JOURNAL OF MATERIALS SCIENCE 29 (1994) 640–644

Lattice dynamics and specific heat of Al–Si and Al–Ge solid solutions

T. SOMA, I. KITABATAKE, H. M. KAGAYA
Department of Applied Physics and Mathematics, Mining College, Akita University, Akita 010, Japan

A simplified treatment has been proposed to study quantitatively the lattice dynamics of Al–Si and Al–Ge alloy systems by solid-solutioning under pressure. The volume and electron density effects on the lattice dynamics of the pure constituents aluminium, silicon or germanium are considered, and the phonon dispersion relations of the local and band modes were obtained. Then, the concentration dependence of the local and band mode frequencies were calculated for the $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ systems. Using the local and band mode frequencies, the lattice specific heat at constant volume was determined theoretically, and results obtained for the temperature-dependent specific heat of matrix aluminium were found to be in good agreement with the experimental data. The concentration dependence of the specific heat could then be predicted quantitatively for $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ alloy systems.

1. Introduction

The formation and physical properties of solid solutions under pressure by rapid quenching from the liquid state are interesting in the field of materials science and technology. Recently, we [1] have studied the solid solubility of silicon and germanium in aluminium under pressure using microscopic electronic theory, and the bulk properties and the solid solubility of the Al–Si and Al–Ge systems obtained were consistent with the experimental data. We then, presented [2] the concentration dependence of elastic moduli for Al–Si and Al–Ge solid solutions. Up to this time, theoretical studies on the lattice dynamics of the alloy system have been devoted to the Rb–K system, because both constituents were alkali metals and the lattice dynamics of the pure constituents have been investigated in detail. Classifying roughly, there are two theoretical treatments. One is the coherent-potential approximation, which is a mean-field type of approach employed to describe the electron density of states in random alloys. Along this line, some research [3–5] on the mass defect and the differences of force constants, etc., have been reported, and neutron scattering cross-sections for various momentum transfers have been calculated in comparison with experimental data. The other is computer-simulation calculation [6, 7] in a molecular dynamics system, which consists of many particles involving randomly chosen solute atoms. The latter obtains the dynamical structure factor, but the effort in computer-simulation procedures is enormous. In the present work, we did not use a rigorous description of the lattice vibrations for the alloy systems, but we have presented a simplified treatment to estimate quantitatively the phonon mode frequencies and thermal properties of Al–Si and Al–Ge alloy systems.

2. Lattice dynamics of Al–Si and Al–Ge alloy systems

The $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ alloy systems form substitutional solid solutions over the α-phase region, and the crystal binding of the solid solution is unchanged compared with that of pure aluminium metal. The bulk properties of these alloys were reproduced in the virtual crystal approximation, and the idea of the average atomic potential was suitable for the static properties. In the dynamical treatment we could not treat the dynamics of the hypothetical pseudo-alloy atom directly from the idea of the average atomic potential, because the constituent atoms thermally vibrate. In fact, it is well known that local and band vibrational modes corresponding to the lattice vibration of the solute and solvent atoms are observed. But, the lattice site of the solute and solvent atoms in the substitutional solid solution is not determined and theoretical treatment of the lattice dynamics encompasses many difficulties. Some research [3–7], mentioned in Section 1 has as a future goal the calculation of the macroscopic thermal properties by summing up the contributions from the individual vibrational modes over braches and wave number space.

We introduce, instead, the following simplifying approximation. When $Al_{1-x}Si_x$ solid solution is formed, aluminium atoms in the solid solution are in a state of volume compression compared with those in pure aluminium and silicon atoms in a state of volume expansion compared with those in fcc silicon [1]. On the other hand, when $Al_{1-x}Ge_x$ solid solution is formed, aluminium atoms in the solid solution are in a state of volume expansion compared with those in pure aluminium, and germanium atoms in a state of volume compression compared with those in fcc germanium [1]. Therefore, we consider apparently the

