Molecular Dynamics Simulation of Hydrogen-Induced Amorphization: Softening Effect by Incorporation of Hydrogen

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Hydrogen-induced amorphization (HIA) of C15 Laves phase compound was studied by the constant-pressure molecular dynamics (MD) simulation using empirical Lennard-Jones interatomic potentials. The CeNi_2H_x alloys were modeled with periodic boundary conditions. The crystal system was heated to the thermodynamic melting point. The potential energy increased during the thermodynamic melting, while it decreased during amorphization. This finding shows that amorphization is driven by the potential relation, *i.e. mechanical melting* while thermodynamic melting is driven by thermal motion. We found that hydrogen incorporation softens the system and facilitates amorphization. We also found the existence of a critical amount of hydrogen to induce amorphization.

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I. Introduction

Microstructure control by the use of the transition process from an amorphous to a crystalline state is one method to improve performance of various metallic materials through the microstructure refinement. Therefore, the preparation of amorphous state alloys is important in this field. Recently Aoki *et al.*⁽¹⁾ observed the formation of amorphous metallic alloys during hydrogenation of the AB_2 Laves phases ($\text{A}=\text{rare earth}$, $\text{B}=\text{Fe, Co, Ni}$), called *hydrogen-induced amorphization* (HIA). In view of industrial applications, hydrogen-induced amorphization is one of probable methods to prepare amorphous alloys since hydrogenation and dehydrogenation can be done easily and rapidly without any traces in materials. To effectively utilize hydrogen-induced amorphization for microstructural control, it is necessary to reveal the mechanism of it. Thus, our goal is to understand the microscopic mechanism by using computer simulations.

The characteristic feature in hydrogen-induced amorphization is that the compounds of specific structures such as L_{12} , D_{019} , C_{23} , B_{82} and C15 become amorphous⁽²⁾, while the amorphization by solid state reaction is independent of the crystal structure.

The C15 Laves phases AB_2 are so called *size factor compounds* and are constructed from the close packing of the hard spheres with the ideal ratio R_A/R_B of 1.225⁽¹⁾, where R_A and R_B are the Goldschmidt radii of A and B atoms. The atomic radii r of A and B atoms calculated from the lattice parameters of C15 Laves phase (*i.e.* $r_A = \sqrt{3}a/8$, $r_B = \sqrt{2}a/8$, where a is the lattice constant) are adjusted to satisfy this ratio. The deviation of the ratio from the ideal one, 1.225, leads to the expansion or compression of the A and B atoms. One can validate it by the sign of $r-R$ ⁽¹⁾. In C15 Laves phases, all A

(rare earth) atoms are compressed and B (transition metal) atoms are compressed or expanded. As Aoki *et al.*⁽¹⁾ pointed out, combinations where the atomic size ratio R_A/R_B is larger than 1.37 show hydrogen-induced amorphization without exception. The Fe, Co and Ni compounds show it while Al compounds do not show it. In the combination which shows hydrogen-induced amorphization, all A (rare earth) and B (Fe, Co, Ni) atoms are compressed and expanded, respectively. It is interesting that this required ratio 1.37 is much larger than that⁽¹⁾ required for the formation of the amorphous alloys by rapid quenching (1.10). The hydrogen-induced amorphization is considered to be controlled not only by the crystal structure, but also by atomic size ratio. Because hydrogen-induced amorphization depends on the size effect phenomenologically as described above, it is interesting to reveal the common physics by using the empirical *pair wise* interatomic potentials. Thus in the present study, the interatomic interactions of the system are modeled by the Lennard-Jones (L-J) potential, focusing on the C15 Laves compounds which have been well studied by Aoki *et al.*⁽¹⁾

II. Method

We used the L-J 12-6 potential,

$$u(r) = 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\}. \quad (1)$$

The L-J potential parameters of Ce and Ni were obtained from the cohesive energies and lattice constants of pure fcc crystals. For hydrogen, the pair potential part used in the Embedded-Atom Method (EAM) was applied⁽³⁾⁽⁴⁾. Only the repulsion was taken into account to reveal the size effect of hydrogen. The parameters used are shown in **Table 1** and the potential relations are shown in **Fig. 1**. Note that the atomic size of Ce is larger

Table 1 The parameters in the Lennard-Jones 12-6 potential; $u(r) = A/r^{12} - B/r^6$ are shown. As for hydrogen, only repulsion is taken into account. For the different species pairs, the geometric combination rule was used; $A_{ij} = \sqrt{A_{ii}A_{jj}}$, $B_{ij} = \sqrt{B_{ii}B_{jj}}$.

