JOURNAL OF MATERIALS SCIENCE 28 (1993) 5836–5842

Elastic and superconducting properties of supersaturated Al–Si and Al–Ge solid-solution alloys treated under a 5.4 GPa pressure

A. MATSUMURO, K. MURATA*, K. SAKAI
Department of Mechanical Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya-shi 464-01, Japan

M. SENOO
Department of Mechanical Engineering, Mie University, Tsu-shi 517, Japan

Supersaturated Al–Si and Al–Ge solid solutions having up to a 10 at% solute concentration were treated at 5.4 GPa. The variations in the elastic moduli, superconducting transition temperature T_c and other physical properties were obtained. Using the resonance method the moduli of the solid solutions in both alloy systems decreased with increasing solute concentration, in contrast with those of the two-phase states which increased. The maximum value of T_c was determined as 6.6 K for an Al–15 at% Si solid solution. It was confirmed that the dependence of T_c on the valence electron concentration was remarkably greater than that of other non-transition and noble metal alloys. Using low-temperature specific-heat experiments as a basis, the superconducting properties were discussed in terms of the electronic specific heat coefficient and the Debye temperature in comparison with other metallic superconductors.

1. Introduction

Pressure is an important thermodynamic parameter affecting the phase stability of elements and their alloys, with a high hydrostatic pressure particularly exerting considerable influence on a material's resultant phase diagram and physical properties. Rapid development of high pressure/temperature experimental techniques has occurred following research directed at accurately determining the high-pressure phase diagrams of many alloy systems. The methodologies employed include utilization of the quenching method and *in situ* observations under high pressure using high-energy synchrotron radiation, conventional X-ray diffraction (XRD) and four-probe d.c. electrical resistance measurements.

The solubility of the second element in Al in both Al–Si and Al–Ge systems was previously shown to be greatly extended using the four-probe resistance method at a pressure of 5.4 GPa [1, 2]. In the Al–Si system the Si solid-solution limit in Al was significantly increased from 1.6 at % at 580 °C and 0 GPa to greater than 15 at % at 560 °C and 5.4 GPa, whereas in the Al–Ge system that of Ge in Al increased from 2.8 at % at 424 °C and 0 GPa to 13.0 at % at 359 °C and 5.4 GPa. The solid-solution phases obtained under high pressure/temperature were quenched at atmospheric pressure and room temperature, thereby easily obtaining supersaturated solid solutions containing much higher solute concentrations than those formed under atmospheric pressure. It should be noted, however, that only a few studies have focused on quantifying the physical and mechanical properties of supersaturated solid solutions, e.g. Degtyareva *et al.* [3] reported that the superconducting transition temperature increased from 1.2 K for pure Al to 7.2 K for an Al–15 at % Ge solid solution and to 10.6 K for an Al–18 at % Si solid solution treated at pressures up to 10 GPa.

This led to the present paper which estimates variations in the elastic moduli, superconducting transition temperature, and other physical properties of Al–Si and Al–Ge solid solutions after undergoing solid-solutioning at 5.4 GPa. The elastic moduli were measured using a resonance method developed by the authors [4]. Properties contributing to the superconducting transition were also determined by low-temperature specific-heat measurements.

2. Experimental procedure

The samples in both alloy systems were prepared by casting 99.99 at % pure Al, 99.999 at % pure Si and 99.999 at % pure Ge at atmospheric pressure to the following compositions: Al–5, 10, 15, 20, 25 at % Si, and Al–2.5, 5, 7.5, 10, 15 at % Ge. After being lathe-machined into a cylinder (6 mm dia. × 6 mm long), the samples were fully annealed in an Ar atmosphere at

---

* *Present address*: NTT Co. Ltd, Morinosato Wakamiya, Atsugi-shi 243-01, Japan.

400 °C for the Al–Si alloy system and 300 °C for Al–Ge.

These Al–Si and Al–Ge samples were solution-treated for 10 h at 5.4 GPa and 600 and 400 °C, respectively, then rapidly cooled to room temperature by de-energizing the heater current and reducing the pressure to atmospheric. High pressure was hydraulically applied in three dimensions using a force-generating apparatus comprised of six tungsten carbide anvils. The pressure vessel volume was 15 mm × 15 mm × 15 mm. Fig. 1 shows a schematic illustration of the experimental set-up. The pressure scale was calibrated using the conventional pressure standards of the phase transitions of Bi (2.55 GPa), Tl (3.67 GPa) and Ba (5.50 GPa), while the temperature was calibrated by a Pt/Pt–13% Rh thermocouple. Fig. 2 shows the solid-solutioning pressure cell, where the pyrophyllite cube (20 mm × 20 mm × 20 mm) acts as the pressure-transmitting medium. The carbon heater and sample are insulated by boron nitride. The structure and lattice parameters of the solution-treated samples were examined using XRD experiments with MoK_α.

Measurements of elastic moduli were performed by three-dimensional resonance of a small cylindrical sample (2–10 mm) as previously described in detail [4]. The shear modulus G and Young's modulus E of the polycrystalline samples were determined at a measurement accuracy of about ±0.1%. The sample density was measured by the Archimedes method using water.

