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Solid solubility of silicon and germanium in aluminium under pressure

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The solid solubility of silicon and germanium in aluminium under pressure are investigated using the microscopic electronic theory based on pseudopotentials and using the virtual crystal approximation. Obtained results for the lattice constant and the solid solubility under pressure in the Al–Si and Al–Ge systems are in good agreement with the few available experimental data, in spite of our not introducing any adjustable parameter except for the lattice constant of pure aluminium crystal. The heat of solution and the pressure–volume relation in the Al–Si and Al–Ge systems are presented theoretically.

1. Introduction

The increase of the solid solubility in alloy systems under pressure is an interesting subject in materials science and technology. Experimentally, a substantial increase in the solubility of silicon and germanium in aluminium has been observed [1–3] under pressure by rapid quenching from the liquid state. It is noticeable that the extension of the silicon and germanium solubility in aluminium produces a drastic increase in the superconducting transition temperature [3]. However, a theoretical study from first principles to estimate quantitatively the solid solubility under pressure and the bulk properties of the Al–Si and Al–Ge systems, has not been reported. In the present work, we apply microscopic electronic theory based on pseudopotentials to the Al–Si and Al–Ge systems. The pseudopotential method has initially been derived from the OPW formalism, and it has been widely used for calculations of different properties of metals and alloys. The second-order perturbation theory using rather weak model pseudopotentials has been succeeded in elucidating the metallic bonding. We have proposed [4] a local Heine–Abarenkov model pseudopotential for pure aluminium crystal, and obtained a cohesive energy and an equation of state in good agreement with the experimental data. Previously, we have reported [5] the corresponding model pseudopotential for solute silicon and germanium with the diamond structure. The Al–Si and Al–Ge system has an fcc phase when the solid solution is formed. Therefore, we consider that the crystal binding of Al–Si or Al–Ge is unchanged compared with that of pure aluminium. The main problem remains to determine both the atomic configuration and the pseudopotential in the solid solution. We employed models of a completely disordered alloy for the solid solution $Al_{1-x}Si_x$ or $Al_{1-x}Ge_x$ with arbitrary atomic concentration, x. Then, using only the pseudopotentials in aluminium, silicon and germanium, we formulated the electronic model for Al–Si and Al–Ge solid solutions in virtual crystal approximation (VCA). Finally, we investigated quantitatively the bulk properties of these systems such as the lattice parameter, heat of solution, Helmholtz free energy, solid solubility and the pressure–volume relation.

2. Formulations

In 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 $Al_{1-x}Ge_x$, using the local Heine–Abarenkov model potential [4, 5], the average bare potential form factor with wave number q, $V_b^{VCA}(q)$ is given by

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

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, R_M^i and u_i (i = Al, Si or Ge) are valency, ionic core radius and potential depth for aluminium, silicon or germanium. Then, Ω, the atomic volume related to average valency $Z = (1-x)Z^{Al} + xZ^{Si\,or\,Ge}$, lattice constant a in the fcc phase and interelectronic distance r_s, is given by

$$\Omega = \frac{a^3}{4} = Z\frac{4\pi r_s^3}{3} \quad (3)$$

In the framework of the usual second-order perturbation based on pseudopotentials, the total energy per atom, $E^{VCA}(\Omega, x)$, in the $Al_{1-x}Si_x$ or $Al_{1-x}Ge_x$ alloy system is obtained in VCA by extending from pure metallic crystal [4] and given by

$$E^{VCA}(\Omega, x) = E_i(\Omega, x) + E^{(0)}(\Omega, x) + E^{(1)}(\Omega, x) + E^{(2)}(\Omega, x) \quad (4)$$

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where E_{i} is the Madelung energy, i.e. the total Coulomb energy of positively charged ions in a uniformly negatively charged background, and given by

$$E_{\mathrm{i}}(\Omega, x) = -\frac{\alpha Z^{5/3}}{r_{\mathrm{s}}} \quad (5)$$

where α is the Madelung constant equal to 1.79175 for the f c c phase. $E^{(0)}$ is the energy of the free electron gas consisting of the kinetic, exchange and correlation energies and given by

$$E^{(0)}(\Omega, x) = Z\left(\frac{2.21}{r_{\mathrm{s}}^2} - \frac{0.916}{r_{\mathrm{s}}} + E_{\mathrm{corr}}\right) \quad (6)$$