0022–2461

lattice vibrations of aluminium, silicon or germanium atoms in the solid solution as those in pure aluminium, fcc silicon or fcc germanium crystals at the equilibrium lattice constant, a_0 [1], and the electron density, $n = Z/\Omega_0$, of the solid solutions with fcc phase. Here, the equilibrium atomic volume, Ω_0 related to average valency, $Z = (1 - x)Z^{\mathrm{Al}} + x \cdot Z^{\mathrm{Si\ or\ Ge}}$ and the interelectronic distance, r_s is given by

$$\begin{aligned} \Omega_0 &= \frac{a_0^3}{4} \\ &= \frac{Z}{n} \\ &= Z\frac{4\pi r_s^3}{3} \end{aligned} \tag{1}$$

The normal vibrational modes with the branch i, the wave vector $\boldsymbol{q}$ and the frequency $\nu_i^{\mathrm{j}}(\boldsymbol{q}, x)$ with concentration, x, of silicon or germanium fixed, are determined by solving the secular equation

$$|D_{\mathrm{j}}^{\alpha\beta}(\boldsymbol{q}, x) - M_j \nu_i^{\mathrm{j}}(\boldsymbol{q}, x)^2 \delta_{\alpha,\beta}| = 0 \tag{2}$$

where j = Al, Si or Ge. The dynamical matrix $D_{\mathrm{j}}^{\alpha\beta}(\boldsymbol{q})$ is given by

$$\begin{aligned} D_{\mathrm{j}}^{\alpha\beta}(\boldsymbol{q}) &= N\sum_{\boldsymbol{G}}(\boldsymbol{q} + \boldsymbol{G})_\alpha(\boldsymbol{q} + \boldsymbol{G})_\beta V_{\mathrm{eff}}^{\mathrm{j}}(\boldsymbol{q} + \boldsymbol{G}) \\ &\quad - N\sum_{\boldsymbol{G} \neq 0} G_\alpha G_\beta V_{\mathrm{eff}}^{\mathrm{j}}(\boldsymbol{G}) \end{aligned} \tag{3}$$

where

$$V_{\mathrm{eff}}^{\mathrm{j}}(\boldsymbol{q}) = \frac{1}{N}\sum_{\boldsymbol{r}_l} V_{\mathrm{eff}}^{\mathrm{j}}(\boldsymbol{r}_l)\mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}_l} \tag{4}$$

In Equation 3, $\boldsymbol{G}$ is the reciprocal lattice vector and in Equation 4, $\boldsymbol{r}_l$ is the equilibrium position vector of the lth ion. Within the second-order perturbation theory based on pseudopotentials, the effective potential $V_{\mathrm{eff}}^{\mathrm{j}}(r)$ is obtained from the pairwise two-body force between ions and given by

$$V_{\mathrm{eff}}^{\mathrm{j}}(r) = \frac{Z_{\mathrm{j}}^2 e^2}{r} - \frac{2Z_{\mathrm{j}}^2 e^2}{\pi}\int_0^\infty F^{\mathrm{j}}(q)\frac{\sin(qr)}{qr}\mathrm{d}q \tag{5}$$

where

$$F^{\mathrm{j}}(q) = \left(\frac{\Omega_0 q^2}{4\pi Z_{\mathrm{j}} e^2}\right)^2 \frac{V_{\mathrm{b}}^{\mathrm{j}}(q)^2}{\varepsilon(q)} \frac{\chi_0(q)}{1 - 4\pi e^2 f(q)\chi_0(q)/q^2} \tag{6}$$

In Equation 6, the details of $V_{\mathrm{b}}^{\mathrm{j}}(q)$, $\varepsilon(q)$, $\chi_0(q)$ and $f(q)$ are the same as those in our previous work [1]. The dynamical matrix, $D^{\alpha\beta}(\boldsymbol{q})$, is given by

$$D^{\alpha\beta}(\boldsymbol{q}) = D_{\mathrm{ion}}^{\alpha\beta}(\boldsymbol{q}) + D_{\mathrm{el}}^{\alpha\beta}(\boldsymbol{q}) \tag{7}$$

