# FORMATION OF Al–Si AND Al–Ge SOLID SOLUTIONS AND EQUATION OF STATE

Toshinobu Soma, Yutaka Funayama and Hiroko-Matsuo Kagaya

Department of Applied Physics and Mathematics, Mining College, Akita University, Akita 010, Japan

The pressure effect on the solid solubility of the Al–Si and Al–Ge systems is studied using the electronic theory based on pseudo-potentials and the virtual crystal approximation for the disordered alloy. The atomic concentration $x$-dependence of the equilibrium volume satisfying energy-minimum condition for $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ solid solutions with f c c lattice is in good agreement with an available experimental data. The equation of state of these alloy systems is presented quantitatively and the compression effect on the heat of solution is investigated. The heat of solution $\Delta E_s (x, P)$ for $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ solid solutions under pressure $P$ is small for the Al-rich region and decreases as the crystal is compressed. Consequently, using the Helmholtz free energy of formation under pressure $F'_s (x, P, T)$, we predict the extended solid solutions under pressure in Al–Si and Al–Ge alloy system is consistent with the experimental tendency.

## 1. INTRODUCTION

AT ATMOSPHERIC pressure, Al–Si and Al–Ge systems are simple eutectic ones, and the Al-rich solid solutions are limited to 1.6 at % Si and 2.8 at % Ge [1]. Under pressure by rapid quenching from the liquid state, an increase in solubility limit of Si and Ge in Al has been observed [2–4]. It is exciting that the extension of the Si and Ge solubility in Al increases drastically the superconducting transition temperature [4]. The difference of lattice constant between Al and a hypothetical f c c Si (with the same density as diamond Si) is 6.5%, and the corresponding one between Al and a hypothetical f c c Ge 10.8%. However, the crystal volume of a hypothetical f c c Si and Ge satisfying the energy-minimum condition is smaller than that of diamond Si or Ge. Therefore, it is of interest to estimate quantitatively the possible extension of Al–Si and Al–Ge solid solution with f c c phase under pressure.

The pseudopotential method has been widely used for calculations of different properties of metals and alloys, and the second-order perturbations theory using rather weak model pseudopotentials has been succeeded in the understanding of the metallic bonding. Previously, we have proposed a local Heine–Abarenkov model pseudopotential for the solvent Al metal [5], and solute Si or Ge crystal [6], and obtained the bulk properties such as cohesive energy, equation of state in good agreement with the experimental data. The Al–Si and Al–Ge systems have a f c c phase when

the solid solution is formed. Therefore, we consider that the crystal binding of Al–Si or Al–Ge system is unchanged compared with that of pure Al metal. Then, we need to determine both the atomic configuration and the pseudopotential in the solid solution. For the former, we assumed the completely disordered alloy for the solid solution $Al_{1-x}Si_x$ or $Al_{1-x}Ge_x$ with arbitrary atomic concentration $x$. For the latter, using only the pseudopotentials in Al, Si or Ge, we formulate the electronic model for Al–Si or Al–Ge solid solution in the virtual crystal approximation (hereafter referred to as VCA). In the present work, we study the compression effect on the solubility limit of Si and Ge in Al under pressure and report the resultant results for the equilibrium volume, equation of state, heat of solution and phase boundary between solid solution and phase mixture of these alloy systems.

## 2. SOLID SOLUTION IN VCA AND EQUATION OF STATE

In the VCA, the disordered alloy is replaced by a monatomic periodic lattice composed of the average atomic potential. In the case of $Al_{1-x}Si_x$ or $Al_{1-x}Ge_x$ alloy, using the local Heine–Abarenkov model potential for solvent Al [5] and solute Si or Ge [6], the average bare potential form factor $V_b^{VCA} (q)$ is given by