The electrical resistivity was measured by the d.c. four-probe method from 4 to 300 K using a rectangular sample (0.5 mm × 1 mm × 5 mm) cut from the cylindrical one. The current passing through the longitudinal direction was adjusted to $< 1\,\mathrm{A\,cm^{-2}}$. The diamagnetic susceptibility was measured from 1.5 to 25 K by an a.c. mutual inductance bridge. The superconducting transition temperature T_c was defined in both methods as the midpoint of the transition.

The low-temperature specific-heat measurements (1.6–6 K) were taken using an adiabatic calorimeter developed by Mizutani *et al.* [5]. The sample value was 0.03 mol. In this temperature range the specific heat is conventionally expressed as $C/T = \gamma + \alpha T^3$, where α and γ are respectively the lattice and electronic specific heat coefficients. As commonly known, γ is related to the density of states of the conduction electrons at the Fermi level $N(E_F)$, and α to the Debye temperature θ_D by $\theta_D = (12\pi^4 R/5\alpha)^{1/3}$, where R is the gas constant. The specific-heat measurements were then least-squares fitted to the above relationship.

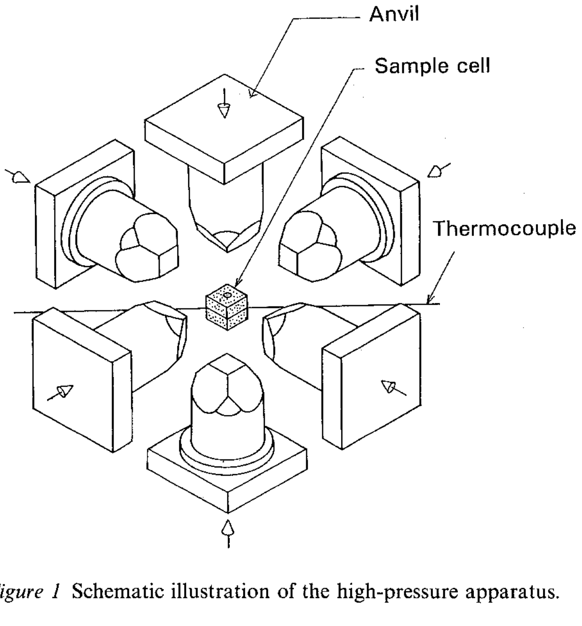

Figure 1 Schematic illustration of the high-pressure apparatus.

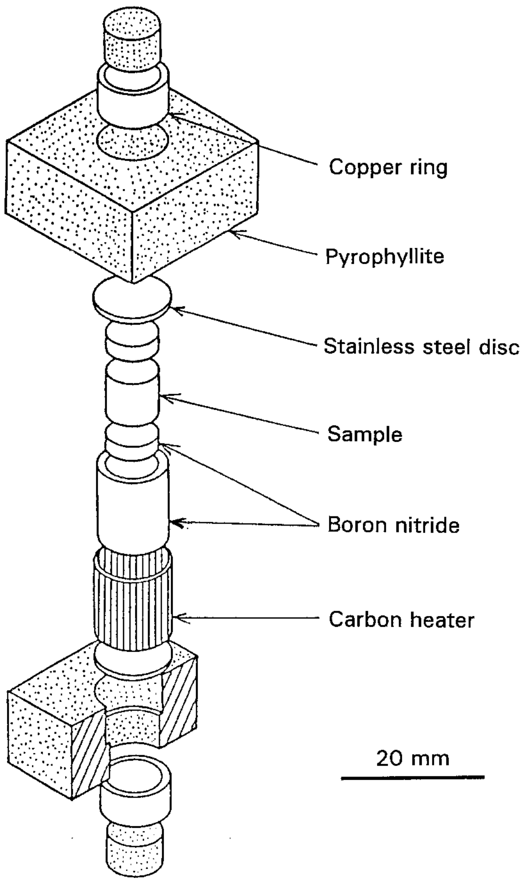

Figure 2 Sample test assembly used with the high-pressure/temperature solid-solutioning technique.

3. Results and discussion

3.1. Elastic modulus measurements

Fig. 3 shows shear moduli G versus the solute concentrations (at %) of the Al–Si and Al–Ge annealed two-phase alloys before solid-solutioning and afterwards. In both the systems the two-phase state shows increasing moduli with the solute concentration c. This occurs because the diamond structure of Si and Ge has a larger modulus than that of pure Al. However, the modulus as estimated by linear extrapolation of the Al–Ge alloy system is substantially larger than the experimental value of pure Al, possibly due to the modulus being affected by the residual solute atoms of Ge in Al even after annealing. In contrast, the shear moduli of the solid solutions in both systems significantly decrease with increasing solute concentration, having slopes of -0.32 and $-0.57\,\mathrm{GPa\,(at\,\%)^{-1}}$ for the Al–Si and Al–Ge systems, respectively. Variations