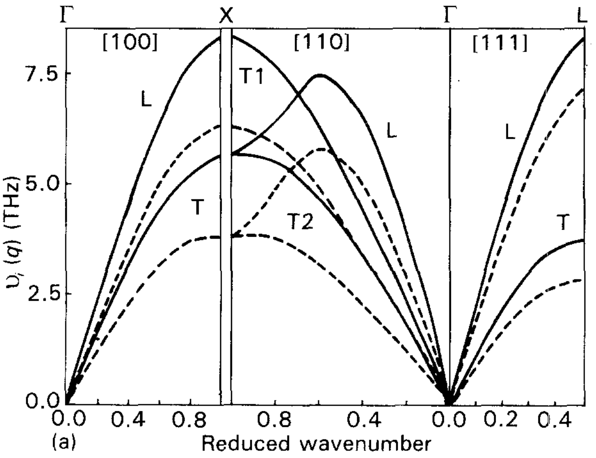
where $D_{\mathrm{ion}}^{\alpha\beta}(\boldsymbol{q})$ and $D_{\mathrm{el}}^{\alpha\beta}(\boldsymbol{q})$ are the contributions from the direct electrostatic interaction of ions and from the indirect two-body interaction of ions. The contribution $D_{\mathrm{ion}}^{\alpha\beta}(\boldsymbol{q})$ is obtained with Ewald's method given by

$$\begin{aligned} D_{\mathrm{ion}}^{\alpha\beta}(\boldsymbol{q}) &= \sum_{\boldsymbol{G}}(\boldsymbol{q} + \boldsymbol{G})_\alpha(\boldsymbol{q} + \boldsymbol{G})_\beta \frac{4\pi Z^2 e^2}{\Omega_0(\boldsymbol{q} + \boldsymbol{G})^2}\mathrm{e}^{-(\boldsymbol{q}+\boldsymbol{G})^2/4\eta} \\ &\quad - \sum_{\boldsymbol{r}_l \neq 0} Z^2 e^2 \mathrm{e}^{i\boldsymbol{q}\cdot\boldsymbol{r}_l}\left\{\frac{r_l^\alpha r_l^\beta}{r_l^5}\left[3\,\mathrm{erfc}\,(\eta^{1/2} r_l)\right.\right. \\ &\quad \left. + 6\left(\frac{\eta r_l^2}{\pi}\right)^{1/2}\mathrm{e}^{-\eta r_l^2} + 4\left(\frac{\eta^3 r_l^6}{\pi}\right)^{1/2}\mathrm{e}^{-\eta r^2}\right] \\ &\quad \left. - \frac{\delta_{\alpha,\beta}}{r_l^3}\left[\mathrm{erfc}\,(\eta^{1/2} r_l) + 2\left(\frac{\eta r_l^2}{\pi}\right)^{1/2}\mathrm{e}^{-\eta r_l^2}\right]\right\} \\ &\quad - \frac{4\pi Z^2 e^2}{3}\left(\frac{\eta}{\pi}\right)^{3/2}\delta_{\alpha,\beta} \end{aligned} \tag{8}$$

where η and $\mathrm{erfc}(\eta^{1/2} r_l)$ are a converging parameter and complementary error function, respectively. The contribution $D_{\mathrm{el}}^{\alpha\beta}(\boldsymbol{q})$ is given by

$$\begin{aligned} D_{\mathrm{el}}^{\alpha\beta}(\boldsymbol{q}) &= -\sum_{\boldsymbol{G}}(\boldsymbol{q} + \boldsymbol{G})_\alpha(\boldsymbol{q} + \boldsymbol{G})_\beta F(|\boldsymbol{q} + \boldsymbol{G}|) \\ &\quad + \sum_{\boldsymbol{G} \neq 0} G_\alpha G_\beta F(G) \end{aligned} \tag{9}$$

This simplified treatment for the lattice dynamics in Equation 2 has been applied to alkali alloy systems [8], and a few local and band mode frequencies of the $\mathrm{Rb}_{0.71} - \mathrm{K}_{0.29}$ alloy did not deviate quantitatively from those [7] of the coherent-potential approximation and by the molecular dynamics simulation. Using the equilibrium lattice constant, a_0[1], and the electron density, n, in Equation 1, we can show the phonon curves obtained for local (silicon or germanium) and band (aluminium) modes of $\mathrm{Al}_{0.85}\mathrm{Si}_{0.15}$ and $\mathrm{Al}_{0.85}\mathrm{Ge}_{0.15}$ alloys in Fig. 1a and b. In this figure and what follows, the results with the Vashishta–Singwi screening function [1] are given.