$E^{(1)}$ is the first order perturbation energy in terms of pseudopotentials, and in our model with the local Heine–Abarenkov potential it becomes

$$E^{(1)}(\Omega, x) = \frac{2\pi Z e^2}{\Omega}[(1-x)Z^{\mathrm{Al}}(R_{\mathrm{M}}^{\mathrm{Al}})^2(1+\tfrac{2}{3}u^{\mathrm{Al}}) + xZ^{\mathrm{Si\,or\,Ge}}(R_{\mathrm{M}}^{\mathrm{Si\,or\,Ge}})^2(1+\tfrac{2}{3}u^{\mathrm{Si\,or\,Ge}})] \quad (7)$$

$E^{(2)}$ is the second-order term usually called the band-structure energy, and is given by

$$E^{(2)}(\Omega, x) = -\frac{\Omega}{2}\sum_{G\neq 0}\frac{V_{\mathrm{b}}^{\mathrm{VCA}}(G)^2}{\varepsilon(G)} \times \frac{\chi_0(G)}{1-4\pi e^2 f(G)\chi_0(G)/G^2} \quad (8)$$

where G is the reciprocal lattice vector of the f c c lattice. In estimating Equation 8, the electronic dielectric function $\varepsilon(q)$ and the factor $f(q)$ including the electronic exchange and correlation effects are important, and are given by

$$\varepsilon(q) = 1 + \frac{4\pi e^2}{q^2}\frac{\chi_0(q)}{1-4\pi e^2 f(q)\chi_0(q)/q^2} \quad (9)$$

and

$$\chi_0(q) = \frac{k_{\mathrm{F}}}{4\pi^2}\left[1 + \frac{1-(q/2k_{\mathrm{F}})^2}{q/k_{\mathrm{F}}}\ln\left|\frac{1+q/2k_{\mathrm{F}}}{1-q/2k_{\mathrm{F}}}\right|\right] \quad (10)$$

where k_{F} is the Fermi wave number. In the present work, we adopt the following three approximations of the exchange correction $f(q)$ to the dielectric screening function $\varepsilon(q)$. First, the modified Hubbard type [6] $f(q) = q^2/2(q^2 + \xi k_{\mathrm{F}}^2)$, and second, the Kleinman–Langreth type [7, 8] $f(q) = q^2/4(q^2 + \xi k_{\mathrm{F}}^2) + q^2/4\xi k_{\mathrm{F}}^2$, where the parameter ξ is obtained from the compressibility sum rule of an electron gas with the Nozières–Pines formula [9] for the correlation energy, E_{corr}. Third, the Vashishta–Singwi type [10], $f(q) = A\{1 - \exp[-B(q/k_{\mathrm{F}})^2]\}$. These three different forms produce the variations in the obtained results corresponding to calculated accuracy.

The equilibrium volume $\Omega_0^{\mathrm{VCA}}(x)$ with fixed atomic fraction x is determined by satisfying the zero-pressure condition given by

$$\left.\frac{\mathrm{d}E^{\mathrm{VCA}}(\Omega, x)}{\mathrm{d}\Omega}\right|_x = 0 \quad (11)$$

The equilibrium lattice constant, $a_0^{\mathrm{VCA}}(x)$, is converted from $\Omega_0^{\mathrm{VCA}}(x)$ using Equation 3. Then, the pressure, P, is obtained from the first derivative of the crystal energy, E^{VCA}, with respect to the crystal volume, Ω, and given by

$$P(x) = -\left.\frac{\mathrm{d}E^{\mathrm{VCA}}(\Omega, x)}{\mathrm{d}\Omega}\right|_{\Omega^{\mathrm{VCA}}(x)} \quad (12)$$