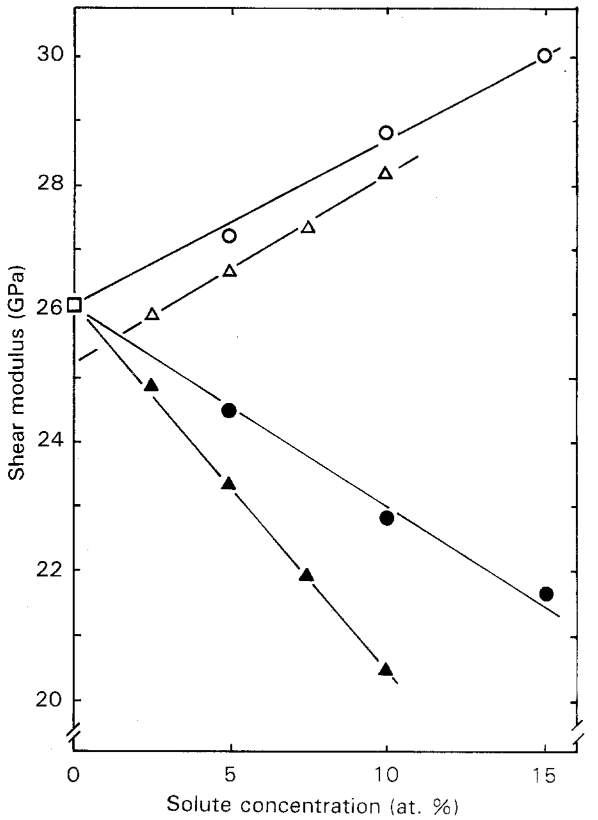

Figure 3 Shear modulus versus the solute concentration of the Al–Si and Al–Ge two-phase alloys and solid solutions: (●) Al–Si solid solution, (▲) Al–Ge solid solution, (○) Al–Si two-phase alloy, (△) Al–Ge two-phase alloy.

in Young's modulus E are shown in Fig. 4 in comparison with those reported by Elliot and Axon [6]. Notice the same features as described for Fig. 3, with slopes of -0.81 and $-1.4\,\mathrm{GPa\,(at\,\%)^{-1}}$ being respectively obtained for the Al–Si and Al–Ge systems. The slope from Elliot and Axon is surprisingly positive and rapidly increases with the solute concentration, an unusual result which is considered to be due to the sample containing a low solute concentration of up to 1 at % Si and/or a large measurement error.

Fig. 5 shows the temperature dependence of the shear moduli for Al–Si and Al–Ge solid solutions in which the low-temperature values of the elastic moduli were determined by the resonance method [4]. As expected, the moduli of both solid solutions increase as the temperature is decreased, having a zero slope at absolute zero and a linear behaviour at high temperatures. These results indicate that no low-temperature phase transition occurs in either solid solution.

Assuming the Debye theory, the Debye temperature θ_D of solid solutions at 0 K is estimated as

$$\theta_D = \frac{h}{k_B}\left(\frac{9N}{4\pi V}\right)^{1/3}\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)^{1/3} \qquad (1)$$

where h is Planck's constant, k_B the Boltzmann constant, N/V the number of atoms per unit volume, and v_l and v_t are the sound propagation velocities for a longitudinal and transversal wave, respectively. The sound velocities in an isotropic solid are determined by the independent elastic moduli G and E and the density ρ. The elastic moduli at 0 K were extrapolated from the measured moduli using Varshini's equation [7], whereas the solid solution densities at 0 K were estimated from the measured density at 293 K by assuming that the coefficients of linear expansion are the same as for pure Al [8]. Fig. 6 shows the results in comparison with those obtained by the specific heat measurements discussed in the next section. The value for pure Al agrees well with results from Lazarus [9], $\theta_D = 425$ K. The Debye temperatures of the Al–Si and Al–Ge solid solutions clearly indicate a linear decrease

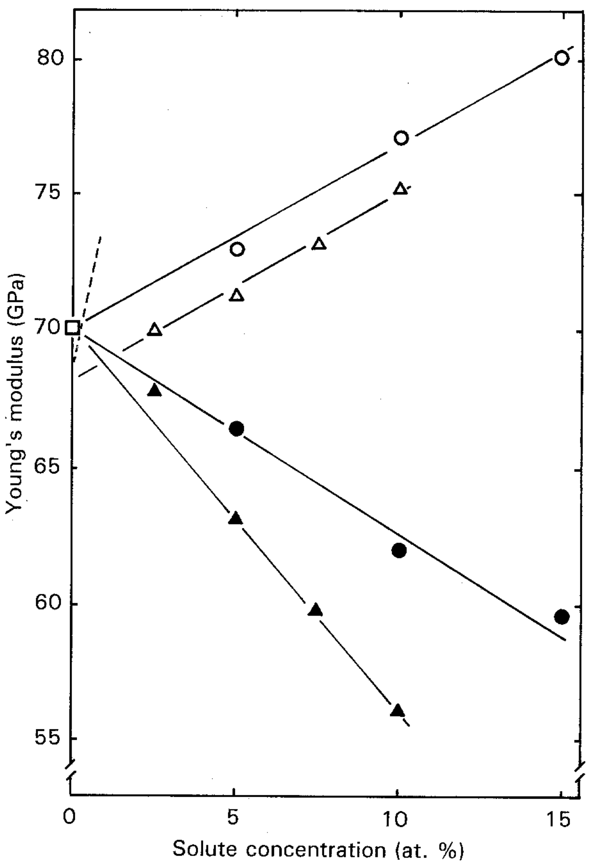

Figure 4 Young's modulus versus the solute concentration of the Al–Si and Al–Ge two-phase alloys and solid solutions: (●) Al–Si solid solution, (▲) Al–Ge solid solution, (○) Al–Si two-phase alloy (△) Al–Ge two-phase alloy; also (- - -) Al–Si results from Elliott and Axon [6].