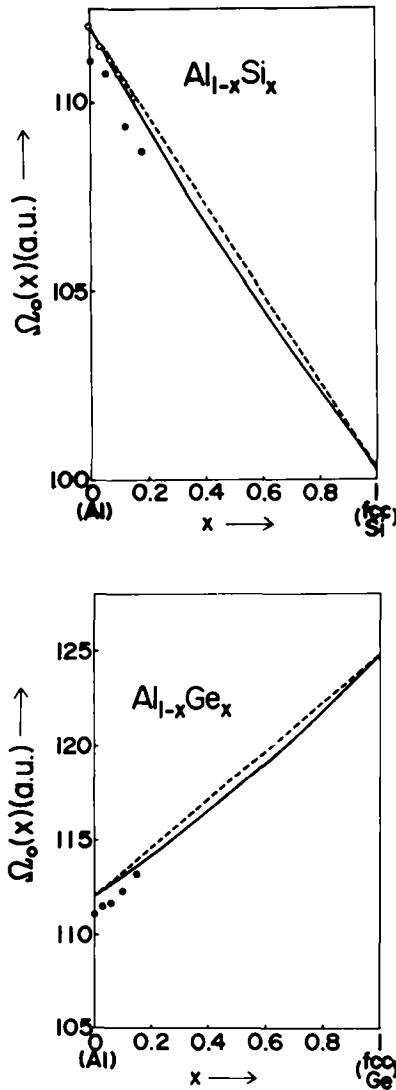$$V_b^{VCA}(q) = (1 - x)V_b^{Al}(q) + x \cdot V_b^{Si \text{ or } Ge}(q), \tag{1}$$

Fig. 1. The equilibrium atomic volume $\Omega_0(x)$ vs $x$ for (a) $Al_{1-x}Si_x$ and (b) $Al_{1-x}Ge_x$ systems. The dashed curve corresponds to that according to Vegard's law, and the points $\bigcirc$ [2] and $\bullet$ [4] are experimental data.

and

$$V_b^i(q) = -\frac{4\pi Z_i e^2}{\Omega q^2}$$
$$\times \left\{(1 + u_i)\cos(qR_M^i) - u_i \frac{\sin(qR_M^i)}{qR_M^i}\right\}, \quad (2)$$

where $Z_i$ ($i = $ Al, Si or Ge) and $\Omega$ are valency and atomic volume, and then, $R_M^i$ and $u_i$ are two parameters corresponding to core radius and potential depth. The system $Al_{1-x}Si_x$ or $Al_{1-x}Ge_x$ is composed of a monatomic fcc-type lattice in VCA, and the total crystal $E$ is given in the usual second-order pertur-

bation theory [5]. Using the average potential $V_b^{VCA}(q)$ in equation (1), we can calculate the total energy $E^{VCA}(\Omega, x)$ as a function of the volume $\Omega$ with fixed concentration $x$. The equilibrium volume $\Omega_0(x)$ is determined by satisfying the zero-pressure condition given by

$$\frac{dE^{VCA}(\Omega, x)}{d\Omega}\bigg|_x = 0. \quad (3)$$

We show the equilibrium volume $\Omega_0(x)$ of $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ system obtained from equation (3) in Fig. 1(a) and (b) where the results with Vashishta–Singwi screening function [5] are given in what follows. Those with other screening functions are almost the same, and the maximum deviation of $\Omega_0(x)$ in Fig. 1 remains to be about $\pm 0.1$ a.u. at $x = 0.5$. The experimental error of the crystal volume over the region of $x \lesssim 0.2$ amounts to $\pm 0.3$ a.u. for these alloy systems [2–4]. Our obtained data of equilibrium volume for $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ systems are consistent with the experimental tendency [2–4], and we see that the disordered system of solid solutions $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ is well defined in the electronic theory using the VCA and the local Heine–Abarenkov model pseudopotential.

The pressure $P(x)$ for $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ systems is obtained from the first derivative of the crystal energy $E^{VCA}$ with respect to the crystal volume $\Omega$ and given by

$$P(x) = -\frac{dE^{VCA}(\Omega, x)}{d\Omega}\bigg|_{\Omega(x)}. \quad (4)$$

We show the obtained data of the pressure–volume relation representatively for $Al_{0.85}Si_{0.15}$ and $Al_{0.85}Ge_{0.15}$ system in Fig. 2(a) and (b). At the finite temperature $T$, the thermal pressure $P_t$ is also considered and defined as the deviation from the corresponding one at absolute zero temperature given [7] by

