First-Principles Calculation on Dissociation of Hydrogen Molecule in Nickel *

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The behavior of hydrogen in Ni was investigated using the first-principles calculations. It was found that there exists only atomic hydrogen in Ni. The hydrogen resides the octahedron, and the lattice constant expands linearly with the concentration of hydrogen. On the basis of a statistical thermodynamic model, the dependency of hydrogen solubility on temperature in Ni was also investigated, and it was found that magnetization does not favor the dissolution of hydrogen, which is in agreement with the experimental results.

1. Introduction

In order to protect our environment from the car fumes, many scientists and engineers are attempting to develop various new types of power systems to replace the gasoline and/or diesel engines, among which the nickel hydrogen cell is attracting more and more attention.[1] Therefore, the study of the interaction between hydrogen and nickel is very important for materials science and engineering. We reported a quantitative treatment for some typical experimental results of hydrogen solubility near Curie point in Fe, Co and Ni, on the basis of the statistical thermodynamic model developed by ourselves.[2] Recently, we performed a series of first-principles calculations to study the effects of hydrogen on the magnetism of magnetic metals in both forms of cluster and bulk materials and it was found that the strong hybridization among the orbitals of H and Ni atoms suppresses the ferromagnetism completely.[3] On the basis of the first-principles calculation results, we modified our statistical thermodynamic model and re-treated the experimental data of the Ni–H system in a wide range of temperature.[4]

The main aim of the present paper is to present our results of the first principles calculation on the dissociation of hydrogen molecule and position of hydrogen atom in nickel, and the effect of hydrogen on the lattice expansion of nickel. It should be pointed out that there were several theoretical studies on the interaction of hydrogen with transition metals.[5-9] These studies, particularly the pioneer work conducted by Adachi and Imoto,[5] are very instructive for the further first-principles studies.

It is worthwhile mentioning that first-principles study is very useful for us to have a deep understanding of the nature of interaction between hydrogen and metals. For the solubility of hydrogen in metals, however, it is not suitable because of the heavy computation. Therefore, it is also necessary for us to carry out phenomenological or statistical studies. The results of first-principles calculations are discussed in the next

section and those of the statistical thermodynamic treatment are described in the third one. The final section ends with a brief summary of the present work.

2. First-Principles Calculation and Discussion

2.1 Computational methods

We used *ab initio* ultrasoft pseudopotential scheme with plane-wave basis (Vienna Ab initio Simulation Program (VASP)),[10] in which the finite-temperature local-density functional theory developed by Mermin[11] is used and the variational quantity is the electronic free energy. Finite-temperature leads to broadening of the one-electron levels that is very helpful to improve the convergence of Brillouin-zone integrations. The electron-ion interaction is described by a fully nonlocal optimized ultrasoft pseudopotential,[12, 13] which has been extensively tested for transition metals.[14] The minimization of the free energy over the degrees of freedom of electron densities is performed using the conjugate gradient iterative minimization technique.[15] About 150 irreducible k points were used in Brillouin zone. 400 eV has been used as cut-off energy in the plane-wave expansion of the pseudo-wavefunctions. The number of k points and the cut-off energy are large enough to obtain a good convergence for all the cases in our calculations. The exchange-correlation energy of valence electrons is adopted in the form of Ceperly and Alder[16] as parameterized by Perdew and Zunger.[17]

2.2 Dissociation of hydrogen molecule on single Ni atom

In order to assess the accuracy of our calculations, we first compute the equilibrium bond length of free hydrogen molecule H_2. We put H_2 in the supercell with 1 nm × 1 nm × 1 nm, the obtained equilibrium bond length is 0.07659 nm which is in agreement with the experimental value of 0.07500 nm.[18] For pure Ni, the optimized lattice constant is 0.34300 nm, in a reasonable agreement with the experimental value of 0.35200 nm.[19]

Before the investigation of hydrogen behavior in bulk Ni, we consider at first the simplest case: H_2 absorbed on a single Ni atom. The equilibrium configuration is found to be a triangle with C_{2v} symmetry, Ni–H bond length is 0.14100 nm,

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while H–H distance is 0.16800 nm, which is much larger than the bond length of H_2, indicating that H_2 has already been dissociated into hydrogen atom.

2.3 Dissociation of hydrogen in bulk Ni

Now, we put H_2 inside the bulk Ni with three different initial orientations of H_2. Case 1: the H_2 is put in the center of the cell with orientation parallel to [001] direction; Case 2: H_2 is oriented along [111] direction with one H atom in the center of the cell and Case 3: H_2 is oriented along [110] direction, being asymmetric with respect to the basal atoms. And then we fully optimize the atomic positions and lattice constants for all these three cases. The result shows us that the equilibrium atomic distance between the two H atoms becomes much larger than that of free H_2, the values for Case 1, 2 and 3 are 0.11880 nm, 0.18549 nm and 0.24985 nm, respectively.

It can be seen from the above that in all three cases, the H_2 is dissociated in bulk Ni, which is the same as in the case of H_2 on the single Ni atom.