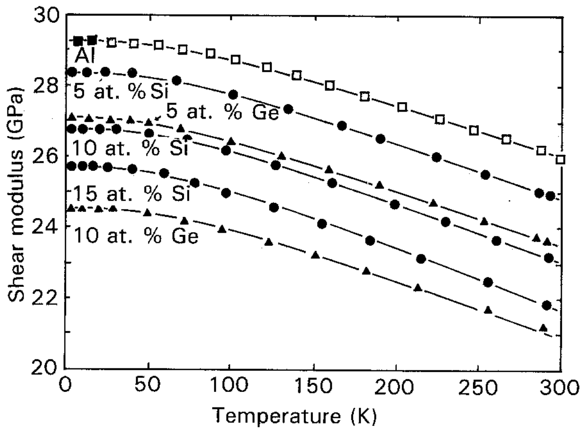

Figure 5 Temperature dependence of the shear modulus for Al–Si and Al–Ge solid solutions and pure aluminium.

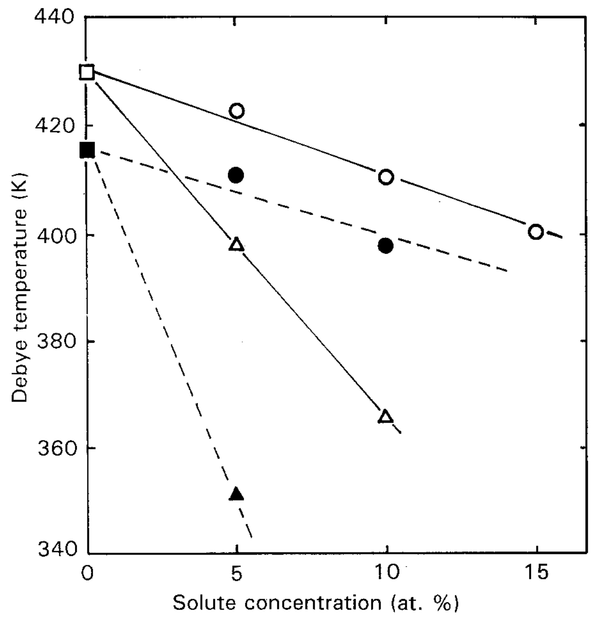

Figure 6 Debye temperature versus the solute concentration of (○, ●) Al–Si and (△, ▲) Al–Ge two-phase alloys and solid solutions. Results determined from elastic modulus (open symbols) and specific heat measurements (filled symbols) are shown.

with increasing solute contents and correspond to variations in the elastic moduli.

The lattice constant a versus solute concentrations for the solid solutions is shown in Fig. 7. For the solid solutions of Ge in Al, lattice expansion increases with an increasing solute concentration, whereas for that of Si in Al, the constant decreases because of the difference in the atomic sizes when dissolved in Al. The slopes are 0.16×10^{-12} and -0.12×10^{-12} m (at %)$^{-1}$ for the Al–Ge and Al–Si systems, respectively, being in good agreement with other reported values obtained using the conventional quenching technique at atmospheric pressure [10, 11]. Notice that although the absolute values of the lattice strains of the solid solutions are approximately the same, their signs are opposite.

The effect of the lattice strain leads to a decrease in the elastic modulus, with Zener [12] concluding that when an internal strain occurs in a solid solution the slope of the shear modulus $\partial G/\partial c$ is expressed as

$$\frac{1}{G}\left(\frac{\partial G}{\partial c}\right) = \frac{4\varepsilon_a^2}{k_B N}\left(\frac{\partial G}{\partial T}\right) \qquad (2)$$

where ε_a is the internal strain $(1/a)(\partial a/\partial c)$, $\partial G/\partial T$ the slope of the shear modulus of pure Al versus temperature, and N the number of atoms per unit volume. The value of ε_a was estimated using variations in the lattice constants (Fig. 7), and $\partial G/\partial T$ was determined to be -0.015 GPa K^{-1} from Fig. 5. As a result, Zener's value of $\partial G/\partial c$ was estimated as -0.016 GPa (at %)$^{-1}$ for Al–Si solid solutions and -0.034 GPa (at %)$^{-1}$ for Al–Ge ones. It should be noted that these values are less than 10% of the experimental data presented for both alloy systems; hence the decrease in G due to Si and Ge solutioning in Al is not influenced by size effects. Therefore, the interactions between Al and Si or Al and Ge atoms play the most important role in the decrease of the elastic moduli.

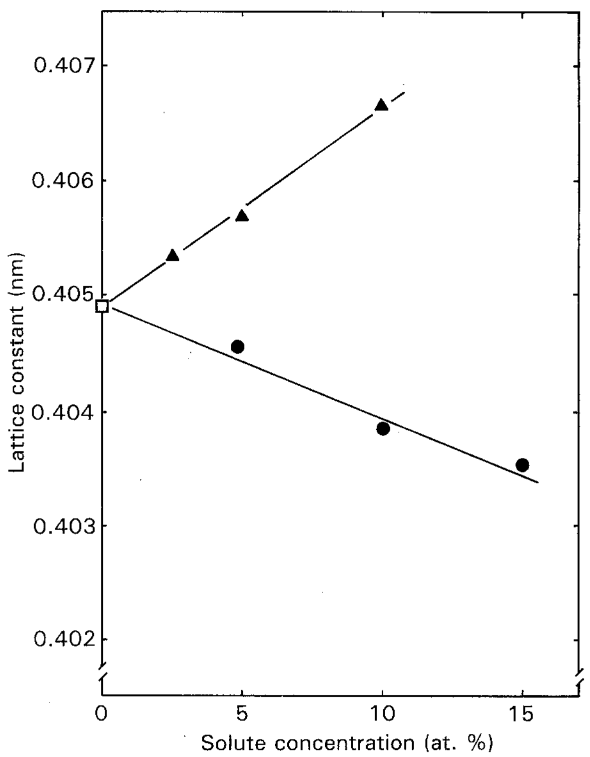

Figure 7 Lattice constant versus the solute concentration of (●) Al–Si and (▲) Al–Ge two-phase alloys and solid solutions.