Atom	$\epsilon/\text{kJ}\cdot\text{mol}^{-1}$	σ/nm	$A/10^{-12}\text{ nm}^{12}\cdot\text{kJ}\cdot\text{mol}^{-1}$	$B/10^{-6}\text{ nm}^6\cdot\text{kJ}\cdot\text{mol}^{-1}$
H	—	—	5	0
Ni	70.76	0.22	3008178	29212
Ce	69.08	0.32	284144044	280016

Fig. 1 The Lennard-Jones 12-6 interatomic potential energies of Ce-Ni-H system are shown. The energies are in $\text{kJ}\cdot\text{mol}^{-1}$ and the distances are in nm.

than that of Ni and that the minimum values of the energies of Ce and Ni are not very different. We confirmed that the C15 Laves phase structure of CeNi_2 was stable by this potential.

We simulated CeNi_2 systems (64Ce and 128Ni atoms) with x hydrogen atoms, *i.e.* $\text{Ce}_{64}\text{Ni}_{128}\text{H}_x$, by *NPT* molecular dynamics method. The periodic boundary condition was applied to simulate the bulk. Parrinello-Rahman method was used to control the pressure⁽⁵⁾ with 1253 fictitious mass of unit cell in units of atomic mass. The cutoff length was 0.71 nm with 0.1 nm spline width and 0.05 nm buffer width. A fifth-order polynomial was used for the switching function. It is arranged so that the first and second derivatives are zero at both the inner and outer range of the switching region. Thus, the interaction energy and its first and second derivatives are continuous, although higher derivatives are not. Hydrogen atoms were distributed by simulated annealing and minimization techniques while fixing Ce and Ni atomic positions. By monitoring the radial distribution functions and coordination numbers, it was found that the hydrogen atoms were located at $2\text{Ce}+2\text{Ni}$ tetrahedral sites. This structure was used as the initial configuration in MD simulations. The instantaneous temperature calculated from the kinetic energy was controlled by the heat-bath contact method⁽⁶⁾. It was elevated from 100 K by 100 K increment. At each temperature, 20000 MD steps were carried out using 0.3 fsec time-step.

Fig. 2 The total volume V of $\text{Ce}_{64}\text{Ni}_{128}\text{H}_x$ as a function of temperature is shown. The volume is in nm^3 and the temperature is scaled by the melting temperature of $\text{Ce}_{64}\text{Ni}_{128}$; T_m .

III. Results

1. Volume and potential change

Figure 2 shows the average of the volume as a function of the average of the instantaneous temperature. The temperature is scaled by the melting temperature of a non-hydrogenated $\text{Ce}_{64}\text{Ni}_{128}$ crystal. For the non-hydrogenated system, the volume expands as the temperature increases and the crystal structure is maintained until melting. A sharp discontinuous change in volume is observed in melting. For the $x=37$ system, crystallinity is maintained until melting as well as the non-hydrogenated system, while the melting temperature is lowered by comparing with the non-hydrogenated system. On the other hand, for $x=39$ system, amorphization takes place at only $0.1T_m$ before melting, which is confirmed by the structure analysis. This suggests that a critical amount of hydrogen is required to induce amorphization. For the $x=42$ system, amorphization takes place at lower temperature; the amorphization temperature decreases as the number of hydrogen atoms increases. For the $x=96$ system, amorphization takes place once hydrogen is incorporated. Note that the sharpness of the discontinuous volume change in melting of the amorphous state becomes blurred as the number of hydrogen atoms increases, and it is difficult to determine the precise phase transition temperature. Volume expansion is observed both in amorphization and melting.

