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Role of hydrogen in heat conduction in zirconium hydride

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Phonon contribution to heat conduction of $ZrH_{1.6}$ is studied by a molecular dynamics method. The vibration modes of particles in Zr-H system are separated to two modes, low frequency mode from the vibration of host metal (Zr) and another related to the high frequency vibration of H. The role of hydrogen in heat conduction was analyzed by molecular dynamics calculations. In the transient condition such as pulse heating, the high frequency mode by H plays an important role in controlling temperature of the system in a short time (0.05psec) at high temperatures (1300 to 2900K). At the temperature of 760K, the heat conduction was calculated based on the Green-Kubo formula of statistical linear-response theory. It is revealed that the heat conduction by H is not a dominant process in the equilibrium condition. Nonequilibrium molecular dynamics was also used to analyze the heat conduction. The comparable contributions of Zr and H on the heat conduction were shown.

Key words: zirconium hydride, molecular dynamics, thermal conductivity

1. INTRODUCTION

Metal-hydrides have very high hydrogen atom density, which is equivalent to that of liquid water. Since zirconium nuclide has a small cross section of neutron capture reaction, zirconium hydride is widely employed as a neutron moderator in nuclear reactors [1]. Heat conduction is one of the most important properties of the neutron moderator. A nuclear reactor operates under not only steady state conditions but also transient conditions. In this paper, heat conduction in Zr-H system was analyzed under steady state, transient and equilibrium conditions.

In metal-hydrides heat conduction occurs not only by lattice vibration but also by electron [2]. In experimental studies, lattice vibration contribution was roughly estimated by subtraction of electron contribution from total conductivity using Wiedemann-Franz relationship [3,4]. In this paper, the heat conduction by lattice vibration mode has been evaluated by molecular dynamics simulation. We have focused attention on the role of hydrogen in the heat conduction in Zr-H system. Vibration modes of particles in Zr-H system are separated to two modes, low frequency mode from vibration of the host metal (Zr) and another which is related to high frequency vibration of H. Steady state and transient energy flows were analyzed by nonequilibrium molecular dynamics (NEMD). Energy flow under the equilibrium conditions was analyzed by equilibrium molecular dynamics (EMD).

2. Model system

Our model system is a cubic cell (L=76.32 Å) containing 42,475 atoms (16,384 zirconium atoms and 26,091 hydrogen atoms). Crystalline d-zirconium hydride with H/Zr ratio of 1.6 is used for calculations. The d-zirconium hydride has fcc structure, CaF_2-type, in which hydrogen atoms occupy tetrahedral positions. At room temperature the lattice parameter is 4.775. The pair potentials in zirconium hydride system are given as a function of atomic distance, r, by the following equation (see Fig.1) [5]:

$$\varphi(r) = \varphi_0(r)-\varphi_0(r_{cut}) + (r_{cut}-r)\varphi_0'(r_{cut}), \quad (1)$$

$$\varphi_0(r) = - p_0(1 + (r - r_0))\exp(-\alpha(r - r_0)), \quad (2)$$

where $\varphi_0'(r)$ is the first derivation of $\varphi_0(r)$. The cutoff distance, r_{cut} is set to be 6.5 Å. The parameters of the pair potentials are summarized in Table 1.

Table1 Parameters of pair potentials in zirconium hydride system

	p_0(eV)	α(Å^{-1})	r_0(Å)
H-H	0.141	1.771	2.445
Zr-Zr	1.445	1.263	3.487
Zr-H	0.039	2.286	2.810

3. Calculations and results

3-1. Steady state heat-flow condition (NEMD)

Thermal conductivity of $ZrH_{1.6}$ has been calculated by NEMD [6,7]. Figure 2 is a schematic representation of the unit cell used to compute thermal conductivity under the periodic boundary conditions. The unit cell is divided into many layers perpendicular

to the x-axis. The layers are grouped into 'hot', 'cold', and 'middle' regions. The energy flows in the x-direction from the hot to the cold regions through the middle region. Temperatures in the hot and cold regions are controlled by the stochastic thermostat. Heat, $\Delta\varepsilon$, is added in the hot region and the same amount of heat is removed from the cold region in stationary condition. Figure 3 shows a typical time-averaged temperature profile used to compute the thermal conductivity. The non-linear temperature profile is observed in layers near the heat source and the heat sink regions. In the intermediate region, temperature profile is fit with a linear function as shown in Fig.3. The phonon thermal conductivity was calculated by the Fourier's law,