$$P_t = P_{ph}(T) - P_{ph}(T = 0), \quad (5)$$

and

$$P_{ph}(T) = \frac{1}{\Omega}\sum_{i,q} h v_i(q)\left\{\frac{1}{2} + \frac{1}{e^{hv_i(q)/kT} - 1}\right\}\gamma_i(q), \quad (6)$$

where $v_i(q)$ and $\gamma_i(q)$ are the vibrational frequency and the mode Grüneisen parameter with mode $i$ and wavevector $q$. At high temperatures, the influence of the thermal pressure $P_t$ is not negligible, and the reformulation of the volume scale is necessary when considering the thermal pressure $P_t$. Using previous results for $v_i(q)$ [8] and $\gamma_i(q)$ [9], the quantitative influence of the thermal pressure on the pressure–volume

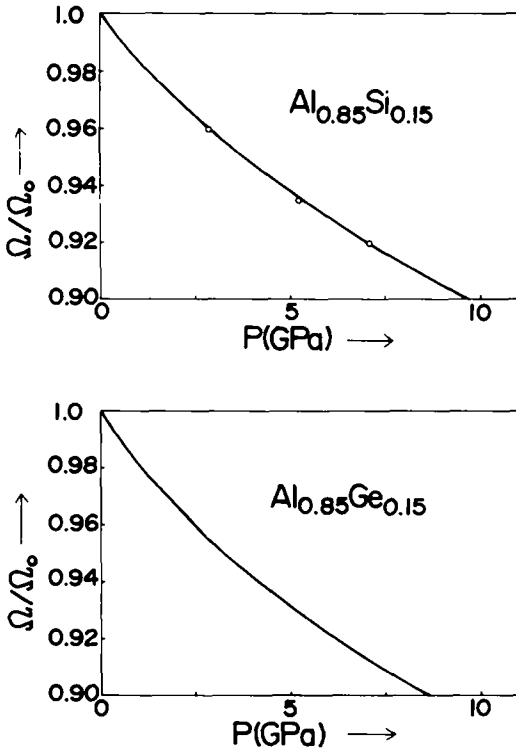Fig. 2. The compressed volume ratio $\Omega/\Omega_0$ vs $P$ for (a) $Al_{0.85}Si_{0.15}$ and (b) $Al_{0.85}Ge_{0.15}$ systems. The points O are the observed data [3].

relation for pure Al metal remains to be about 0.1 GPa at $T = 933.4\,K$ (melting temperature under atmospheric pressure) at the compressed volume $\Omega/\Omega_0 = 0.9$. The maximum deviation of pressure $P(x)$ due to other screening functions in Fig. 2 amount to about $\pm 0.1\,GPa$ at $\Omega/\Omega_0 = 0.9$, and comparable to the experimental error [3]. From Fig. 2(a), we see that our obtained data for equation of state of $Al_{0.85}Si_{0.15}$ system are in good agreement with the available observed data [3].

## 3. HEAT OF SOLUTION AND SOLUBILITY LIMIT UNDER PRESSURE

The heat of solution $\Delta E_s(x, P)$ for $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ systems under pressure $P$ is defined as the energy difference between the corresponding energy $E^{VCA}(x, P)$ of the hypothetical solid solution with f c c phase and that of the phase mixture $E_{mix}(x, P)$, and given by

$$\Delta E_s(x, P) = E^{VCA}(x, P) - E_{mix}(x, P), \qquad (7)$$

and

$$E_{mix}(x, P) = (1 - x)E^{Al}(x = 0, P)$$
$$+ x \cdot E^{Si\,or\,Ge}(x = 1, P), \qquad (8)$$


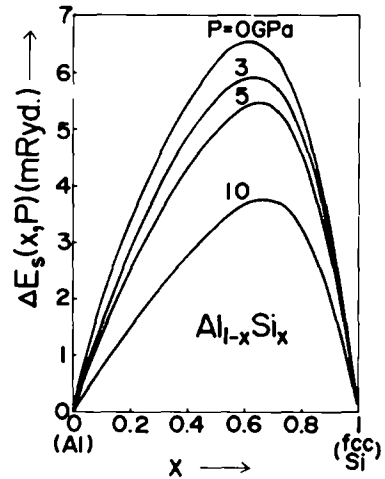
Fig. 3. The heat of solution $\Delta E_s(x, P)$ vs $x$ for the $Al_{1-x}Si_x$ system under pressure $P = 0, 3, 5$ and 10 GPa.