Figure 3 shows the average potential energy as a function of the average instantaneous temperature. While the potential energy increases in melting, it decreases discontinuously in amorphization for $x=39$ and $x=42$ systems. The slope of the potential increase of amorphous states with increasing temperature is greater than that of crystal states. The decrease in potential energy during hydrogen-induced amorphization is vali-

Fig. 3 The total potential energy U of $\text{Ce}_{64}\text{Ni}_{128}\text{H}_x$ as a function of temperature is shown. The energy is in $\text{kJ}\cdot\text{mol}^{-1}$ and the temperature is scaled by the melting temperature of $\text{Ce}_{64}\text{Ni}_{128}$; T_m .

dated by experiments; Aoki *et al.* have demonstrated that the crystalline hydride (c- GdFe_2H_x) is less stable than the amorphous a- GdFe_2H_x synthesized by hydrogenation, because the former transforms to the latter exothermally⁽¹⁾⁽⁷⁾⁽⁸⁾. This indicates that the amorphous product by hydrogen-induced amorphization has a lower free energy than the corresponding crystalline one⁽¹⁾. The contrast between melting and amorphization suggests that the melting is thermal process governed by entropic effects, whereas amorphization can be viewed as an energetic (or mechanical) process in which the potential relation governs the transition. Thus it can be said that melting to the liquid state is *thermodynamic melting*, while amorphization is potential-driven *mechanical melting*.

2. Amorphous structure

We monitored the radial distribution functions $g(r)$ of $\text{Ce}_{64}\text{Ni}_{128}\text{H}_{40}$, as shown in Fig. 4. The first peak in $g(r)$ among cerium atoms in Fig. 4(a) shifts to the right, indicating that the compression of cerium atoms is relaxed. The expansion of nickel atoms is also relaxed as shown in Fig. 4(b). As a result, the distances which give the potential minimum in Fig. 1 are naturally reflected in the location of the first peaks of $g(r)$ in the amorphous state. Moreover, the height of the first peaks of $g(r)$ of Ce-Ce and Ni-Ni become similar and the relation of the potential minimum is also naturally reflected. By the relaxation of crystal structure, the potential relation becomes to be realized more effectively in average. Recalling that the potential energy decreases discontinuously during amorphization, one can say that the amorphization is a relaxation process where the effective use of the potential relation is realized *in average*. Since it is difficult to realize such an effective use without density fluctuations, density fluctuations are essential in amorphous structure.

3. Amorphization temperature

Figure 5 shows the phase diagram as a function of

Fig. 4 The radial distribution functions $g(r)$ of $\text{Ce}_{64}\text{Ni}_{128}\text{H}_{40}$ are shown. The dashed and solid lines show $g(r)$ for crystal and amorphous state, respectively. The interatomic distances r are in nm.

Fig. 5 The phase diagram at given temperature, T , and the number of hydrogen atoms, x , of $\text{Ce}_{64}\text{Ni}_{128}\text{H}_x$ is shown. S_{xx} is the tensile stress applied to the MD cell and it lowers the amorphization temperature. The temperature T is scaled by the melting temperature, T_m , of $\text{Ce}_{64}\text{Ni}_{128}$. Refer to text.

temperature and the number of hydrogen atoms. The critical number of hydrogen atoms to induce amorphi-

zation seems to be $x=38$ in our model; Amorphization does not take place if the number of hydrogen atoms is less than 38 and melting occurs before amorphization. Note that the amorphous-liquid coexistence curve cannot be defined precisely, as we pointed out. The phase transition from amorphous to liquid becomes blurred as the amount of hydrogen increases. Thus in Fig. 5, we draw the amorphous-liquid phase transition as a line for the sake of convenience. The error bars correspond to the 100 K temperature increment in MD simulation.

If one extrapolates the crystal-amorphous curve to the liquid region, one can imagine that the amorphization temperature is much higher than the thermodynamic melting temperature in $\text{Ce}_{64}\text{Ni}_{128}\text{H}_x$ system for $x < 38$. Hydrogen incorporation may induce a mechanical instability in the system, lowering the amorphization temperature. If this were the case, an applied stress would be expected to have the same effect as incorporation of hydrogen.

To examine this possibility, we studied the effect of an external stress on hydrogen-induced amorphization. The cross in Fig. 5 shows the result under the tensile stress S_{xx} along x -direction. While the $x=37$ system does not show the amorphization, the same system does become amorphous under a tensile stress of 7 GPa. This suggests that tensile stress and hydrogen atoms act in a similar way to lower the amorphization temperature. The incorporation of hydrogen atoms imposes local stress in the system, and this similarity suggests that hydrogen-induced amorphization is a mechanical process.