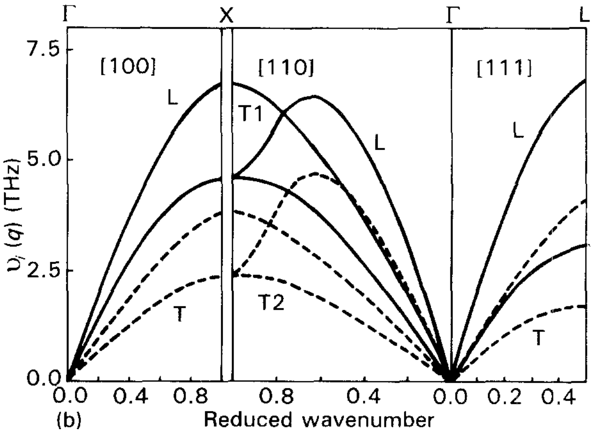


Figure 1 Calculated phonon dispersion relations for (– – –) local and (——) band modes for (a) $\mathrm{Al}_{0.85}\mathrm{Si}_{0.15}$ and (b) $\mathrm{Al}_{0.85}\mathrm{Ge}_{0.15}$ alloys.

Then, we give the calculated results for the concentration dependence of the local and band mode frequencies in the $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ alloy system in Fig. 2 representatively at X and L points. Our predicted phonon frequencies in Fig. 2 have a calculated accuracy $|\Delta\nu_i| \leqslant 0.1$ THz due to other screening functions [1]. From Fig. 2, our calculated data of $\nu_i(\boldsymbol{q})$ for matrix aluminium are in good agreement with experimental data [9].

3. Specific heat of Al–Si and Al–Ge alloy systems

Using the local $\nu_i^{\mathrm{Si\ or\ Ge}}(\boldsymbol{q})$ and band mode frequencies $\nu_i^{\mathrm{Al}}(\boldsymbol{q})$, we can express the energy contribution from the