In treating the solid solubility in the alloy system, the estimation of the heat of solution, $\Delta E(x)$, is essential. The heat of solution, $\Delta E(x)$, for $\mathrm{Al}_{1-x}\mathrm{Si}_x$ or $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ is defined as the energy difference between the solid solution $E^{\mathrm{VCA}}[\Omega_0^{\mathrm{VCA}}(x), x]$ and the phase mixture $E_{\mathrm{mix}}(x)$ given by

$$\Delta E(x) = E^{\mathrm{VCA}}[\Omega_0^{\mathrm{VCA}}(x), x] - E_{\mathrm{mix}}(x) \quad (13)$$

and

$$E_{\mathrm{mix}}(x) = (1-x)E^{\mathrm{Al}}(\Omega_0^{\mathrm{Al}}, x = 0) + xE^{\mathrm{Si\,or\,Ge}}(\Omega_0^{\mathrm{Si\,or\,Ge}}, x = 1) \quad (14)$$

The pressure effect on the heat of solution, $\Delta E(x, P)$, is obtained using Equation 12, namely the pressure, P–volume relation $\Omega^{\mathrm{VCA}}(x)$, and given by

$$\Delta E(x, P) = E^{\mathrm{VCA}}(x, P) - E_{\mathrm{mix}}(x, P) \quad (15)$$

and

$$E_{\mathrm{mix}}(x, P) = (1-x)E^{\mathrm{Al}}(x = 0, P) + xE^{\mathrm{Si\,or\,Ge}}(x = 1, P) \quad (16)$$

The Helmholtz free energy, $F_{\mathrm{s}}(x, P, T)$, for the solid solution under pressure, P, at the temperature, T(K), is given by

$$F_{\mathrm{s}}(x, P, T) = E(x, P, T) + kT[(1-x)\ln(1-x) + x\ln(x)] \quad (17)$$

In the following section, we treat the Helmholtz free energy of formation, $F_{\mathrm{s}}'(x, P, T)$, for the solid solution under pressure, given by

$$F_{\mathrm{s}}'(x, P, T) = F_{\mathrm{s}}(x, P, T) - E_{\mathrm{mix}}(x, P, T) = \Delta E(x, P) + kT[(1-x) \times \ln(1-x) + x\ln(x)] \quad (18)$$

where the vibrational contribution to the internal energy and the thermal entropy were assumed to be independent of the alloy composition. The behaviour of $F_{\mathrm{s}}'(x, P, T)$ against x with fixed P and T(K) determines the solubility limit.

3. Numerical resuls and discussion

First, the variation of the equilibrium lattice constant $a_0^{\mathrm{VCA}}(x)$ of the $\mathrm{Al}_{1-x}\mathrm{Si}_x$ and $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ systems with x, obtained from Equations 3 and 11 is shown in Figs 1a and b, where the results with the Vashishta–Singwi screening function are given below. The results for other screening functions are almost the same, and the maximum deviation of a_0^{VCA} in Fig. 1 is about ±0.0001 nm at $x = 0.5$. The experimental error in the lattice constant over the region of $x \leqslant 0.2$ amounts to ±0.0003 nm for these alloy systems [1–3]. The equilibrium lattice constants $a_0^{\mathrm{VCA}}(x)$ obtained here deviate

