrahedral pores located in different coordination spheres of substitutional impurities (VASP software [17, 18]). All calculations were performed for a ferromagnetic cubic bcc supercell containing 54 atoms using PAW potentials [19] and the GGA-PBE generalized gradient approximation [20] with a cutoff for the energy of plane waves at 450 eV. Figure 5 shows the calculation results obtained according to the Eq. (2). It should be noted that the change in electron density is positive after the addition of hydrogen in all the cases. This indicates that hydrogen in bcc iron is a donor to partially transfer its electron density to the collectivized states of the matrix. It is also clear that all the impurities form a general linear trend, although with some scatter, probably due to the unavoidable calculation errors. This result is main in this work. Ab initio calculations showed for the first time that there is a universal relationship: the energy of hydrogen dissolution is the lower, the less the inserted hydrogen atom changes the electron density in a tetrahedral pore. Such a relationship led probably to the success of the effective environment methods.

The bond energy of a hydrogen atom with a substitutional impurity for 3d impurities is equal to the difference between the dissolution energies of hydrogen in pure iron and in iron containing substitutional impurities. Considering that the first value is the same

for all impurities, then all the factors related the influence of impurities on the dissolution energy in bcc Fe discussed above also affect the bond energy. The bond energy, therefore, will be as much as higher, the lower the perturbation of electron density during the dissolution of hydrogen in alloy, in comparison with the value of  $0.0175 \text{ \AA}^{-3}$  for pure iron. Of course, the impurities with a large atomic radius, which, locally expanding the matrix lattice around themselves, decrease the pressure on a hydrogen atom incorporated to decrease the charge transfer from it and to change the electron density, will possess this property. The second mechanism, however, is also possible, when doping leads to a shift of the Fermi level of the system to a local minimum of the density of states, which makes the transfer of electron density from hydrogen to the matrix to be unfavorable. High bond energy observed during the doping with Cu and Zn impurities is probably due to this fact.

### CONCLUSIONS

The influence of low concentrations of Mg, Al, Si, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Pd, and Cd substitutional impurities on the dissolution energy of hydrogen in bcc iron and the energy of capture of hydrogen by them was studied within the density functional theory. The energies of the H–Pd (0.087 eV) and the H–Zr bonds (0.17 eV) were found in this case for the first time.

We showed that the highest energy of hydrogen capture corresponds to the Y, Sc, Zr, Cd, Ti, and Mg substitutional impurities. The analysis showed that the bond energy of hydrogen with alloying impurities in bcc iron will be the higher, the smaller the perturbation of electron density arises during the dissolution of hydrogen in the doped alloy. The impurities that allow strong capture of hydrogen, therefore, should be searched in two directions. First of all, one should consider the impurities that either decrease the density of electronic states (DOS) of alloy at the Fermi level or are able to locally increase the volume of tetrapores in the matrix lattice near them due to the high atomic radius.

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### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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