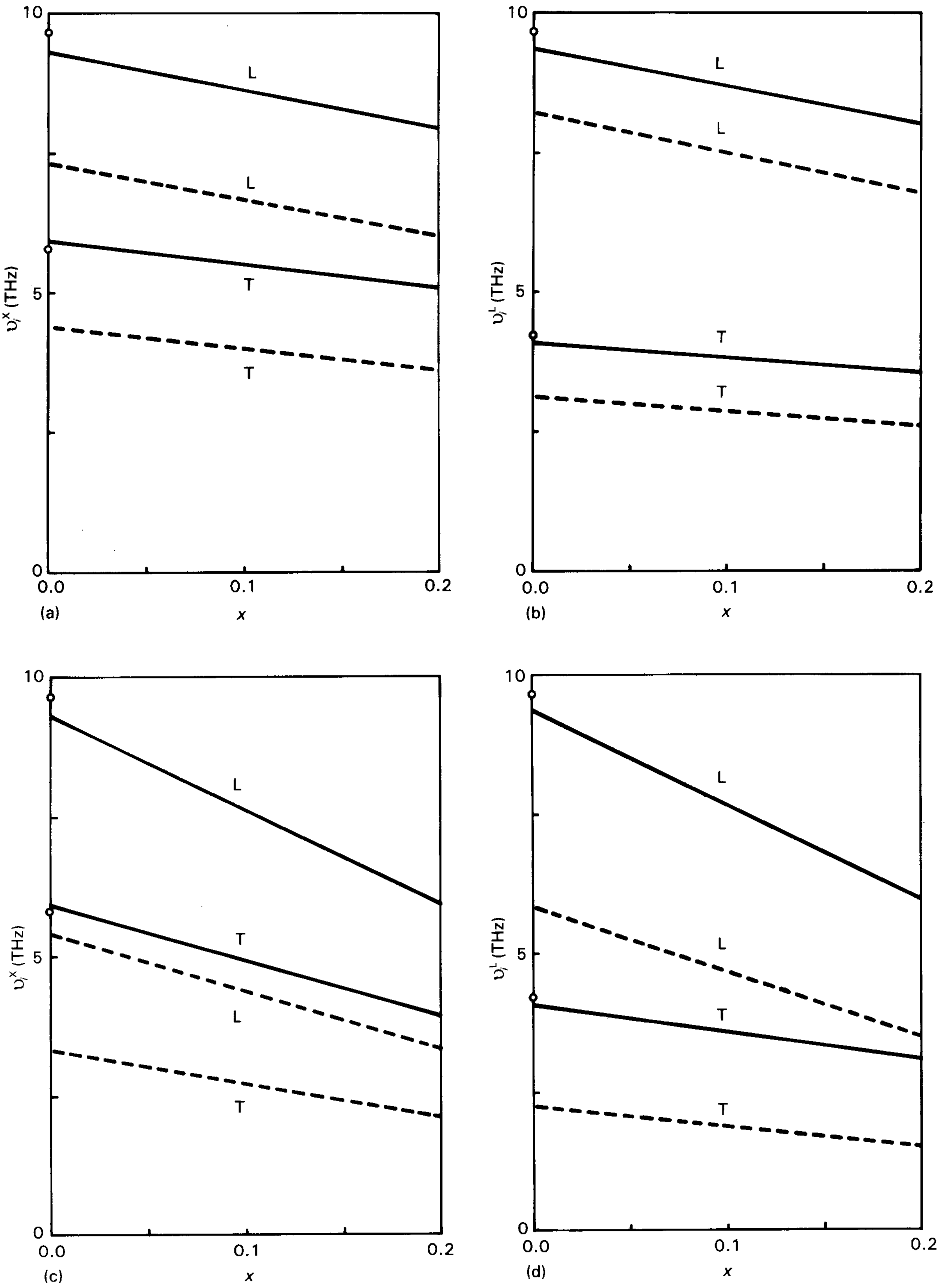


Figure 2 The concentration, x dependence of the (– – –) local and (——) band mode frequencies for (a, b) $Al_{1-x}Si_x$ and (c, d) $Al_{1-x}Ge_x$ alloys at X and L points. The points for matrix aluminium are the experimental data [9].

lattice vibrational term, U, for the solid solution $Al_{1-x}Si_x$ or $Al_{1-x}Ge_x$ as

$$U = (1-x)U^{\mathrm{Al}} + x\,U^{\mathrm{Si\ or\ Ge}} \tag{10}$$

where $U^{\mathrm{Si\ or\ Ge}}$ are contributions from local and band modes, and

$$U^{\mathrm{j}} = N\sum_{i,\boldsymbol{q}} h\nu_i^{\mathrm{j}}(\boldsymbol{q})\left\{\frac{1}{2} + \frac{1}{\exp[h\nu_i^{\mathrm{j}}(\boldsymbol{q})/kT] - 1}\right\}$$

$$\mathrm{j} = \mathrm{Al,\ Si\ or\ Ge} \tag{11}$$

Using Equations 10 and 11, the lattice specific heat at constant volume, C_v, is given by

$$C_v = (1-x)C^{\mathrm{Al}} + x\,C^{\mathrm{Si\ or\ Ge}} \tag{12}$$

where

$$C^{\mathrm{j}} = \sum_{i,\boldsymbol{q}} \frac{Nk(h\nu_i^{\mathrm{j}}(\boldsymbol{q})/kT)^2}{\{\exp[h\nu_i^{\mathrm{j}}(\boldsymbol{q})/kT] - 1\}^2}\exp(h\nu_i^{\mathrm{j}}(\boldsymbol{q})/kT) \tag{13}$$

