§36. Determination of Solution Energy of Hydrogen in $Be_{12}Ti$ by First Principles Electronic-structure Methods

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For the neutron multiplier, beryllium metal (Be) is a reference material in the blanket design. However, it may not be applicable to the DEMO blanket, which requires high temperature and neutron dose, because of high reactivity and large swelling. Therefore, it is necessary to develop an advanced material for a neutron multiplier that has high temperature resistance and high radiation resistance. Berylides such as $Be_{12}Ti$ and $Be_{12}V$ have been suggested as promising candidates for advanced neutron multipliers from the viewpoints of high melting point, high beryllium content, fast decay of gamma dose rate and good chemical stability, etc.

The behaviour of hydrogen isotopes in the neutron multiplier will influence the safety of the reactor. Furthermore, the generated hydrogen isotope causes problems for the neutron multiplier with respect to tritium retention.

In this work, the interaction of atomic hydrogen with $Be_{12}Ti$ has been studied by means of first principles electronic-structure methods.

All the calculations were performed using the density functional theory (DFT) method as implemented in the SIESTA code[1]. The electron exchange and correlation are treated within the generalized gradient approximation (GGA) of the Wu-Cohen modification of Perdew−Burke−Ernzerhof (PBE-WC) function[2]. The electron-ion interactions were described by normconserving Troullier Martins pseudo potentials factorized in the Kleinman-Bylander form. The valence wave functions were expanded in a basis set of localized atomic orbitals, and both single-ζ (SZ) and double-ζ polarized (DZP) basis sets were used for the purpose of comparison. The calculations were carried out in a supercell containing 52 atoms. The convergence of the calculations has been tested, and we found a $4 \times 4 \times 4$ k-point grid and a 200 Ry cutoff for the real space mesh can give well converged results.

Relaxation is performed until all the Hellmann−Feynman forces are converged to 0.01 eV/Å. Electronic convergence is achieved when the difference between the total energies of the last two consecutive steps is less than 10^{-4} eV.

To build the lattice energy–volume curves, the lattice energy was computed as a function of the lattice volume. Fig. 1 shows the lattice energy–volume curves for $Be_{12}Ti$, and Table 1 lists the parameters of the corresponding fitted Murnaghan equations of state for the sake of comparison[3]. It was fitted by the Levenberg-Marquardt algorithm to the resulting lattice energy–volume curves, yielding directly the parameters E_0, V_0, B_0, and B_0'. The calculated lattice parameter, a =b= 7.625 Å, c=4.319 Å were slightly large as

compared with experimental values, 3.6% and 4.7% respectively. The bulk modulus, B = 100 GPa, were found to be in good agreement with the experimental values of 117 GPa in the framework of the density functional theory.

The solution energy ΔE_s of a H atom was calculated as follows:

$$\Delta E_s = E_{tot}(Be_{12}Ti\text{-}H) - E_{tot}(Be_{12}Ti) - \frac{1}{2}E_{tot}(H_2) \qquad (1)$$

were $\Delta E_{tot}(Be_{12}Ti\text{-}H)$ is the total energy of the system with hydrogen in $Be_{12}Ti$, $\Delta E_{tot}(Be_{12}Ti)$ is that of $Be_{12}Ti$ perfect crystal, and $E_{tot}(H_2)$ is that of an H_2 molecule.

Hydrogen atoms accommodated with in twenty different sets of lattice site, resulting in solution energy of +0.1 eV $\sim$ +0.7 eV. These results indicate that $Be_{12}Ti$ intermetallic alloy is endothermic hydrogen occluding metal. Since the endothermic alloys have "positive" solution energy and fast diffusion, hydrogen reemission occurs earlier with increase temperature. Consequently the hydrogen retention coefficient decrease.

Method	a=b (Å)	c(Å)	a/c	B (Gpa)
This work	7.625	4.391	1.7365	100.1
Exp.	7.360	4.195	1.754	117

Table 1. The comparison of the equilibrium structural parameters from this work and from experiments.
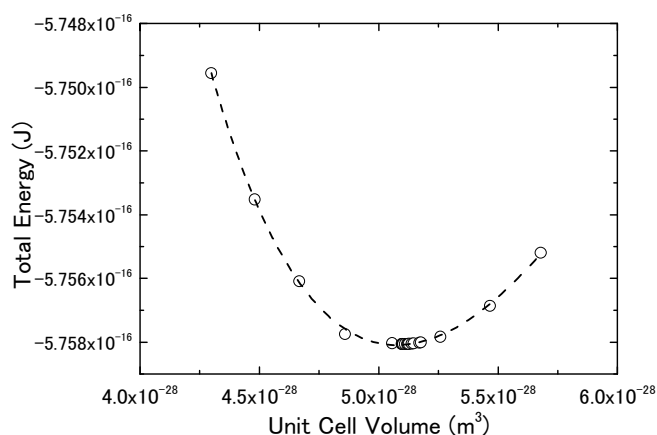

Fig.1. Total energy as function of the volume calculated in this work. The points are from the SIESTA calculations; the dashed line is the fit of the Murnaghan equation of state.

1) E. Artacho, Phys. Status Solidi B 215 (1999) 809
2) Z. Wu and R.E. Cohen, PRB 73 (2006) 235116
3) C. Li and P. Wu, Chem. Mater. 13 (2001) 4642-4648