where the conversion to the crystal volume $\Omega(x)$ from the pressure $P(X)$ is performed by using equation (4). In Fig 3, we show the heat of solution $\Delta E_s(x, P)$ of $Al_{1-x}Si_x$ system under pressure $P = 0, 3, 5$ and 10 GPa. From Fig. 3, we see that the heat of solution $\Delta E_s(x, P)$ for the $Al_{1-x}Si_x$ system is not symmetric as a function of $x$ and shifted towards the f c c Si-rich region. For the $Al_{1-x}Ge_x$ system, this trend of $\Delta E_s(x, P)$ vs $x$ is somewhat reduced and the maximum of $\Delta E_s(x, P)$ is about 10% smaller than that for the $Al_{1-x}Si_x$ system. For both of the Al–Si and Al–Ge system, $\Delta E_s(x, P)$ decreases as the crystal is more compressed. Then, we show in Fig. 4 the ratio
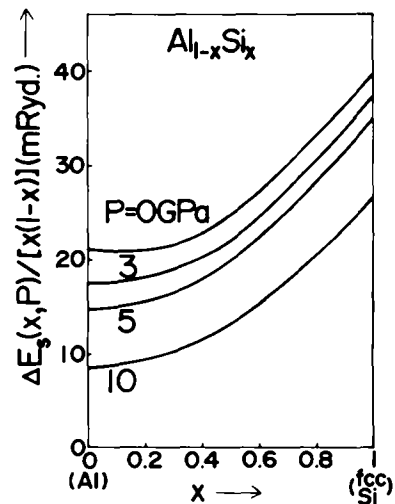


Fig. 4. The ratio of the heat of solution $\Delta E_s(x, P)/[x(1 - x)]$ vs $x$ for the $Al_{1-x}Si_x$ system under pressure $P = 0, 3, 5$ and 10 GPa.
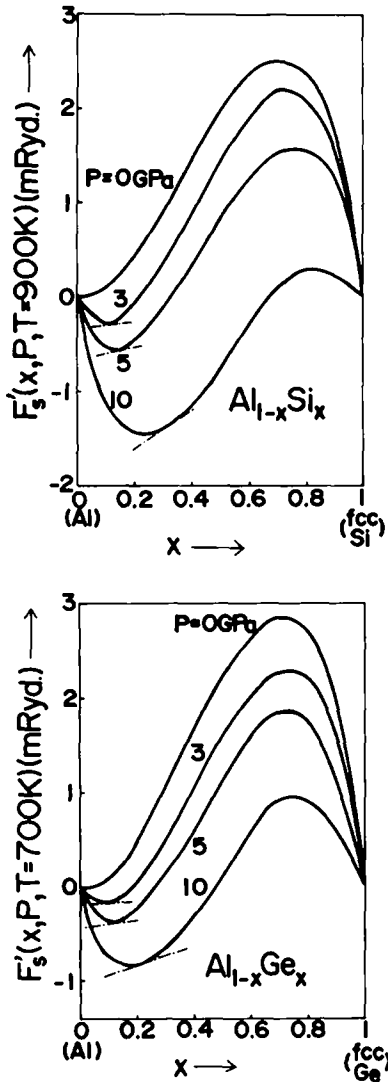
Fig. 5. The Helmholtz free energy of formation $F_s'(x, P, T = 900\,K)$ vs $x$ for (a) $Al_{1-x}Si_x$ and $F_s'(x, P, T = 700\,K)$ vs $x$ for (b) $Al_{1-x}Ge_x$ system under pressure $P = 0, 3, 5$ and $10\,GPa$.

$\Delta E_s(x, P)/[x(1 - x)]$ at $P = 0, 3, 5$ and $10\,GPa$ for the $Al_{1-x}Si_x$ system, and the nonlinear dependence of $\Delta E_s(x, P)/[x(1 - x)]$ vs $x$ is found. The maximum deviation of the numerical data in Figs. 3 and 4 remains to be about $\pm 0.1\,mRyd$ at $x = 0.6$.