As a result of changes in the band structure, the precise effects of atomic interactions on the elastic moduli generally vary with respect to the valence electron concentration per atom Z when an atom having a different number of valence electrons is solutioned in the solvent atom. Smith [13] reported that the elastic moduli for solid solutions consisting of Cu and Ag with a monovalent solvent metal decrease with increasing Z. Fig. 8 shows Young's moduli versus Z for the present Al alloys and those of the Al–Cu [14] and Al–Li [15] alloys. These Young's moduli indicate the effective values for the valence interaction, from which Zener's values are subtracted. All the Al alloy systems show an approximately linear relation with a negative slope, being similar to that of the Cu and Ag solid solutions [13]. However, the slope for the Al–Ge alloy system is steeper than in the other alloy systems by an amount that is outside the experimental error. The reason for this difference has not been clarified. Since only the Al–Ge solid solutions have positive internal strains, in contrast with the other Al alloys, the influence of the change in the mean atomic volume may be an important phenomenon to investigate to determine the reason, although only if Zener's estimation is a good one. Noble *et al.* [15] also suggested that variations in Young's moduli with the solute concentration $\partial E/\partial c$ were closely related to deviations of the mean atomic volume from Vegard's law, which predicts a linear dependence of the atomic volume on concentration for solutions comprised of pure solvent and pure solute.

3.2. Superconducting properties

Fig. 9 shows the typical temperature dependence of the electrical resistivity of an Al–15 at % Si solid solution

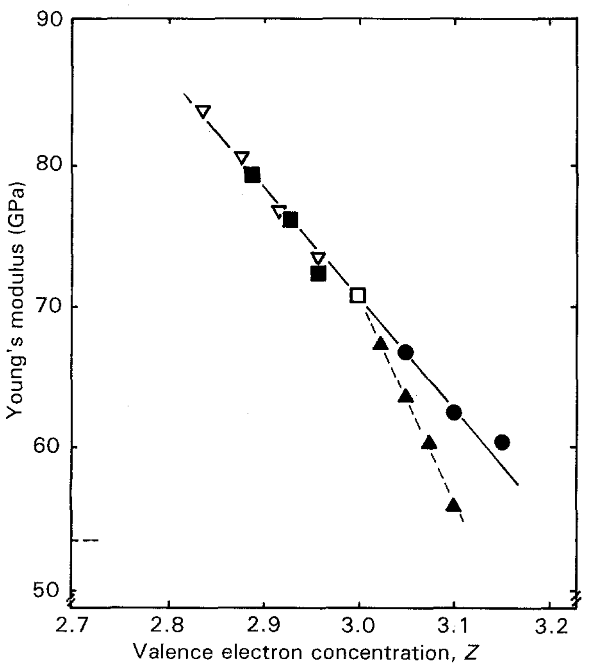

Figure 8 Young's modulus versus the valence electron concentration Z of (□) pure Al and solid solutions based on aluminium: (●) Al–Si, (▲) Al–Ge, (▽) Al–Cu, (■) Al–Li.

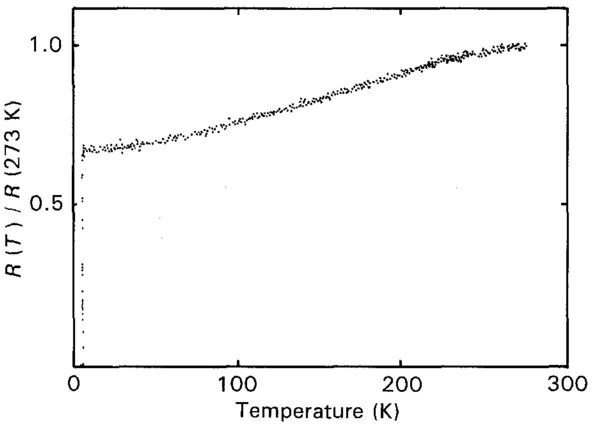

Figure 9 Typical temperature dependence of the electrical resistivity for Al–15 at % Si solid solutions.

from 4 to 300 K. The observed T_c was 6.6 K with a width of 0.4 K. Fig. 10 shows T_c for the Al–Si and Al–Ge solid solutions versus the valence electron concentration Z. XRD patterns of diamond-structure Si and Ge were also observed for Al–20 at % Si ($Z = 3.2$), Al–25 at % Si (3.25) and Al–15 at % Ge (3.15) because their solute concentrations exceeded the solubility limits shown in their respective high-pressure phase diagrams [1, 2]. Within these limits, T_c linearly increased with increases in Z for both systems. The resultant slopes were obtained to be 33 K Z^{-1} for the Al–Si solid solution and 27 K Z^{-1} for Al–Ge. Fig. 11 compares our values of T_c for the Al–Si and Al–Ge solid solutions with those obtained by Degtyareva *et al.* [3] and those from other non-transition alloys [3] and the α-phase f.c.c. solid solutions of Au–Ga [16], Ag–Ga [16] and Cu–Ga [16]. Good correlation with Degtyareva *et al.* is apparent. Moreover, the strong dependence of T_c on Z is shown to be much greater in the Al–Si and Al–Ge systems than in the non-transition and noble metal alloys.