We note that the phase diagram in Fig. 5 does not reflect equilibrium condition. For certain hydrogen contents, the amorphous state is potentially more stable than the crystalline one, as shown later. This suggests that there exists an activation barrier to hydrogen-induced amorphization. A phase can exist in a region where it is thermodynamically unstable if it is metastable. By this one means that it corresponds to a local minimum in the free energy. Eventually one may reach a state point where the metastable phase becomes unstable. This is the *limit of metastability of the phase*. Mechanical melting corresponds more closely to the limit of metastability than to the thermodynamic melting point which occurs when the two phases have the same free energy. We suppose that one will see the change when the free energy barrier becomes comparable to kT . The limit of metastability is when the free energy barrier goes to zero and the mechanical melting temperature is when the activation energy becomes comparable with kT . The mechanical melting is probably nearer the limit of metastability.

This is illustrated in a simple model in a paper⁽⁹⁾. They also measured the free energy profiles and hence the thermodynamic melting points for some Sutton-Chen metals⁽¹⁰⁾.

We should think about finite size effect; *free energy barriers tend to increase with system size* until they reach a constant corresponding to nucleation in an infinite phase⁽¹⁰⁾. In really small systems the mechanism can be a

simultaneous rearrangement of all the atoms. In a larger system part will melt/disorder and there will be two phases present spanning the cell; at thermodynamic melting the free energy barrier is essentially the free energy of this interface. As the system size increases the interface becomes bigger and the free energy barrier larger. Eventually the system is large enough that the size of the critical nucleus is the determining factor. This may be dealt with in nucleation theory. Our system is quite small and so either the first or the second condition must apply. Note that this is all a potential effect and not a kinetic effect.

IV. Discussion

We discuss the mechanism of the amorphization from viewpoint of the softening effect of the material. The softness of the material can be measured by the bulk modulus which is the second derivative of the energy with respect to the volume. We calculated the potential energy as a function of cell length at 0 K using a conjugate gradient (Polak Ribiere) optimization technique at each volume. Figure 6 shows the potential energies of $\text{Ce}_{64}\text{Ni}_{128}$, *unrelaxed* and *relaxed* $\text{Ce}_{64}\text{Ni}_{128}\text{H}_x$ systems; the

Fig. 6 The total potential energies, U , as a function of cell lengths, the L for $\text{Ce}_{64}\text{Ni}_{128}\text{H}_x$ ($x=39$ or 192) are shown. For *amorphous* state (triangle up) in the $x=39$ case, the optimized structure of the *relaxed* system (circle) at 1.49 nm was used for the initial structures during geometry optimization.

positions of hydrogen atoms were relaxed for both systems, while Ce and Ni atoms were fixed for unrelaxed systems. Figure 6 shows the potential energy curves as a function of cell length for the $x=39$ and $x=192$ systems. As a result of hydrogen incorporation, the potential energy increases, as does the equilibrium lattice constant. As for the relaxed $x=39$ system, crystallinity cannot be maintained and the structure is destroyed in the attractive region. A discontinuous decrease in potential energy is observed during the transition at a cell length of about 1.49 nm. As for relaxed $x=192$ system, the crystal becomes unstable and is destroyed in the repulsive region at a cell length of about 1.42 nm. By fitting these curves, one can calculate the equilibrium lattice constant and the bulk modulus. Murnaghan's equation of state⁽¹¹⁾ was used to fit the curves,

$$E(V) = \frac{B_0 V}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] + \text{constant}. \quad (2)$$

B_0 and B'_0 are the bulk modulus and its pressure derivative at the equilibrium volume V_0 . This equation of state has been examined and found to be quite accurate for various crystals under moderate compression⁽¹¹⁾. Curves were fit for cell lengths between 1.35–1.65 nm for unrelaxed systems. A narrower region was used for the other systems.