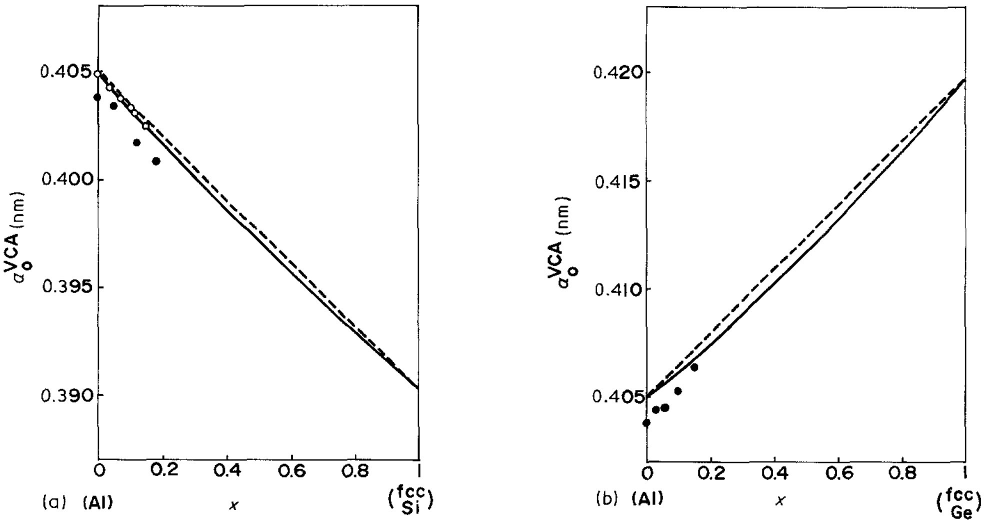

Figure 1 The variation of equilibrium lattice constant $a_0^{\mathrm{VCA}}(x)$ with x for (a) $\mathrm{Al}_{1-x}\mathrm{Si}_x$, and (b) $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ systems. (○) [1] and (●) [3] observed data, (– – –) Vegard's law.

from that according to Vegard's law (as shown by the broken lines in Fig. 1), and the slope $\Delta a/(a\Delta x)$ below $x = 0.2$ is -0.040 for $\mathrm{Al}_{1-x}\mathrm{Si}_x$ and 0.031 for the $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ system. The experimental slope $\Delta a/(a\Delta x)$ for $\mathrm{Al}_{1-x}\mathrm{Si}_x$ alloy was -0.038 [1] and -0.042 [3], and that for $\mathrm{Al}_{1-x}\mathrm{Ge}_x = 0.042$ [3]. Our obtained data of lattice constants are consistent with the observed data for $\mathrm{Al}_{1-x}\mathrm{Si}_x$, and those for $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ show a somewhat smaller increase with atomic fraction, x, than the observed data.

Next, we calculated the crystal energy in VCA, $E^{\mathrm{VCA}}(x, P)$, of the hypothetical $\mathrm{Al}_{1-x}\mathrm{Si}_x$ and $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ solid solution under the corresponding pressure, P, and found the heat of solution, $\Delta E(x, P)$, of the $\mathrm{Al}_{1-x}\mathrm{Si}_x$ and $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ systems under pressure $P = 0$, 3, 5 and 10 GPa, to be as shown in Figs 2a and b. From Fig. 2, we see that the heat of solution for the $\mathrm{Al}_{1-x}\mathrm{Si}_x$ and $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ systems has a maximum near $x = 0.6$ and decreases as the crystal became more compressed. This tendency of $\Delta E(x, P)$ is closely related to the formation of the solid solution over the aluminium-rich region under pressure. The ratio $\Delta E(x, P)/[x(1-x)]$ at $P = 0, 3, 5$ and 10 GPa for the $\mathrm{Al}_{1-x}\mathrm{Si}_x$ and $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ systems is shown in Figs 3a and b, where $\Delta E(x, P)/[x(1-x)]$ deviates largely from the linear dependence with the atomic fraction x. In the quasi-chemical model of binary alloys $\mathrm{A}_{1-x}\mathrm{B}_x$ [11], using three independent A–A, B–B and A–B bonds, the ratio $\Delta E(x)/[x(1-x)]$ is constant. However, this model is applicable only to alloy systems composed of metals with approximately equal atomic size, and not to the Al–Si or Al–Ge systems. The maximum deviation of our resultant data in Figs 2 and 3 remains at about ± 0.1 mRy ($1\ \mathrm{Ry} = 2.179\,72 \times 10^{-18}$ J) at $x = 0.6$.

Thirdly, using numerical data in Fig. 2, we show the results obtained for $F_s'(x, P, T = 700\,\mathrm{K})$ for the $\mathrm{Al}_{1-x}\mathrm{Si}_x$ system under pressure $P = 0$, 3, 5 and 10 GPa in Fig. 4a, and for $F_s'(x, P, T = 600\,\mathrm{K})$ for the $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ system in Fig. 4b. In Fig. 4, the point on the tangent of $F_s'(x, P, T)$ drawn through the point ($x = 1$, $F_s' = 0$) denotes the determined phase boundaries between the solid solution and the phase mixture under the corresponding pressure, P, and at the characteristic temperature T(K). From Fig. 4, we see that the solid solution is not formed under atmospheric pressure ($P = 0$ GPa) at $T = 700$ K for the $\mathrm{Al}_{1-x}\mathrm{Si}_x$ system and at $T = 600$ K for the $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ system. From similar analysis of $F_s'(x, P, T)$ at different temperatures from that in Fig. 4, the solubility