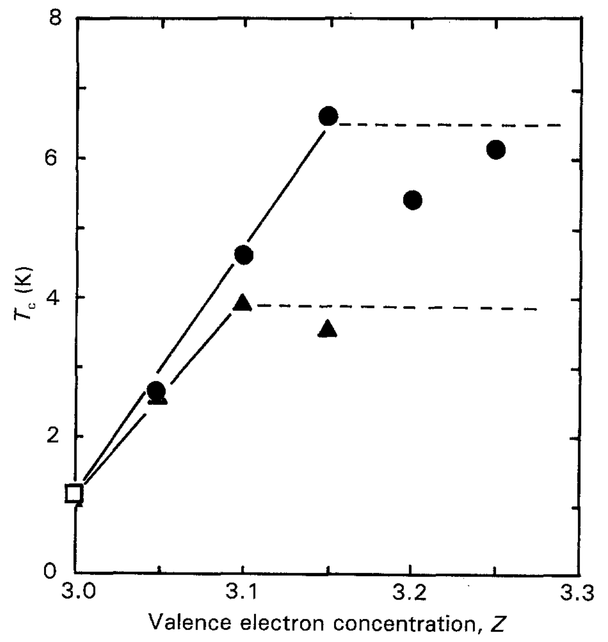

Figure 10 Superconducting transition temperature T_c versus the valence electron concentration Z for (●) Al–Si and (▲) Al–Ge solid solutions.

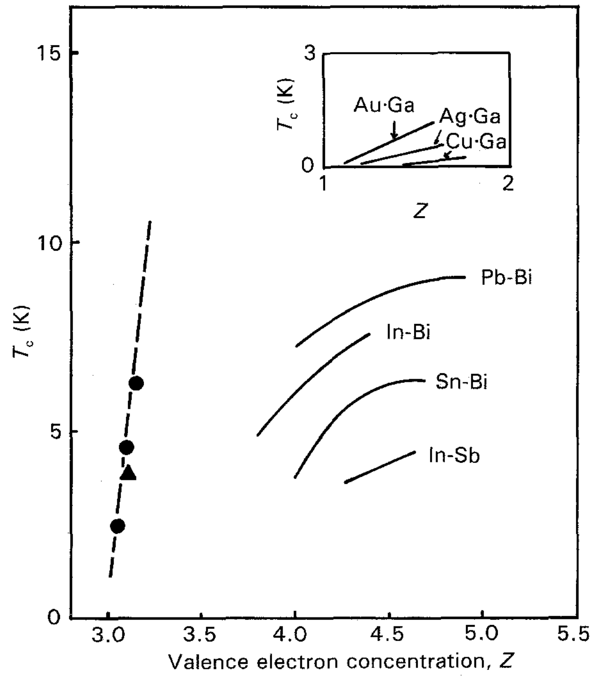

Figure 11 Superconducting transition temperature T_c versus the valence electron concentration Z for (●) Al–Si and (▲) Al–Ge solid solutions, together with (---) the results of Degtyareva *et al.* [3] and data for other non-transition alloys and α-phase f.c.c. solid solutions (see text). The inset only illustrates the general tendencies of T_c versus Z.

Fig. 12 shows typical results of the specific heat measurements for an Al–5 at % Si solid solution under zero magnetic field, plotted as C/T versus T^2. Also shown is the extrapolation of the least-squares fit. The peak below 8 K^2 is obviously due to the superconducting state, with T_c being estimated as 2.6 K in good agreement with the diamagnetic susceptibility measurements. Other solid solutions showed similar

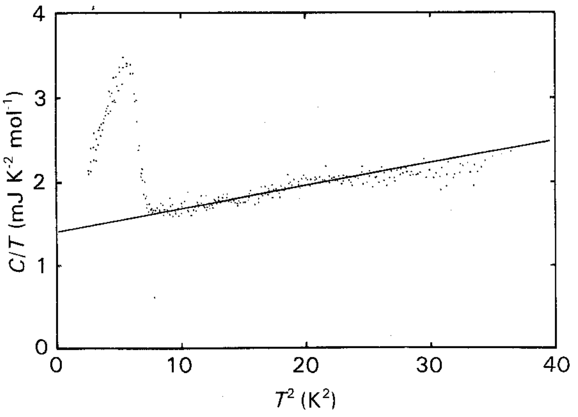

Figure 12 Typical specific heat measurements in zero magnetic field for Al–5 at % Si solid solutions. The least-squares fit to $C/T = \gamma + \alpha T^3$ is also shown.

