On the specific heat of Al–Si and Al–Ge alloys—A simulation study

P MURUGAN and K RAMACHANDRAN*

Department of Theoretical Physics, Madurai Kamaraj University, Madurai 625 021, India

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Abstract. The large variation in specific heats with concentration between temperatures 50 K and 200 K for Al–Si and Al–Ge alloys are analysed in detail by lattice dynamical and Monte Carlo approaches. The large deviation from linearity at low temperatures does not seem to be due to the Debye's low temperature contribution. It is shown that an anharmonic vibration in the above solid solutions, particularly at 200 K, is the cause for the small variation in the specific heat.

Keywords. Specific heat; lattice vibration; localized modes; anharmonic lattice mode; band modes; normal modes; simulation; Monte Carlo.

1. Introduction

The study on specific heats of alloys by experiments and theory is not new. When such solid solutions are formed, the localized or resonant vibrational modes also contribute to the specific heats. Recently, Soma *et al* (1994) have presented a simplified treatment for Al–Si and Al–Ge alloys where the lattice vibration of Al, Si or Ge atoms are replaced with those of pure Al, fcc Si or fcc Ge crystals, having the lattice constant and electron density of the alloy. They have also obtained the phonon dispersion curves of the local and band modes for $\text{Al}_{0.9}\text{Si}_{0.1}$ and $\text{Al}_{0.9}\text{Ge}_{0.1}$ along with their concentration dependences. Employing these results, the variation of specific heat with temperature for these alloys are obtained.

The interesting results of the investigations in these alloys are (i) the variation of the specific heat with concentration (x) is monotonic and (ii) the deviation at low temperature, from linearity, is quite large.

In general, the variation of specific heats in the low temperature region would obey the Debye- T^3 law and hence it will deviate from the linear variation. However, according to Soma *et al* (1994) such large deviations are related to the unusual variation in the slope of the graph, compared to specific heats at high temperatures.

Unified theoretical approach for the estimation of local or band mode is not available in literature and the computations of the thermal properties of these solid solutions, from first principles is available mainly to $\text{Rb}_{1-x}\text{K}_x$ systems.

In general, two treatments are available in the literature for such $\text{Rb}_{1-x}\text{K}_x$ alloys: (i) coherent potential approxi-

mation (Janucci *et al* 1977) and (ii) computer simulation in molecular dynamics (Janucci *et al* 1978).

We present a simple lattice dynamical approach and a Monte Carlo simulation for the evaluation of specific heat variation with temperature and concentration for the alloys Al–Si and Al–Ge, with a view to examine the wide variation in the low temperature region.

This study is motivated by the fact that an increase in solid solubility of Si and Ge in Al has been observed under pressure by rapid quenching from liquid state (Mii *et al* 1976), and the physical properties of Al–Si and Al–Ge systems form an interesting subject.

2. Lattice dynamical study

The aim of this investigation is to study the specific heat variation with temperature for the alloys. The specific heat can be computed from Maradudin *et al* (1971)

$$C_v = 3R \frac{\int \frac{g(\omega) y^2 \exp(y) d\omega}{[\exp(y) - 1]^2}}{\int g(\omega) d\omega}, \quad (1)$$

where $y = \hbar\omega/kT$, $g(\omega)$ is the number of phonons having the phonon frequencies between ω and $\omega + d\omega$ and R the universal gas constant.

The phonons for Al, Si and Ge are worked out employing the shell model (Woods *et al* 1960). The parameters have been worked out from the elastic constants, zone centre frequencies and polarizabilities and are available for Al, Si and Ge. These parameters are given in table 1.

The phonons are obtained by solving the dynamical matrix $D_{\alpha\beta}$, taking into account the long range and the

*Author for correspondence

short range interactions extending upto the second nearest neighbours

$$|D_{\alpha\beta}(q, k) - \alpha_j^2(q, k)\delta_{\alpha\beta}| = 0, \quad (2)$$

where α and β are the directions, j the branch index.

The phonon dispersion curves obtained in this study agree well with the experimental results. The frequency distribution $g(\omega)$ is plotted and the specific heats are now calculated using (1) for various temperatures. The results are presented in figure 1 for Al, Si and Ge.