The sums over $\boldsymbol{q}$ in Equations 12 and 13 are calculated by the following sampling method. Considering the symmetry of the irreducible 1/48th portion of the Brillouin zone, it is sufficient to determine the phonon frequencies in the range $\boldsymbol{q} = 2\pi(q_x, q_y, q_z)/(16a_0)$, where q_x, q_y, q_z are positive integers and satisfy the inequalities $0 \leqslant q_x \leqslant q_y \leqslant q_z \leqslant 8$ and $q_x + q_y + q_z \leqslant 12$. We show the predicted temperature dependence of the specific heat, C_v, for matrix aluminium in Fig. 3. In the harmonic approximation, C_v becomes $3Nk$ at high temperatures. Experimentally, C_v at high temperatures near the melting point, T_m, deviates from the constant value $3Nk$ [10]. This deviation is produced by the introduction of the anharmonic contributions from higher than cubic terms (for example, see [11]). At temperatures from low to about 850 K, we obtain good agreement of the calculated results of C_v for matrix aluminium with the observed data [10] in Fig. 3. Then, we can show the concentration, x, dependence of C_v for the $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ alloy systems at the representative temperatures 100 and 300 K as in Fig. 4a and b. The maximum deviation of specific heat, C_v, obtained in Fig. 4a and b is about ± 0.02 and $\pm 0.05\,\mathrm{J\,mol^{-1}}$

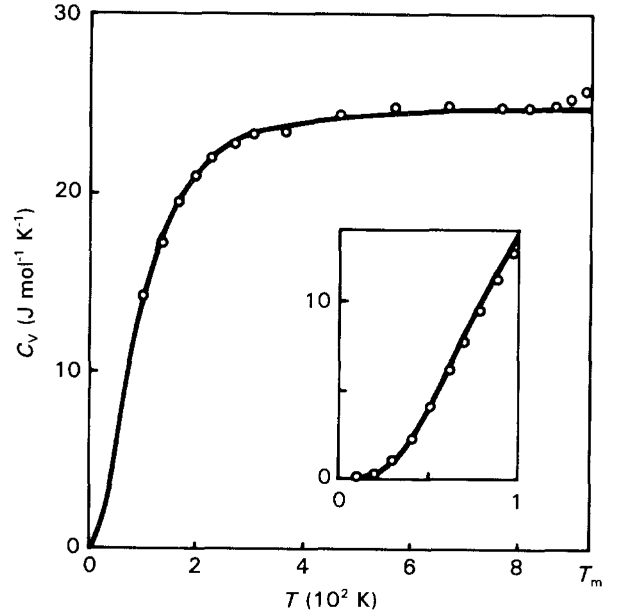


Figure 3 Specific heat at constant volume, C_v, versus temperature for matrix aluminium. The points are the observed data [10].