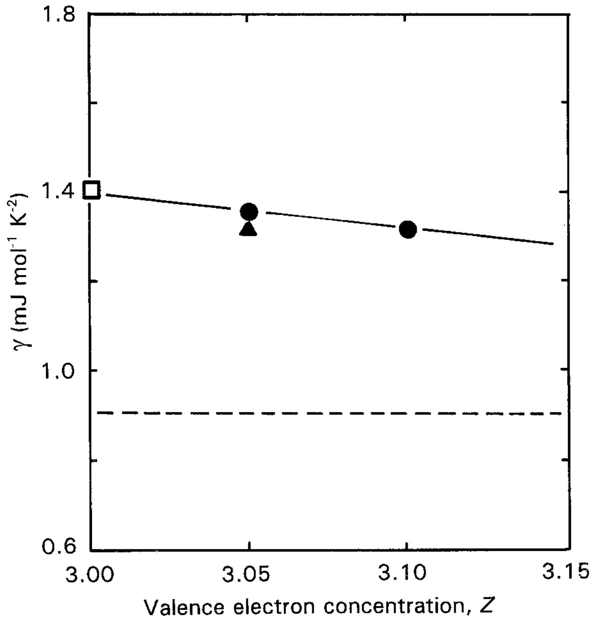

Figure 13 Electronic specific heat coefficient γ versus the valence electron concentration Z for (●) Al–Si and (▲) Al–Ge solid solutions, together with (- - -) predictions from free electron theory.

results. From the extrapolated line, $\gamma = 1.34 \pm 0.02\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$ and $\theta_D = 411 \pm 2\ \mathrm{K}$ were obtained. Fig. 13 shows γ versus Z, as well as the calculated values obtained by assuming a free electron approximation. For pure Al $\gamma = 1.36 \pm 0.01\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$, in good agreement with Aoki *et al.* [17] where $\gamma = 1.37 \pm 0.02\ \mathrm{mJ\,mol^{-1}\,K^{-2}}$.

In both systems the variation of γ with respect to Z is considerably small, being quite similar to the relationship obtained by the free electron alloy model. This suggests that for supersaturated Al–Si and Al–Ge solid solutions having up to a 10 at % solute concentration, the electronic states at the Fermi level are almost the same as in pure Al, and therefore both solid solutions have free electron-like band structures. The values of θ_D obtained from the specific heat measurements are also shown in Fig. 6. The value for pure Al, $\theta_D = 415.6 \pm 0.6$ K, agrees well with the value of 408 K reported by Howlling *et al.* [18]. However, the Debye temperature determined from the elastic moduli is different from the value obtained from the specific heat measurements. Since different experimental techniques correspond to different averages over the distributions of the phonon frequency, an exact agreement should not be expected. Nonetheless, in both measurements the Debye temperature shows a similar dependence on the electron concentration, i.e. it monotonously decreases with increasing Z and its slope in the Al–Ge alloy system is greater than that of Al–Si. Similar corresponding features were also found in the elastic moduli G and E.

The specific heat measurement can explain the resultant superconductivity phenomenon if the nearly free electron model is applied to the solid solutions. The dependence of the electron phonon coupling constant λ on Z was investigated using a simple jellium model containing the parameters of Z and ionic mass M. Using this model, the ionic plasma frequency Ω_p is expressed as

$$\Omega_p = \left(\frac{NZ^2e^2}{\varepsilon_0 M}\right)^{1/2} \tag{3}$$

where N, e and ε_0 are respectively the ion density, the proton charge and the permittivity of free space. The dimensionless ratio of $\ln(k_B T_c/\hbar\Omega_p)$ represents the exponential factor contained in McMillan's equation [19] shown below, and therefore approximates λ:

$$T_c = \frac{\theta_D}{1.45}\exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right) \tag{4}$$

where μ^* is the effective Coulomb repulsion parameter, being assumed to be 0.1 for simple metals. The dependence of $\ln(k_B T_c/\hbar\Omega_p)$ on Z is estimated using the measured T_c values, and Fig. 14 compares the results with those for other solid solutions consisting of the simple noble metals. The value for each alloy system linearly increases with increasing solute concentrations and the slope for the Al–Si and Al–Ge alloy systems is clearly steeper than in other non-transition superconductors such as Pb–Bi, Pb–Tl and Sn–Bi [20]. On the other hand, the dependence on Z corresponds to the results for noble metal alloys such as Au–Ga [14], Ag–Ga [5] and Cu–Ga [5]. It is therefore concluded that the electron–phonon interactions of Al–Si and Al–Ge solid solutions are the same as those occurring in the noble metal alloys having valence electrons in the s- or p-orbital state. Table I summarizes the θ_D/Z ratio of several alloy systems, where the ratio for the Al–Si and Al–Ge solid solutions is remarkably larger than those from the noble metal alloys.

The decrease in the Debye temperature is consequently believed to play a major role in the great enhancement of T_c with respect to solute concentration in both the Al–Si and Al–Ge systems.

4. Conclusions

Supersaturated Al–Si and Al–Ge solid solutions up to 10 at % solute contents were prepared under a pressure of 5.4 GPa, with their elastic and superconduct-