So far the calculations have only been for the individual systems of Al, Si or Ge, and the contribution of the defect modes resulting from the formation of the alloy such as $\text{Al}_{0.9}\text{Si}_{0.1}$, will now be analysed. Two methods are considered to study the contribution of defect modes for the specific heats, when alloys Al-Si or Al-Ge are formed.

2.1 Virtual crystal approximation

When a solid solution $\text{Al}_{1-x}\text{Si}_x$ is formed, the effective dynamic matrix is constructed from the effective parameters which are obtained from Vegard's Law, as

$$A_{\text{Al-Si}} = (1-x)A_{\text{Al}} + xA_{\text{Si}}, \quad (3)$$

for the Kellermann's A. Similarly, all the other parameters are worked out to evaluate the phonon frequencies from (2).

Following the usual procedure, the specific heats are obtained for $\text{Al}_{1-x}\text{Si}_x$, using (1), for various temperatures and concentrations from 0 to 0.2 in step of 0.05. The results are presented in table 2 along with the available experimental values.

2.2 Contribution from the defect modes (molecular model)

The alternative method of looking at the contribution of alloying to the specific heat is to work out the defect modes, treating Si as a mass defect in the Al molecule. The molecular model of Jaswal (1965) is followed and the parameters used in the construction of dynamical matrix

are given in table 3. The nearest neighbour environment of Al-Si in the lattice is shown in figure 2.

On solving the dynamical matrix and analysing the displacements and eigen values of the host and defect atoms, the localized modes are identified. Such defect modes are 217 cm^{-1} and 200 cm^{-1} for $x = 0.1$ and 0.2 , respectively, which compare well with results of Soma *et al* (1994). Similar results for Al-Ge alloy are 207 cm^{-1} and 182 cm^{-1} for $x = 0.1$ and 0.2 .

The contribution of these defect modes to the specific heats can be worked out again from,

$$C_v = k_B \sum_{kj} y^2(kj) \frac{\exp(y(kj))}{[\exp(y(kj)) - 1]^2}, \quad (4)$$

Figure 1. Specific heat vs temperature for pure Al, fcc Si and fcc Ge from two approaches along with experimental values of Stedman *et al* (1967), Heish (1954). (MC, Monte Carlo method and LD, lattice dynamical method).

Table 2. Specific heat (in units of $\text{J K}^{-1}\text{mol}^{-1}$) for different concentrations (x) and for different temperatures for Al-Si and Al-Ge alloys (virtual crystal approximation).

Table 1. Shell model parameters.

Parameter	Al	Si	Ge	Unit
e^2/V	1.38	0.5718	0.5088	10^4 dyne/cm
A	6.08	43.61	41.94	e^2/V units
B	1.50	4.5	4.21	e^2/V units
A_1	-0.76	-3.05	-2.05	e^2/V units
B_1	-0.07	-0.3	-0.2	e^2/V units
A_2	-0.76	-3.05	-2.05	e^2/V units
B_2	-0.07	-0.3	-0.2	e^2/V units
Z	0.02	0.2	0.2	e
α_1/V	-0.065	-0.07	-0.07	-
α_2/V	-0.41	-0.187	-0.184	-
d_1	-0.09	-0.05	-0.06	e
d_2	0.54	0.14	0.16	e

Concentration (x)	Temperature		
	50 K	100 K	200 K
<i>(Al-Si alloy system)</i>			
0.0	3.54(3.74)	10.98(12.78)	19.30(20.81)
0.1	3.44(3.54)	10.54(12.12)	18.83(20.08)
0.2	3.34(3.35)	10.11(11.45)	18.35(19.35)
<i>(Al-Ge alloy system)</i>			
0.0	3.54(3.74)	10.98(12.78)	19.30(20.81)
0.1	3.65(3.86)	11.10(12.68)	19.37
0.2	3.76(3.98)	11.22(12.58)	19.43

Experimental values (obtained from Stedman *et al* (1967), Heish (1954)) are shown within brackets.

where $y(kj) = \hbar\omega(kj)/k_B T$ for all kj values. The cumulative effect of this contribution to the specific heat of $(1-x)$ of Al, is given in table 2, for which a graph is also drawn connecting specific heat and concentration. The slopes for temperatures 50 K and 200 K are evaluated from this graph, which are 1.1 and 0.65, respectively (for Al-Ge alloy). This indicates the variation in 50 K is large compared to 200 K (from linearity).