Figure 7 shows the equilibrium cell lengths for *unrelaxed* (circle) and *amorphous* (square) systems. The amorphization cell length (cross) where the crystal structure is destroyed in relaxed systems is also shown. All lengths are scaled by the equilibrium cell length of 1.443 nm for the non-hydrogenated $\text{Ce}_{64}\text{Ni}_{128}$ system. It is known that the equilibrium cell length increases due to incorporation of hydrogen atoms. The amorphization also increases the equilibrium cell length. Although not shown here, if the Ce and Ni atoms are relaxed as well as hydrogen atoms, *i.e.* a *fully relaxed system*, the equilibrium cell length slightly decreases compared to that of the unrelaxed system; the relaxation leads to a

Fig. 7 The equilibrium cell lengths for unrelaxed (circle) and amorphous (square) states of $\text{Ce}_{64}\text{Ni}_{128}\text{H}_x$ are shown. The amorphization cell lengths (cross) are also shown. Lengths are scaled by the equilibrium cell length L_0 for $\text{Ce}_{64}\text{Ni}_{128}$. Refer text.

volume contraction. There is a point at which the unrelaxed curve (circle) and amorphization curve (cross) cross one another. In the region where the cell length of amorphization is less than that of an unrelaxed system, the crystal structure with hydrogen is unstable and amorphization takes place once the hydrogen atoms are incorporated. This is seen in the $x=192$ case in Fig. 6.

The fitted potential energy curve in Fig. 6 also gives the bulk modulus. Figure 8 shows the bulk modulus of *unrelaxed* systems as a function of the number of incorporated hydrogen atoms. The data were scaled by the bulk modulus of the non-hydrogenated $\text{Ce}_{64}\text{Ni}_{128}$ system. It is found that the incorporation of hydrogen makes the material softer. The softening effect is the direct result of the non-linearity of the L-J potential. If interatomic interactions were described a harmonic function, it would not be realized.

Although we do not plot the data, the structural relaxation of cerium and nickel atoms, *i.e.* for *relaxed* systems, makes the material much softer. The role of this softening effect in hydrogen-induced amorphization will be reported in another paper.

Figure 9 shows the *experimental* hydrogen-induced amorphization temperature T_a of cobalt compounds ACo_2 (A =rare earth) reported by Aoki *et al.*⁽²⁾. It is known that the larger R_A/R_{Co} corresponds to lower values of T_a .

Figure 10 shows the bulk modulus B_{ACo_2} calculated from the bulk moduli of *pure* crystals B_A and B_{Co} by the simple combination rule (see Appendix),

$$B_{\text{ACo}_2} = 0.479 B_A + 0.521 B_{\text{Co}}. \quad (3)$$

The data for pure systems were taken from reference⁽¹²⁾. The predicted trend in the bulk modulus of AFe_2 and ANi_2 is similar to that of ACo_2 . From Fig. 10, we observe that a larger ratio R_A/R_{Co} gives a smaller bulk modulus and a softer material. Thus, from Figs. 9 and 10, one can say that *softer materials tend to possess a lower hydrogen-induced amorphization temperature*. Chung *et al.*⁽¹³⁾ also suggested that a correlation exists between

Fig. 8 The bulk modulus B as a function of the number of hydrogen atoms, x , for *unrelaxed* $\text{Ce}_{64}\text{Ni}_{128}\text{H}_x$ is shown. The bulk modulus is scaled by that of $\text{Ce}_{64}\text{Ni}_{128}$; B_0 .

Fig. 9 The dependence of the experimental HIA temperature, T_a , of C15 Laves ACo_2 compounds on the atomic size ratio, $R(A)/R(Co)$, is shown.

Fig. 10 Bulk modulus, B , of ACo_2 C15 Laves phase calculated by combination rule is shown.

Young's modulus and amorphization in AB_2 compounds and discussed the critical lattice constant where hydrogen-induced amorphization occurs. Their suggestion is as follows: *since hydrogen incorporation causes lattice expansion, softer materials deform to the critical lattice constant more readily and hence amorphization occurs more easily*. Their discussion is based on the assumption of a constant Young's modulus, but we found that *the softening occurs by the hydrogen incorporation*. Moreover, we found that the critical lattice constant is not invariant; it is a function of the number of hydrogens (see Fig. 7), and it decreases as the number of hydrogen increases, suggesting that the barrier to hydrogen-induced amorphization decreases as the number of hydrogens increases.