2.4 The stable position of hydrogen in bulk Ni

From the above, in bulk Ni there exists only hydrogen atom, not the molecule. Bulk Ni has a face centered cubic (fcc) structure and there are two types of interstitial sites in the structure for atomic H to reside: octahedral site and tetrahedral site. Which is more stable? In order to solve this problem, we calculated the total binding energy and the lattice constants for both cases. The results show that if we put the H atom in the octahedron, the total binding energy is -29.8554 eV with the lattice constant of 0.34912 nm for a, b and c; while in the tetrahedron, the corresponding values become -29.6265 eV and 0.35150 nm, respectively. Thus, it can be concluded that H atom prefers octahedron to tetrahedron, as shown in Fig. 1. It should be noted, however, that as the energy difference is not too large, the H atom in the octahedron may diffuse into the tetrahedron when at high temperature and/or under high pressure.

2.5 Lattice expansion of Ni with hydrogen

From the previous subsection it is known that the hydrogen atom resides the octahedron. The problem arises: how the lattice constant changes with the hydrogen concentration in Ni hydride? We have calculated for the following cases: the concentration of hydrogen (atomic fraction) being 0, 0.25, 0.5, 0.75 and 1.0. As shown in Fig. 2, the lattice constant expands linearly with the concentration of hydrogen. The relationship between the lattice constant a and hydrogen concentration y_H can be expressed as below:

$$a(y_H) = 0.4025(1 + 0.044(y_H - 0.6)) \text{ (nm)}. \quad (1)$$

3. Statistical Thermodynamic Treatment and Discussion

In the previous section, we discussed dissociation of hydrogen molecule H_2 on single Ni atom and in bulk Ni using
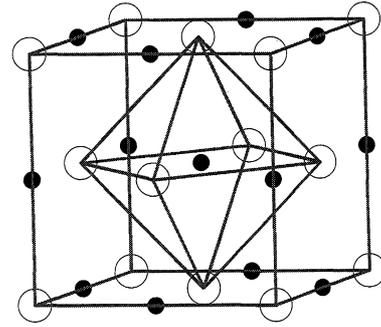

Fig. 1 The interstitial sites for hydrogen in bulk nickel of fcc structure, where the large open circles and the small solid ones represent the nickel and hydrogen atoms, respectively.
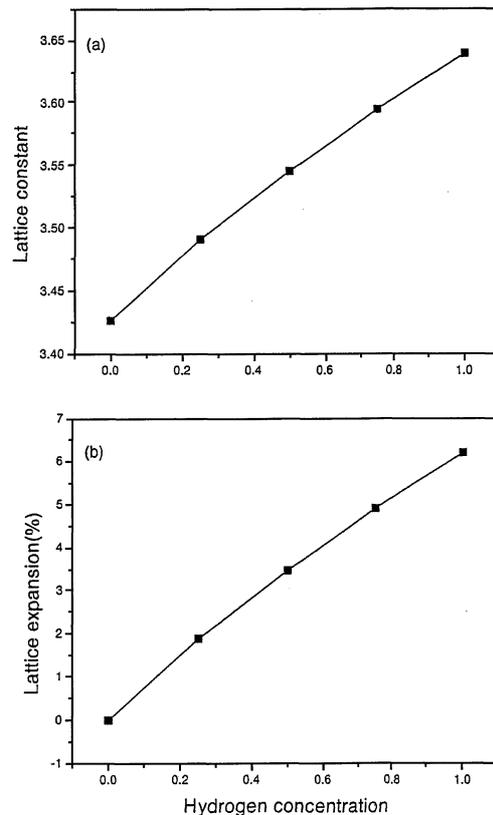

Fig. 2 Lattice constant (a) and lattice expansion (b) changes with the concentration of hydrogen.

the first-principles calculations, and found that the lattice constants of bulk Ni expands linearly with the concentration of hydrogen. As for the solubility of hydrogen in bulk Ni, however, the first-principles calculation is not so suitable, because the calculation is too heavy. Therefore, we developed a statistical thermodynamic model, the so-called extended higher order regular solution model, on the purpose of quantitative analysis of hydrogen solubility in magnetic alloys. Owing to the page limitation, this section only gives the resultant expression of the model with brief explanation, the reader is referred to literature[4] for details.

At the thermodynamic equilibrium condition, we got the following two expressions:

$$RT \ln \frac{1 - y_H}{y_H} = \sum x_i U_{iH} - z \left\{ J\mu^2 + \frac{1}{2}RT \left[(1 + \mu) \ln \frac{1 + \mu}{2} + (1 - \mu) \ln \frac{1 - \mu}{2} \right] \right\}, \quad (2)$$

$$RT \ln \frac{1-\mu}{1+\mu} = 4J\mu. \tag{3}$$

Where R is gas constant; T, absolute temperature; y_H, atomic fraction of hydrogen; x_i, atomic fraction of metallic element i; z, coordination number of hydrogen atom; U_{iH}, molar chemical interaction energy of metallic element i with hydrogen; J, molar exchange; and μ is the magnetization.