This deviation can be due to (i) anharmonic contributions to the specific heats of the alloys leading to the small variation around 200 K and (ii) Debye- T^3 law contributing to the large deviation around 50 K.

Detailed studies on these two aspects are not available in the literature and hence, we analyse the specific heats of alloys using simulation techniques.

3. Monte Carlo and anharmonic lattice dynamics results

Monte Carlo (MC) and anharmonic lattice dynamics (λ^2 and λ^4 perturbation theory, PT) calculations of the thermodynamic properties of Xe have been reported by Shukla *et al* (1992) for a fcc crystal. They have calculated the specific heats, volume expansion, Gruneisen parameter etc and the agreement with MC is good. Similarly they have also estimated the mean square displacement (MSD) and the agreement is found to be good with λ^2 perturbation theory.

In order to see whether the specific heat variation with x , for $\text{Al}_{1-x}\text{Si}_x$ is low at 200 K, a MC simulation is carried out for these alloys taking the anharmonic interactions into account.

3.1 Theory

The specific heat capacity at constant volume is calculated using the fluctuation theory applied to a thermodynamical quantity. For a canonical ensemble the partition function is defined as

$$Z = \sum_n \exp(-U_n/kT). \quad (5)$$

Table 3. Molecular model parameters for Al-Si and Al-Ge alloy.

Parameter	$\text{Al}_{1-x}\text{Si}_x$		$\text{Al}_{1-x}\text{Ge}_x$		Unit
	$x = 0.1$	$x = 0.2$	$x = 0.1$	$x = 0.2$	
$e^2/2$ V	0.6349	0.5746	0.617	0.552	10^4 dyne/cm
Z_{Al}	0.75	0.45	0.80	0.45	e
$Z_{\text{Si(Ge)}}$	-0.25	-0.15	-0.27	-0.27	e
$A_{\text{Al-Al}}$	7.462	7.462	7.462	7.462	10^4 dyne/cm
$B_{\text{Al-Al}}$	0.727	0.727	0.727	0.727	10^4 dyne/cm
$A_{\text{Al-Si(Ge)}}$	7.594	7.725	7.496	7.529	10^4 dyne/cm
$B_{\text{Al-Si(Ge)}}$	0.744	0.761	0.730	0.720	10^4 dyne/cm

The mean energy is

$$\langle U \rangle = \frac{\sum_n U_n \exp(-U_n/kT)}{\sum_n \exp(-U_n/kT)}. \quad (6)$$

Then differentiating the mean energy with respect to temperature and rearranging the terms, we get the specific heat equation

$$\left(\frac{\partial U}{\partial T} \right)_{n,v} = C_v = \frac{\langle (\delta U)^2 \rangle}{k_B T^2}. \quad (7)$$

The potential energy U of the solid is written as the sum of pair potential ϕ :

$$U = \frac{1}{2} \sum_{i \neq j} \phi(r_{ij}), \quad (8)$$

where ϕ is chosen to be Morse potential, ϕ_m . It is true that there will be many body interaction, when there are 256 atoms considered, particularly when conventional lattice dynamical calculations are carried out. But in Monte Carlo simulation technique, where we would not calculate the phonons, the random walk principle is in built. So, Heisenberg or Ising models that are found to be most successful even for molecules and clusters (Binder 1987) use only pair wise interaction. Also, here in our present work, a simple MC technique is aimed and so it is restricted to only pair wise interaction.

$$\phi_m = \epsilon \{ \exp[-2\alpha(r - r_0)] - 2\exp[-\alpha(r - r_0)] \}, \quad (9)$$

where the parameters ϵ , and α can be determined from the experimental values of sublimation energy (L) and bulk modulus (B_T) from

Figure 2. Nearest neighbour, T_d symmetry for $\text{Al}_{1-x}\text{Si}_x$.