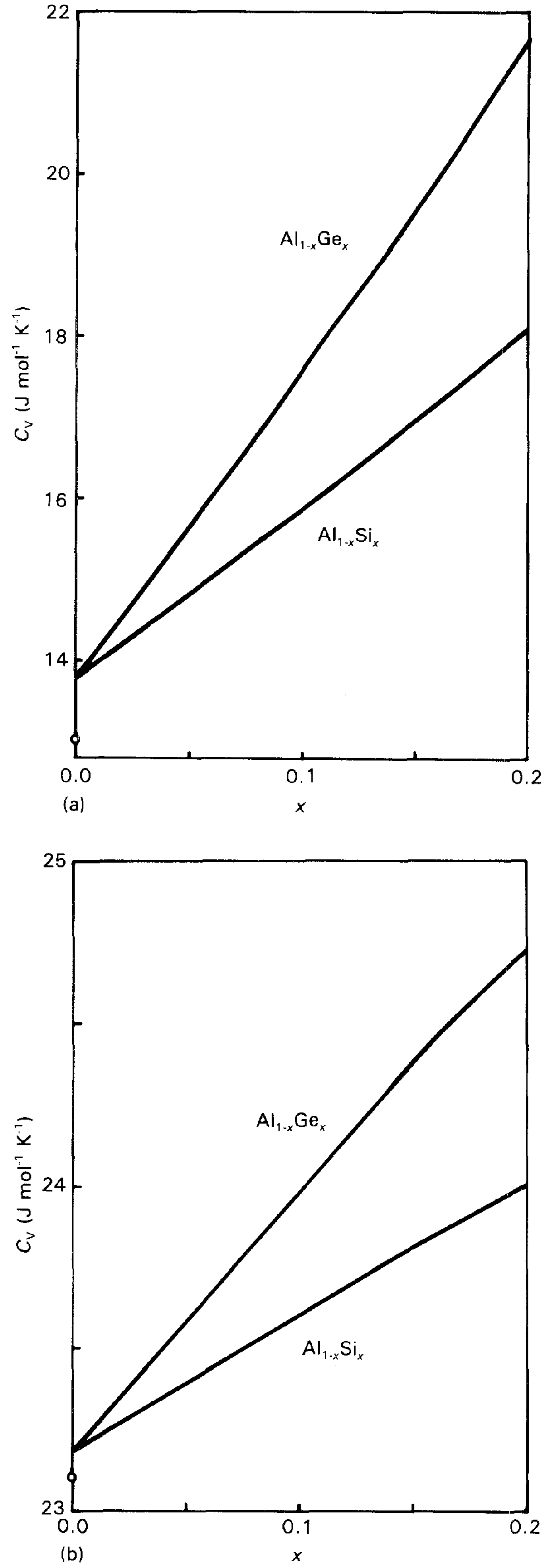


Figure 4 The concentration, x, dependence of the specific heat, C_v, for the $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ alloys at (a) 100 K and (b) 300 K. The points for matrix aluminium are the observed data [10].

K^{-1}. From Fig. 4a and b, we see that the obtained results of C_v for the $Al_{1-x}Si_x$ and $Al_{1-x}Ge_x$ alloy systems are monotonic functions of the atomic fraction, but show a non-linear dependence on x.

4. Conclusion

We have proposed a simplified treatment to study quantitatively the lattice dynamics of Al–Si and Al–Ge alloy systems. We have presented the numerical results of the concentration dependence of the local and band mode frequencies and the lattice specific heat. Our predicted data are useful in studying the thermal and anharmonic properties of these alloy systems, and we hope that there will be further experimental research in this field.

Acknowledgements

The authors thank Mr T. Itoh and Mr S. Nehashi for help in performing the preliminary calculations. The numerical calculations were carried out with ACOS-6 S2000 operating system in the Computer Centre of Tohoku University.

References

1. T. SOMA, Y. FUNAYAMA and H.-MATSUO KAGATA, *J. Mater. Sci.* **25** (1990) 3917.
2. T. SOMA, S. TAKASHIMA and H.-MATSUO KAGAYA, *ibid.* **27** (1992) 1184.
3. M. MOSTOLLER and T. KAPLAN, *Phys. Rev. B* **16** (1977) 2350.
4. W. A. KAMITAKAHARA and J. R. D. COPLEY, *ibid.* **18** (1978) 3772.
5. G. GRÜNEWALD and R. SCHOPOHL, *J. Phys. F* **9** (1979) 1047.
6. G. JACUCCI, M. L. KLEIN and R. TAYLOR, *Solid State Commun.* **24** (1977) 685.
7. *idem, Phys. Rev. B* **18** (1978) 3782.
8. T. SOMA, H. OHSUGI and H.-MATSUO KAGAYA, *Phys. Status Solidi* (*b*) **124** (1984) 525.
9. R. STEDMAN and G. NILSON, *Phys. Rev.* **145** (1966) 492.
10. Y. S. TOULOUKIAN, R. K. KIRBY, R. E. TAYLOR and T. Y. R. LEE, "Thermophysical Properties of Matter, Vol. 4, Specific Heat" (IFI/Plenum, New York, 1970).
11. P. C. TRIVEDI, *J. Phys. F.* **1** (1971) 262.

Received 10 April 1992
and accepted 14 June 1993