$$J_x = -\kappa \partial T/\partial x, \qquad (3)$$

where J_x is the thermal flux, κ is the thermal conductivity, and $\partial T/\partial x$ is the gradient of the temperature along the x-axis. Calculated phonon thermal conductivity (0.015W/cm K) is smaller than the value estimated from the experiments (0.030W/cmK). In the experiments, entire thermal conductivity is measured. There may also be some uncertainty in estimation of the electronic contribution by Wiedemann-Franz relationship. So, it can be noted that a fairly good agreement between calculation and experiments was obtained. This means that appropriate model potential and calculation conditions are used in this simulation.

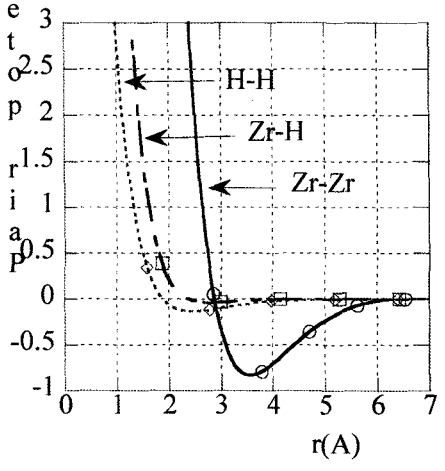

Fig.1 Pair potentials between atoms.

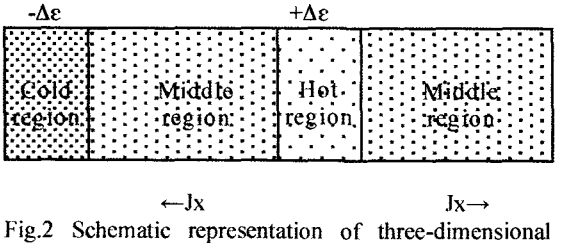

Fig.2 Schematic representation of three-dimensional periodic simulation cell used to calculate the thermal conductivity.

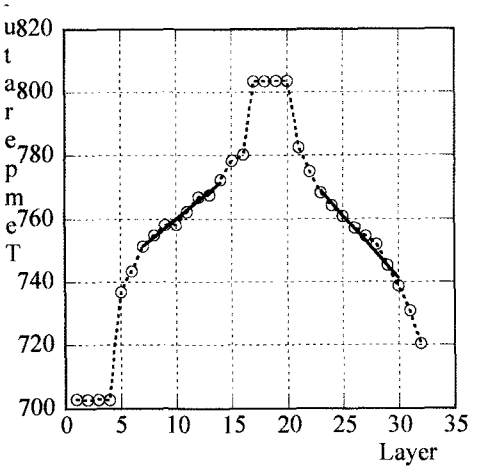

Fig.3 Temperature profile in zirconium hydride system at an average temperature of 750K.

3.2 Transient heat-flow condition (NEMD)

Pulse heating problem has been solved to estimate the two contributions of Zr vibration and H vibration to the heat conduction at high temperature. A heat pulse was introduced into the center layer of the simulation cell by scaling velocities of all atoms there to those corresponding to the temperature of 2900K. The evolution of the local temperature calculated from the kinetic energy of all atoms in the heated layer is shown in Fig.4, where the individual temperatures of Zr and H calculated from their kinetic energy are also shown. In the transient condition at high temperature, H atom quickly responds to heat transfer.

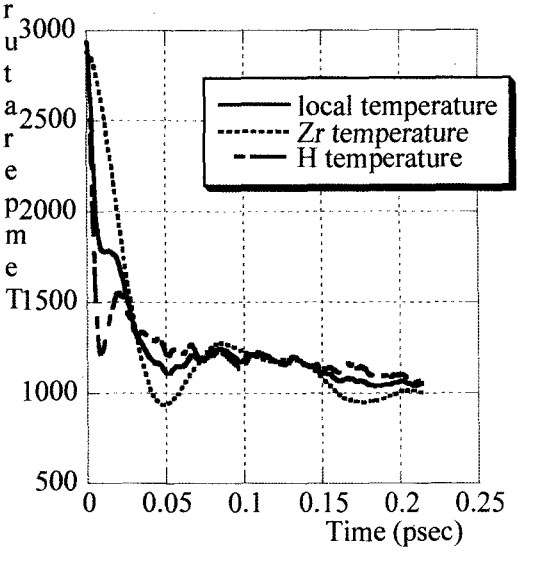

Fig.4 Evolutions of temperatures of pulse heated layer (solid line, local temperature; dotted line, temperature of Zr; short dash line, temperature of H).