$$\varepsilon = U/6N, \quad (10)$$

where ε values are 9.065×10^{-20} J, 12.517×10^{-20} J and 10.672×10^{-20} J for Al, Si and Ge, respectively

$$\alpha = \left(\frac{9B_T r_0}{2\varepsilon} \right)^{1/2}, \quad (11)$$

where r_0 is the lattice constant at equilibrium. The α values are $3.285 \text{ \AA}^{-1}$, $4.023 \text{ \AA}^{-1}$ and $3.972 \text{ \AA}^{-1}$ for Al, Si and Ge, respectively. The specific heat at constant volume, C_v (in terms of R , universal gas constant) is calculated from the fluctuations in the potential energy

$$C_v = \frac{\langle (\delta U)^2 \rangle}{N(k_B T)^2}, \quad (12)$$

where N = number of atoms in the system.

$$\delta U = U - \langle U \rangle, \quad (13)$$

k_B = Boltzmann constant.

3.2 Simulation

To start with simulation is performed for pure Al by considering 256 particle-clusters with periodic boundary conditions using Metropolis algorithm (Metropolis *et al* 1953). The starting configuration is fcc. The positions of pure Al atoms are defined in the three-dimensional co-ordinate system where

$$\vec{r} = \frac{(j+k)}{2} \hat{x} + \frac{(i+k)}{2} \hat{y} + \frac{(i+j)}{2} \hat{z}. \quad (14)$$

For the alloy system, the impurity atoms (Si or Ge) randomly occupy position of pure atoms as isotopic substitution. So, the nearest neighbour distance between the pure atom and impurity atoms are relaxed. The new position of each atom in the alloy system is calculated from the relaxation.

Displacements of the particles from their corresponding fcc positions are computed in the following way. Six random numbers distributed uniformly in the range $\{0, 1\}$ are chosen. The first three random numbers are used to fix the direction of movement. By suitably making three random numbers to 1, 2 and 3, the x , y and z directions are identified.

Having fixed the direction of jumps (which necessitates the updation), then the other three random numbers are used to update the magnitude of the displacement. For example, r_{AB} is the minimum distance between particles A and B (nearest neighbour distance) as the shortest distance between A and any of the particles B.

If the positions of the 256 particles in the lattice are known, the potential energy of the system is computed

from (8). Now, the equilibrium value of any quantity F is

$$\langle F \rangle = \frac{\int F \exp(-U/k_B T) dp^{3N} dq^{3N}}{\int \exp(-U/k_B T) dp^{3N} dq^{3N}}. \quad (15)$$

The MC method of many dimensional integral consists simply of integrating over a random sampling of points instead of over a regular array (Sobol 1975). Hence, to carry out the integration, the N particles would be put in the random position.

To achieve this, the N particles are placed in fcc configuration first, and then, each of the particles are moved in succession according to

$$\begin{aligned} X &\rightarrow X + \eta \xi_1, \\ Y &\rightarrow Y + \eta \xi_2, \\ Z &\rightarrow Z + \eta \xi_3, \end{aligned} \quad (16)$$

where η is the maximum allowed displacement, which is arbitrary and ξ s are the random numbers, which are generated.

Thus the three random numbers generated are used to update the position of the atoms. After updating the positions the change in energy ΔU , due to the motion is computed. If the motion brings the system to lower energy, we allow this motion as successful; otherwise, it is a failure, i.e. if $\xi_1 < \exp(-\Delta U/k_B T)$, this is allowed and the particle is moved to the new position, whereas if $\xi_1 \geq \exp(-\Delta U/k_B T)$, we return to the old positions.

So now

$$\langle F \rangle = \frac{1}{M} \sum_1^M F_j, \quad (17)$$

where F_j is the value of the property F of the system after the j moves.

The maximum allowed displacement in a given trial is chosen to keep the fraction of successful moves at around 25% for temperature 50 K. (However, Shukla *et al* (1992) have reported maximum allowed displacement as 50% for Xe system at temperatures 60–100 K). For higher temperatures maximum displacement can be increased to around 50% of nearest neighbour distance.