The softening effect indicates hydrogen incorporation lowers the second derivative of the potential energy. Since structural fluctuations are governed by the second derivative a reduction in this quantity leads to an increase in fluctuations. In other words, mechanical

instability increases. Therefore, hydrogen-induced amorphization can be realized more easily by the softening effect. Under the condition of cell-volume relaxation, the critical cell length for amorphization can be reached more easily if softening effect occurs and the amorphization is facilitated.

Note that it is not straightforward to explain the tendency of amorphization by the softness of the non-hydrogen-incorporated system. We calculated the bulk modulus of AB_2 (A =rare earth, B =Al, Fe, Co, Ni) by the combination rule and *ab initio* calculations, and found that Al compounds were softer than the others. Despite this however, Al did not show hydrogen-induced amorphization while Fe, Co, Ni compounds did. The manner in which expansion occurs may be the key; Fe, Co and Ni expand while Al contracts in the C15 Laves phase.

The amorphization process includes the local destruction of crystalline structure. We discuss this process in terms of the interatomic potential relations. The L-J potential does not require strong alignment of the atoms in comparison with Coulombic interactions. Therefore, amorphization—the destruction of the crystal structure—is not accompanied by a large increase in potential energy, and thus it is allowed energetically by the L-J potential, but not by the Coulomb potential.

We ignored many-body effects which are an essential feature of interatomic interactions in metals. Many-body effects can be described as a function of density. In the embedded-atom method (EAM), it is described simply as a function of local density around an atom and the three-body effect is purely repulsive⁽¹⁴⁾. When amorphization occurs, the average coordination number decreases. This decrease causes a reduction in repulsion and stabilizes the amorphous structure. The three-body effect also reduces the activation barrier to amorphization. Therefore, amorphization may occur more readily when three-body effects are included.

V. Conclusion

We have presented results from molecular dynamics (MD) simulations of hydrogen-induced amorphization (HIA) in C15 Laves phase compounds using Lennard-Jones interatomic potentials. Hydrogen-induced amorphization was shown to be a potential-driven mechanical process best described as *mechanical melting*. Our findings are supported by several MD results; 1) the potential energy decreases discontinuously during amorphization which is contrary to thermodynamic melting; 2) The interatomic potential relations become naturally reflected in the radial distribution functions for the amorphous state; 3) The effects of hydrogen incorporation and tensile stress have the same effect of lowering the amorphization temperature, suggesting that the effect of the hydrogen incorporation is to create local stress.

The mechanical melting temperature is usually higher than the thermodynamic one, because the origin of it is mechanical instability. Hydrogen incorporation was

found to lower it. If the amount of hydrogen exceeds a critical value, amorphization temperature is lowered below the thermodynamic melting point and the hydrogen-induced amorphization can be observed. In our model for $\text{Ce}_{64}\text{Ni}_{128}\text{H}_x$, the critical number of hydrogen atoms is 38. We found that hydrogen incorporation leads a softening of the material and proposed that this softening effect facilitates amorphization.

The softening effect results from the non-linearity nature of the interatomic potential. Because the softness is expressed by the second derivative of the potential energy with respect to volume, softening corresponds to a lowering of the derivative, leading to structural fluctuations at the finite temperature. As a result, hydrogen incorporation induces mechanical instability, facilitating amorphization.

We also suggested the existence of an activation energy barrier toward hydrogen-induced amorphization. Hydrogen incorporation may lower this barrier, allowing amorphization to occur. Mechanical instability due to hydrogen incorporation facilitates amorphization.

We used a crude model which was described by the simple pair-wise interatomic potentials. These potentials are only a very approximate description of the true potentials. However, the non-bonding interaction part exists in the metallic interaction, and the essential physics reported here may be contained in more complicated model.