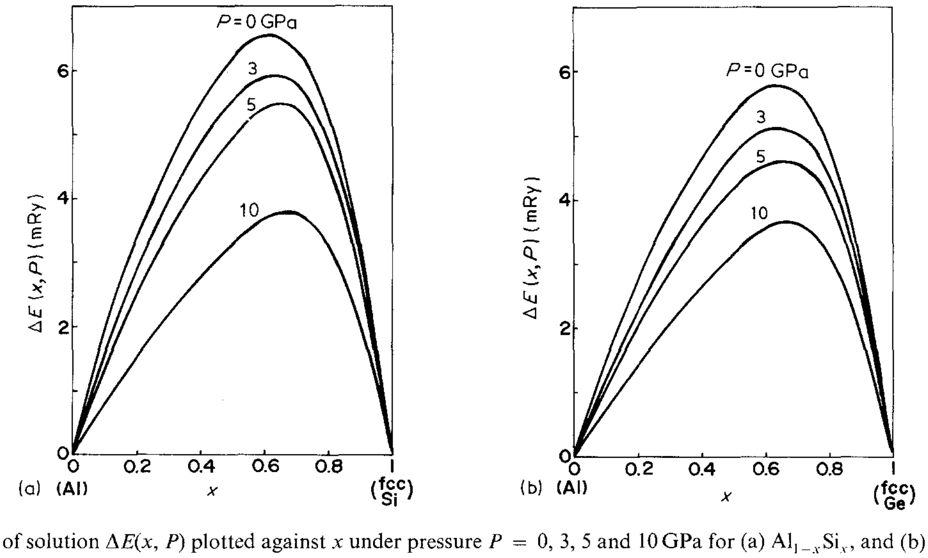

Figure 2 The heat of solution $\Delta E(x, P)$ plotted against x under pressure $P = 0$, 3, 5 and 10 GPa for (a) $\mathrm{Al}_{1-x}\mathrm{Si}_x$, and (b) $\mathrm{Al}_{1-x}\mathrm{Ge}_x$ systems.

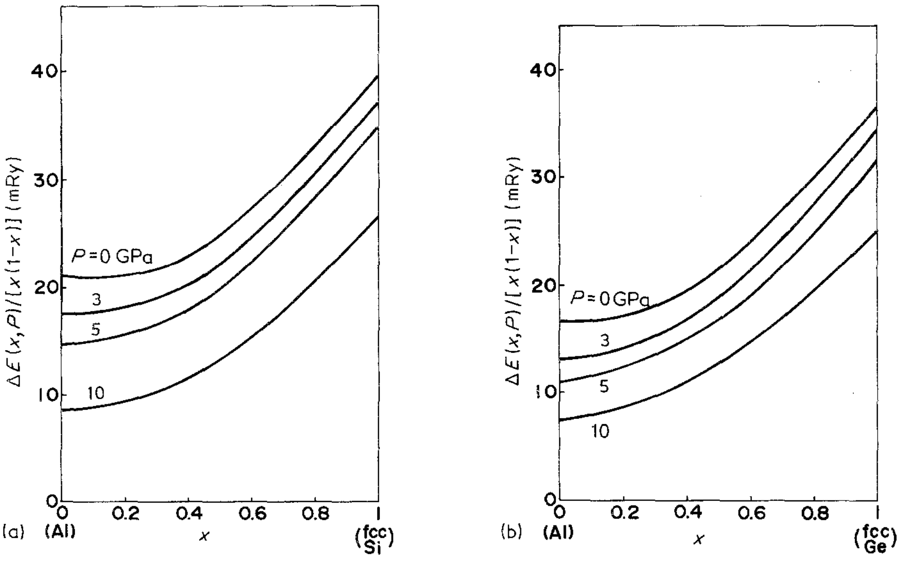

Figure 3 The ratio of the heat of solution $\Delta E(x, P)/[x(1-x)]$ plotted against x, under pressures $P = 0, 3, 5$ and 10 GPa for (a) $Al_{1-x}Si_x$ and (b) $Al_{1-x}Ge_x$ systems.