3.3Equilibrium condition (EMD): thermal conductivity

We also performed the thermal conductivity calculations based on the equilibrium fluctuations of the heat flux. The thermal conductivity (κ) is calculated from the Green-Kubo formula of statistical linear-response theory,

$$k = \frac{1}{3k_B T^2 V}\int_0^\infty \langle J(t)\cdot J(0)\rangle dt, \quad (4)$$

where V is the system volume, k_B is the Boltzmann constant, and T is the system temperature. $J(t)$ is the heat current calculated from

$$J(t) = \sum_i \left[\frac{1}{2}m\dot{r}_i^2(t) + \frac{1}{2}\sum_{j\neq i} V_{ij}\{r_{ij}(t)\}\right]\dot{r}_i(t), \quad (5)$$
$$-\frac{1}{2}\sum_i\sum_{i\neq j}\left[\dot{r}_i(t)\cdot\frac{\partial V_{ij}\{r_{ij}(t)\}}{\partial r_i}\right]r_{ij}(t)$$

where V_{ij} is the interaction potential between atom i and its neighbor atom j. The first term on the right-hand side represents the convective contribution. The second term describes energy transport through interatomic interaction. These terms include velocities, atomic distances and gradient of the potential i.e. forces, which are directly computed in MD simulations.

The thermal conductivity, κ, was calculated by averaging of the summations of the current-current correlation using the following equation;

$$\kappa = \frac{1}{N}\frac{\Delta t}{Vk_B T^2}\sum_n^{N-1}\sum_{m=1}^{M} J(nN_{sift}+m)J(nN_{sift}), \quad (6)$$

where Δt is the MD time step. M is the MD step number to integrate the current-current correlation. The same calculation is repeatedly done N-times after sifting by N_{sift} steps. The total number of MD steps calculated by $M+N\times N_{sift}$ should be sufficiently longer than M to assure good statistical averaging. The present simulation has the total MD step number of 1×10^6. N_{sift} was taken to be 20,000 (=1psec), considering the decay time required for velocity auto-correlation function as seen in Fig.5. M was taken to be 2×10^5 from the decay of the current-current correlation.

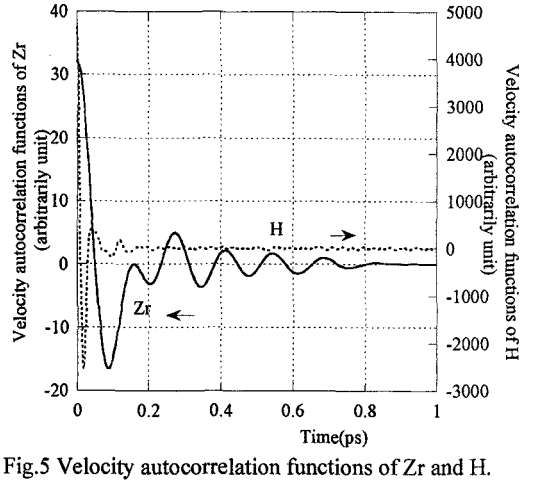

Fig.5 Velocity autocorrelation functions of Zr and H.

In order to better understand the role of hydrogen, the current-current correlation function is calculated by,

$$J(t)J(0) = \{J_{Zr}(t) + J_H(t)\}\{J_{Zr}(0) + J_H(0)\}$$
$$= J_{Zr}(t)J_{Zr}(0) + J_{Zr}(t)J_H(0) + J_H(t)J_{Zr}(0) + J_H(t)J_H(0) \quad (7)$$

where the $J_{Zr}(t)$ and $J_H(t)$ are the components of the heat current due to Zr and H, respectively. Figure 6 shows the evolution of the heat currents with time along the x-, y- and z-axis. The fluctuation of the heat current of H is much larger than that of Zr. This may be understood by the difference in mass between Zr and H. According to Eq. (5), the heat current is calculated by summation of the energies multiplied by the particle velocity. The ratio of averaged velocities of H particles to Zr particles is calculated to be $\sqrt{91.22/1.008}$=9.513.