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REFERENCES

- (1) K. Aoki, X. G. Li and T. Masumoto: *Acta Metall. Mater.*, **40** (1992), 1717–1726.
- (2) K. Aoki and K. Masumoto: *Materia Japan*, **34** (1995), 126–133, *in Japanese*.
- (3) M. Ruda, D. Farkas and J. Abriata: *Phys. Rev. B*, **54** (1996), 9765–9774.
- (4) M. S. Daw and M. I. Baskes: *Phys. Rev. B*, **29** (1984), 6443–6453.
- (5) M. Parrinello and A. Rahman: *J. Appl. Phys.*, **52** (1981), 7182–7190.
- (6) M. Katagiri, M. Tanaka, H. Takaba, A. Miyamoto, Y. Nozue, O. Terasaki, N. Qurke and J. M. Newsam: *Fluid Phase Equil.*, **125** (1996), 1–11.
- (7) K. Aoki, A. Yanagitani and T. Masumoto: *Appl. Phys. Lett.*, **52** (1988), 2122–2123.
- (8) K. Aoki, X. G. Li and T. Masumoto: *Acta Metall. Mater.*, **40** (1992), 221–227.
- (9) R. M. Lynden-Bell: *Mol. Phys.*, **86** (1995), 1353–1373.
- (10) R. M. Lynden-Bell, J. S. V. Duijneveldt and D. Frenkel: *Mol. Phys.*, **80** (1993), 801–814.

- (11) M. T. Yin and M. L. Cohen: *Phys. Rev. B*, **26** (1982), 5668–5687.
- (12) C. Kittel: *Introduction to solid state physics*, 6th ed., John Wiley & Sons, Inc., New York, U.S.A., (1986).
- (13) U.-I. Chung, Y.-G. Kim and J.-Y. Lee: *Philos. Mag. B, Phys. Condens. Matter Electron. Opt. Magn. Prop.*, **63** (1991), 1119–1130.
- (14) M. S. Daw, S. M. Foiles and M. I. Baskes: *Mater. Sci. Rep.*, **9** (1993), 251–310.
- (15) H. Anton and P. C. Schmidt: *Intermetallics*, **5** (1997), 449–465.

APPENDIX A:

Combination Rule of Bulk Modulus

Here we give the combination rule of the bulk modulus of C15 laves phase. The total volume V per formula unit is the summation of the volumes V_A and V_B of Wigner-Seitz cell,

$$V = V_A + 2V_B. \quad (\text{A1})$$

The ratio of V_B and V_A is constant in the volume change, *i.e.*,

$$\xi \equiv \frac{V_B}{V_A} = \text{const.} \quad (\text{A2})$$

Then V can be written by,

$$V = (1 + 2\xi)V_A = \left(\frac{1 + 2\xi}{\xi}\right)V_B. \quad (\text{A3})$$

The total energy per formula unit can be written as,

$$E = E_A + 2E_B. \quad (\text{A4})$$

Since E_A and E_B are only the function of V_A and V_B respectively, we get

$$\frac{d^2E}{dV^2} = \left(\frac{1}{1 + 2\xi}\right)^2 \left(\frac{\partial^2 E_A}{\partial V_A^2}\right)_{V_A} + 2 \left(\frac{\xi}{1 + 2\xi}\right)^2 \left(\frac{\partial^2 E_B}{\partial V_B^2}\right)_{V_B}. \quad (\text{A5})$$

We put eq. (A3) into eq. (A5) and get the combination rule of bulk modulus.

$$\begin{aligned} B_{AB_2} &\equiv V \frac{d^2E}{dV^2} \\ &= \frac{1}{1 + 2\xi} B_A + 2 \frac{\xi}{1 + 2\xi} B_B \end{aligned} \quad (\text{A6})$$

Since the radii of A and B atoms are calculated from the lattice parameters L by, $r_A = \sqrt{3}L/8$ and $r_B = \sqrt{2}L/8$, the ratio $\xi = 0.544$. Then we get,

$$\begin{aligned} B_{AB_2} &= \frac{1}{1 + 2\xi} B_A + \frac{2\xi}{1 + 2\xi} B_B \\ &= 0.479 B_A + 0.521 B_B. \end{aligned} \quad (\text{A7})$$

with the atomic partial bulk moduli

$$B_{A,B} = V_{A,B} \frac{d^2E_{A,B}}{dV_{A,B}^2}. \quad (\text{A8})$$

Equation (A7) gives the combination rule where $B_{A,B}$ are the pure metal data of the components. The arithmetic mean is obtained by setting $\xi = 1$. One can see the theoretical work on the combination rule in a paper⁽¹⁵⁾