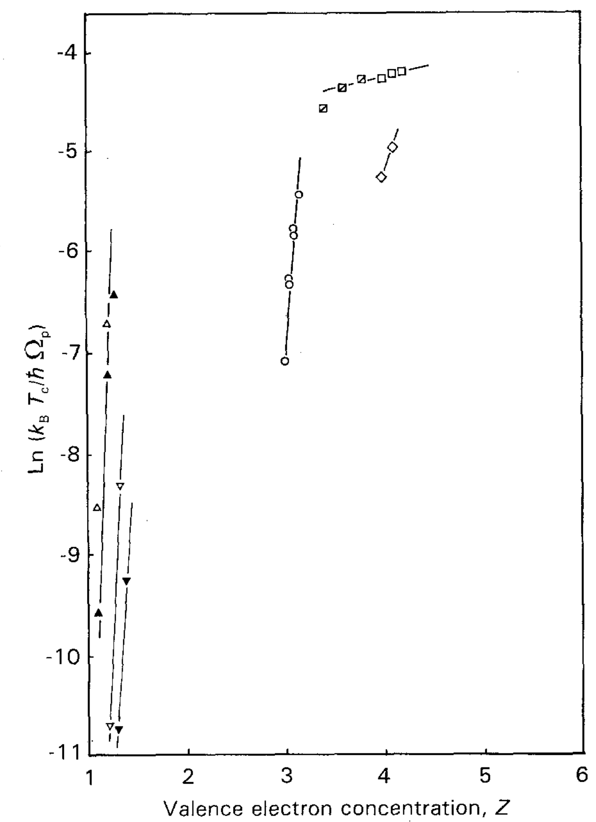

Figure 14 Ratio of the normalized superconducting transition temperature to the characteristic bare phonon temperature ($\hbar\ \Omega_p/k_B$) versus the valence electron concentration Z for (○) Al–Si and Al–Ge, (□) Pb–Bi [20], (▨) Pb–Tl [20], (◇) Sn–Bi [20], (△) Au–Ga [16], (▲) Au–Al [21], (▽) Ag–Ga [16] and (▼) Cu–Ga [16].

TABLE I Dependence of Debye temperature on the valence electron concentration Z

Alloy	Al–Si	Al–Ge	Au–Ga	Ag–Ga	Cu–Ga	Pb–Bi
θ_D/Z	−193	−640	−88	−51	−42	−20

ing properties being subsequently obtained. It was found using the resonance method that the shear modulus G and Young's modulus E for both solid solutions decrease with increasing solute concentration, whereas the moduli of the annealed two-phase state before solid-solutioning increase. The slopes $\partial G/\partial c$ and $\partial E/\partial c$ were respectively calculated as -0.32 and -0.81 GPa(at %)$^{-1}$ for the Al–Si system and -0.57 and -1.40 GPa(at %)$^{-1}$ for Al–Ge.

Within the solubility limits the values of T_c increased linearly with respect to increasing valence electron concentration Z. The dependence of T_c on Z was found to be much greater than in other non-transition and noble metal alloys. The remarkable enhancement of T_c is mainly attributed to the decrease of the Debye temperature with increasing Z.

Acknowledgements

Sincere gratitude is extended to Professors U. Mizutani and S. Matsuo, Nagoya University, for their beneficial suggestions, and to Mr Y. Masanaka, Nagoya University, for his assistance in sample preparations.

References

1. H. MII, M. SENOO and I. FUJISHIRO, *Jpn. J. Appl. Phys.* **15** (1976) 777.
2. M. SENOO, *J. Jpn. Soc. Tech. Plasticity* **27** (1986) 464.
3. V. F. DEGTYAREVA, G. V. CHIPENKO, I. T. BELASH, O. I. BARKALOV and E. G. PONYYATOVSKII, *Phys. Status Solidi A* **89** (1985) K127.
4. A. MATSUMURO, T. NAGASAKA and M. SENOO, *Jpn. Soc. Mech. Eng. Int. J.* **A35** (1992) 220.
5. U. MIZUTANI, S. NOGUCHI and T. B. MASSALSKI, *Phys. Rev. B* **5** (1972) 871.
6. B. J. ELLIOTT and H. J. AXON, *J. Inst. Metals* **86** (1957–58) 24.
7. V. P. VARSHINI, *Phys. Rev. B* **2** (1970) 3952.
8. D. E. GRAY, "American Institute of Physics Handbook", 3rd Edn (McGraw-Hill, New York, 1972) pp. 4–120.
9. D. LAZARUS, *Phys. Rev.* **76** (1949) 545.
10. M. ITAGAKI, B. C. GIESSEN and H. J. GRANT, *Trans. ASM* **61** (1968) 330.
11. H. J. AXON, D. PHIL and W. HUME-ROTHERY, *Proc. Roy. Soc.* **A193** (1948) 1.
12. C. ZENER, *Acta Crystallogr.* **2** (1949) 163.
13. A. D. N. SMITH, *J. Inst. Metals* **80** (1951–52) 477.
14. M. SENOO and T. HAYASHI, *Jpn. Soc. Mech. Eng. Int. J. A* **31** (1992) 664.
15. B. NOBLE, S. J. HARRIS and K. DINSDALE, *J. Mater. Sci.* **17** (1982) 461.
16. R. F. HOYT, *Phys. Rev. B* **14** (1976) 441.
17. R. AOKI and T. OHTSUKA, *J. Phys. Soc. Jpn.* **26** (1969) 651.
18. D. H. HOWLLING, E. MENDOZA and J. E. ZIMMERMAN, *Proc. Roy. Soc.* **A229** (1955) 85.
19. W. L. McMILLAN, *Phys. Rev.* **167** (1968) 331.
20. P. B. ALLEN and R. C. DYNES, *Phys. Rev. B* **14** (1976) 441.
21. T. B. MASSALSKI and U. MIZUTANI, *Prog. Mater. Sci.* **22** (1978) 151.

Received 1 July 1992
and accepted 27 April 1993