Figure 7 shows the thermal conductivity values as a function of integration time of the heat-current correlation function by the Green-Kubo formulation of Eq. (6). As can be seen from this figure, a large number of time steps are necessary to calculate the thermal conductivity through the EMD simulation. Therefore, it is difficult to estimate the value of thermal conductivity from Fig. 7, even though very long run simulation was performed. The contributions of the heat currents of Zr and H, however, might be possible to be discussed as follows. The contributions of , $J_{Zr}(t)J_{Zr}(0)$ and $J_{Zr}(t)J_H(0)$ increase smoothly and reach to converged values. The former may be a main part of the thermal conductivity and larger than the total thermal conductivity by NEMD. The contributions, $J_H(t)J_{Zr}(0)$ and $J_H(t)J_H(0)$ have large fluctuations due to the fluctuation of $J_H(t)$ shown in Fig. 7. It might be noted that the heat current of H produces a small contribution to the thermal conductivity in outcome.

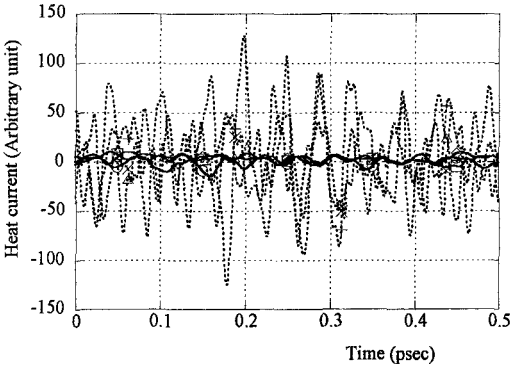

Fig.6 Heat currents by H, $J_H(t)$ in Eq.(7), (dotted line(x:×, y:+, z; Δ), by Zr, $J_{Zr}(t)$, (solid line(x:○, y:□, z; ◊).

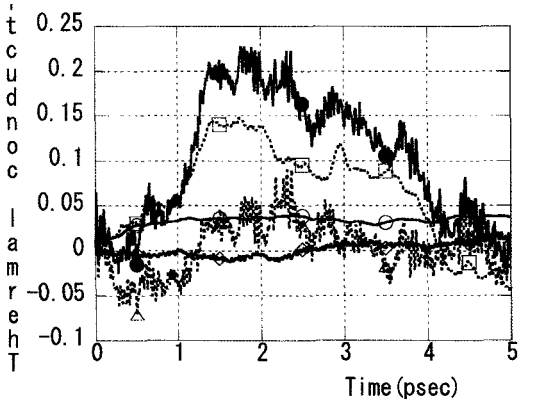

Fig.7 Integrated value (until "Time") of heat correlation function (corresponding to thermal conductivity of $ZrH_{1.6}$ at the temperature of 700K) denoted by ●. There are shown contributions of the first term of right side of Eq.(6), $J_{Zr}(t)J_{Zr}(0)$, (⊖), the second term, $J_H(t)J_{Zr}(0)$, (⊟), the third term, $J_{Zr}(t)J_H(0)$, (⊜), and the fourth term $J_H(t)J_H(0)$, (⊴)

4. Discussion and conclusions

The vibration modes of particles in Zr-H system are separated to two modes, low frequency mode from the vibration of host metal (Zr) and the second which is related to the high frequency vibration of H. The contributions of the two modes to thermal conductivity of $ZrH_{1.6}$ have been studied by NEMD and EMD methods under the steady state, transient and equilibrium conditions. The calculation results under the transient condition show that the high frequency vibration mode strongly affects the local temperature change in a short time period (<0.5psec). On the other hand, although the heat current of H has the large fluctuation, its contribution to thermal conductivity is not so large under the equilibrium condition. The present calculation results show comparable contributions of Zr and H to the thermal conductivity.

A large number of time steps are needed to calculate the thermal conductivity of the Zr-H system by the Green-Kubo method because of the large fluctuation of H heat current. It is worthwhile to point out that the NEMD simulation has an advantage in computation time.

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3.9 References

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