Equation (3) describes the temperature dependence of magnetization μ. Equation (2) can be solved for the hydrogen concentration as a function of temperature and magnetization:

$$y_H = \left\{ 1 + \exp\left\{ \sum \frac{x_i U_{iH}}{RT} - z\left\{ \frac{J\mu^2}{RT} + \frac{1}{2}\left[(1+\mu)\ln\frac{(1+\mu)}{2} + (1-\mu)\ln\frac{(1-\mu)}{2} \right] \right\} \right\} \right\}^{-1}. \tag{4}$$

The energy term in the exponential function is composed of contributions from chemical and magnetic interactions to the dissolution of hydrogen. In the case of a pure magnetic metal, eq. (4) is reduced to

$$y_H = \left\{ 1 + \exp\left\{ \frac{U_{iH}}{RT} - z\left\{ \frac{J\mu^2}{RT} + \frac{1}{2}\left[(1+\mu)\ln\frac{(1+\mu)}{2} + (1-\mu)\ln\frac{(1-\mu)}{2} \right] \right\} \right\} \right\}^{-1}. \tag{5}$$

The exchange interaction parameter J can be determined from the equation:

$$J = -\frac{1}{2}RT_c, \tag{6}$$

which follows from eq. (3) by taking the extremal condition, *i.e.* μ tends to zero as the temperature approaches T_c.

Using above equations, we can make quantitative analyses for the hydrogen solubility in magnetic alloys and pure metals. Here we show an example of hydrogen in pure metal Ni whose magnetic properties have been systematically investigated.[20]

Shown in Fig. 3 are the experimental and calculated results of hydrogen solubility in Ni. In the figure, T_c is the Curie temperature, the open and closed symbols represent the experimental data of Vyatkin, Zhorin and Tseitlin[21] and those of Shapovalov and Boyko,[22] respectively. Different open symbols stand for different specimens used in the experiment. Both single and double curves represent the calculated results. It should be noted that in the ferromagnetic state, the double curve is the extrapolation from that in the paramagnetic state, while the single one is calculated with

the magnetization being taken into account. The calculations were carried out by combining eqs. (3), (5) and (6), using the parameter values: U_{NiH}(in paramagnetic state) $=$ 14.30 kJ/mol, U_{NiH}(in ferromagnetic state) $=$ 12.55 kJ/mol and $T_c = 627$ K.

There is a common feature among the experimental data of the two groups that with the decrease of temperature, the hydrogen solubility drops more rapidly in the ferromagnetic state than in the paramagnetic state. This is in agreement with our calculated results. Thermodynamically, the interchange interaction energies of hydrogen with metals differ from paramagnetic state to ferromagnetic state. The value of U_{NiH} decreases from paramagnetic state to ferromagnetic state, the observed difference being 6.3 ± 1.6 kJ/mol.[21] This is in reasonable agreement with our calculated result of 1.75 kJ/mol.

Thus, we conclude that the effect of magnetic transition on hydrogen solubility in ferromagnetic metal Ni can be described by the combination of eqs. (3), (5) and (6) with appropriate choice of the parameters.

4. Summary

In order to investigate the behavior of hydrogen in bulk of pure transition metal nickel, a series of first-principles calculations were performed. It has been found that there exists only atomic, not molecular hydrogen in Ni. The hydrogen resides the octahedron, and the lattice constant expands linearly with the concentration of hydrogen. On the basis of a statistical thermodynamic model, the dependency of hydrogen solubility on temperature in Ni was also investigated, and it was found that magnetization does not favor the dissolution of hydrogen, which is in agreement with the experimental results.
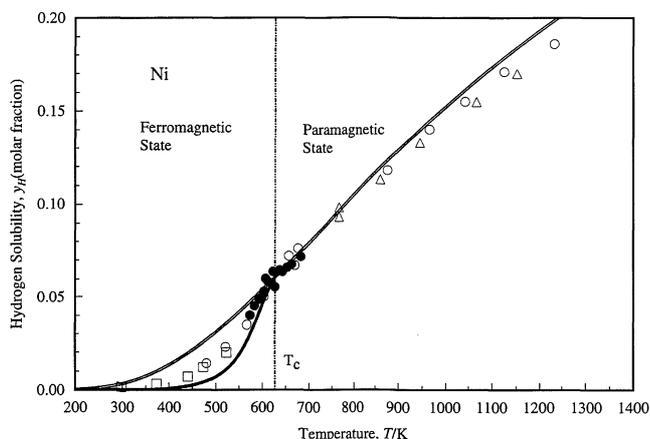
Acknowledgement

Fig. 3   Temperature dependence of hydrogen solubility in nickel. T_c is the Curie temperature. The open and closed symbols represent the experimental data of Vyatkin, Zhorin and Tseitlin[21] and those of Shapovalov and Boyko,[22] respectively. Different open symbols stand for different specimens used in the experiment. Both single and double curves represent the calculated results, of which the single one includes the effect of magnetic transition.

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