In calculating the solubility limit, we must obtain the Helmholtz free energy of formation under pressure $F_s'(x, P, T)$ for $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ systems given by

$$F_s'(x, P, T) = \Delta E_s(x, P)$$
$$+ kT[(1 - x)\ln(1 - x) + (x)\ln(x)], \qquad (9)$$
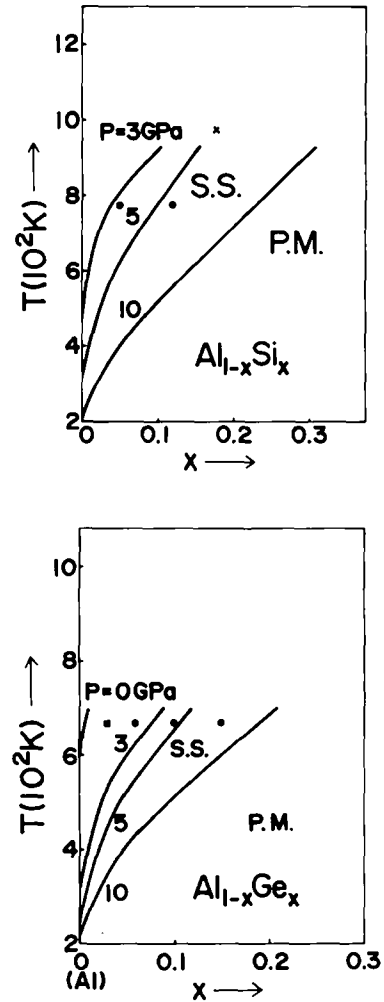
where the vibrational contribution to the internal



Fig. 6. The obtained phase boundaries between the solid solution (S.S.) and the phase mixture (P.M.) for (a) $Al_{1-x}Si_x$ and (b) $Al_{1-x}Ge_x$ system under pressure $P = 0, 3, 5$ and $10\,GPa$. The points ■, ● and x are the solid solution with f c c phase [4] found experimentally under $P = 4.5, 7.0$ and $9.0\,GPa$, respectively.

energy and the thermal entropy are assumed to be independent of the alloy composition. Using the numerical data in Fig. 3, we show the obtained results of $F_s'(x, P, T = 900\,K)$ vs $x$ for $Al_{1-x}Si_x$ system in Fig. 5(a), and $F_s'(x, P, T = 700\,K)$ vs $x$ for $Al_{1-x}Ge_x$ system in Fig. 5(b) under pressure $P = 0, 3, 5$ and $10\,GPa$ in both the cases. The contact points on the common tangents of $F_s'(x, P, T)$ determine phase boundaries between the solid solution and the phase mixture under the corresponding pressure $P$ and the characteristic temperature $T$. In Fig. 5(a), one of the contact points occupies the point $(x = 1, F_s' = 0)$, and the f c c Si-rich solid solution is not formed. Then, from Fig. 5(a), we see that the solid solution is not formed under atmospheric pressure $(P = 0\,GPa)$ at

$T = 900\,\text{K}$ for $Al_{1-x}Si_x$ and, from Fig. 5(b), limited to $x = 0.01$ at $T = 700\,\text{K}$ for $Al_{1-x}Ge_x$ system. From the similar analysis of $F_r'(x, P, T)$ at different temperatures as that in Fig. 5(a) and (b), we show the resultant solubility as that in Fig. 5(a) and (b), we show the resultant solubility limit of $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ system under $P = 0, 3, 5$ and $10\,\text{GPa}$ in Fig. 6(a) and (b). From Fig. 6(a) and (b), we see that the solid solution in Al–Si and Al–Ge system, extended under pressure, is consistent with the observed tendency [2–4]. Our obtained phase boundaries in Fig. 6 have have the calculated accuracy corresponding to $|\Delta x| \lesssim 0.01$ and $|\Delta T| \lesssim 5\,\text{K}$. In Fig 6, because of lack of information on the liquid phase of $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ system, we do not treat the compression effect on the phase boundary between the solid phase and the liquid phase.

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