limit of the $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ systems under $P = 0, 3, 5$ and 10 GPa may be calculated; see Figs 5a and b. From Fig. 5, we predict that extended solid solutions may be formed under pressure in Al–Si and Al–Ge systems. In estimating the melting curve, it is necessary to know the Holmholtz free energy of formation $F_l'(x, P, T)$ for the liquid phase. An increase in the melting point of pure aluminium under pressure has been reported [13], but, because of lack of information on the liquid phase of the $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ systems, it is not possible to treat the phase boundary between the solid and the liquid for these systems. Our resultant phase boundaries in Fig. 5 have a calculated accuracy corresponding to $|\Delta x| \leqslant 0.01$ and $|\Delta T| \leqslant 5$ K.

Lastly, the numerical data of the pressure–volume relation for the $Al_{0.85}Si_{0.15}$ and $Al_{0.85}Ge_{0.15}$ systems are shown representatively in Figs 6a and b. The maximum deviation of pressure P in Fig. 6 is about ± 0.1 GPa at $\Omega/\Omega_0 = 0.9$, and comparable to the experimental error. At the finite temperature T, the thermal pressure, ΔP, is also considered. This effect is estimated using the Mie–Grüneisen equation of state and given [14] by $\Delta P = 3kT\gamma D(\theta/T)/\Omega$ where γ, θ and $D(\theta/T)$ are the Grüneisen parameter, Debye temperature and Debye function, respectively. At high temperatures, the influence of the thermal pressure, ΔP, is not negligible, and the reformulation of the volume scale is necessary when considering the thermal pressure. The quantitative influence of the thermal pressure on the equation of state for pure aluminium amounts to about 0.1 GPa at $T = 933.4$ K (melting point under atmospheric pressure) and at the compressed volume $\Omega/\Omega_0 = 0.9$. From Fig. 6a, we see that our resultant data of equation of state for the $Al_{0.85}Si_{0.15}$ system are in good agreement with the available experimental data [2].

4. Conclusions

The solubility limit of silicon and germanium in aluminium was studied under pressure using the microscopic electronic theory based on pseudo-

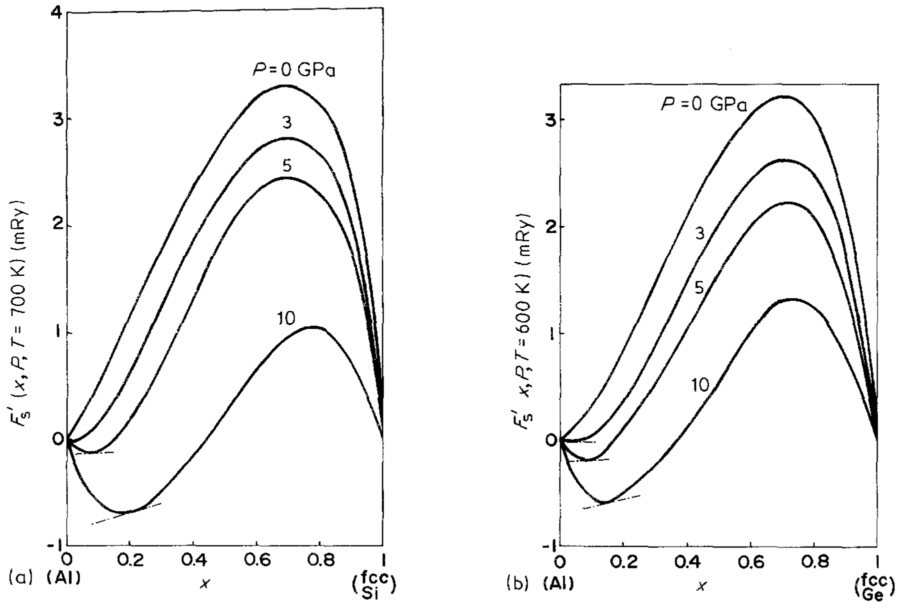

Figure 4 The Helmholtz free energy of formation (a) $F_s'(x, P, T = 700\,K)$ plotted against x for the $Al_{1-x}Si_x$, system and (b) $F_s'(x, P, T = 600\,K)$ plotted against x for the $Al_{1-x}Ge_x$ system, under pressure $P = 0, 3, 5$ and 10 GPa.

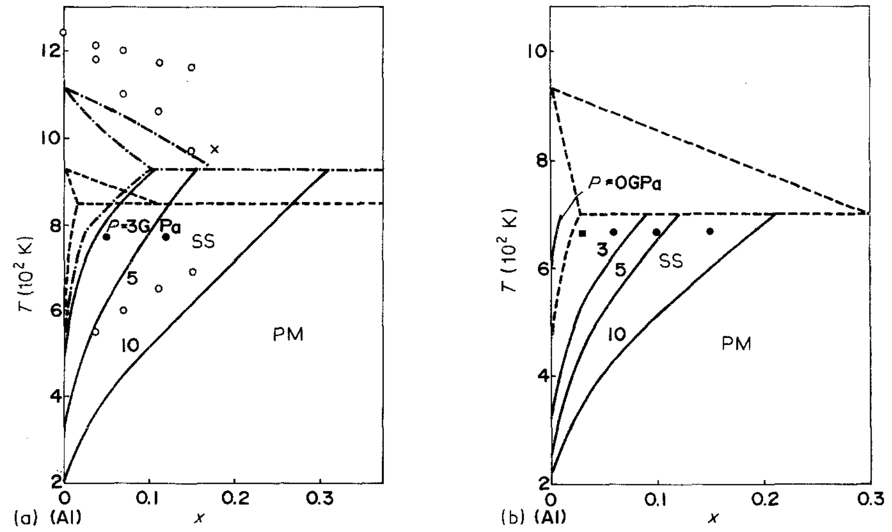

Figure 5 The resultant phase boundaries between solid solution (SS) and phase mixture (PM) under pressure $P = 0$, 3, 5 and 10 GPa for (a) Al$_{1-x}$Si$_x$ and (b) Al$_{1-x}$Ge$_x$ systems. P = (- - -) 0 GPa [12], (—·—) 2.8 GPa [1] and (○) 5.4 GPa [1]. (■), (●) and (x) solid solution with fcc phase [3] obtained experimentally at P = 4.5, 7.0 and 9.0 GPa respectively.

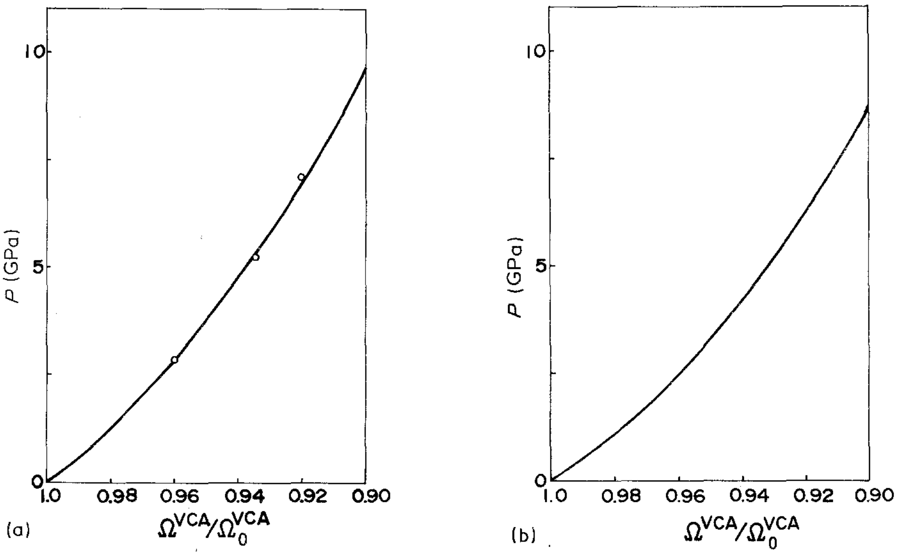

Figure 6 Pressure–volume relation for (a) Al$_{0.85}$Si$_{0.15}$ and (b) Al$_{0.85}$Ge$_{0.15}$ systems. (○) Experimental data [2].

potentials and virtual crystal approximation. The bulk properties and the solid solubility of the Al–Si and Al–Ge systems obtained from first principles are consistent with experimental data. Our treatment is useful in studying the mechanical properties, such as elastic moduli, etc., and the thermal properties, such as specific heat, etc., of these alloy systems.

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