Potential energy is calculated using (9) for the first neighbours only. Canonical averages are calculated for 10,000 further configurations, following success/failure of the jumps and then the specific heats are calculated.

Similarly, for each temperature, the lattice parameter is varied slowly so that the pressure within that volume approaches zero. Then, the corresponding lattice parameter is used for further calculations of the thermodynamic properties.

Simulation results of specific heats for Al compare well with the experimental results (figure 1), and hence, the simulation of specific heats for alloys is attempted.

Sublimation energy and bulk modulus of alloy, for example $\text{Al}_{0.9}\text{Si}_{0.1}$, are obtained from the value of Al and Si using Vegard's law for various temperatures.

Recently, De Caro *et al* (1998) have analysed the validity of Vegard's rule for the lattice parameter and stiffness constant ratios of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ternary compounds by making experimental observations using high resolution X-ray diffraction technique. They have analysed this from concentration $x = 0.0$ to 0.5 . In all cases, the Vegard's rule and the experimental observations agree very well with in the accuracy of the measurements. This prompts us to use Vegard's rule in the modeling and simulation of alloy properties.

The same procedure used for the simulation of pure system (Al), is followed with the new set of parameters for $\text{Al}_{1-x}\text{Si}_x$ and $\text{Al}_{1-x}\text{Ge}_x$ alloys for various temperatures and concentrations.

Figure 3. Specific heat vs concentration for Al-Si (a) and Al-Ge (b) alloys have been reported here (Monte Carlo simulation method (solid line) along with the experimental values (full circle), from Stedman *et al* (1967), Heish (1954)) (Specific heats have been deduced from Vegard's law).

4. Results and discussions

The results obtained from the MC simulation explain most of the observed properties of the specific heat versus concentration and temperature graphs of the alloys.

(I) Variation of specific heat with concentration (up to $x = 0.2$) for temperatures 50 K and 200 K are monotonic (figures 3a-b) whereas below 50 K the variation is not monotonic (figure 4) i.e in figure (4), the variation of specific heat with concentration for temperatures 20, 30 K are drawn. The variations in these temperatures are not so linear compared to 50 K where it is almost a straight line. This is in agreement with the observations of Soma *et al* (1994).

(II) When the variation for 200 K and 50 K are analysed in terms of the slopes, for steepness, they are found to be 0.148 and 0.927, respectively. There is qualitative agreement with the observation of Soma *et al* (1994), even though there is slight variation in magnitudes.

(III) Because MC results on specific heat for alloys are compared with the results of Soma *et al* (1994), it is necessary to study the agreement of pure Al with experimental results (Heish 1954; Stedman *et al* 1967). These are given in figure 1 for temperatures 50 K and 200 K, along with the experimental values.

The MC results agree very well with the experiment of Soma *et al* (1994), particularly for 50 K, justifying the qualitative agreement with results of Soma *et al* (1994).

(IV) Even though Soma *et al* (1994) have claimed that the deviation from linearity is large at 50 K, this MC simulation could reproduce that fact even at temperatures below 50 K.

Figure 4. Specific heat vs concentration for Al-Si alloy for temperature from 20 K to 50 K with various concentrations (x), calculated from Monte Carlo simulation, showing that below 50 K, specific heat has not monotonically increased with concentration.

(V) In order to investigate whether Debye- T^3 law dominates the behaviour of the alloys at 50 K, a study is made on pure Al and Si separately for low temperatures (figure 1). Even though, Debye's contribution is dominant below 50 K for Al-Si alloy, at temperatures 50 K and above, it is not dominant as could be seen from figures 3a-b.

(VI) For the first time, simulation of specific heats for these alloys with our simple model could satisfactorily explain behaviour of the alloys.

Our results clearly demonstrate that at 50 K variation (in terms of slopes) of specific heat is large compared to 200 K and this variation is not due to Debye's low temperature contribution.

Similarly when simulation with anharmonicity is considered, certainly there is a small variation at 200 K, compared to 50 K, but quantitatively in disagreement with Soma *et al* (1994). Since the Debye temperatures, θ_D (at room temperature) of Al, Si and Ge are 400, 570 and 300 K respectively, for the alloys $Al_{0.9}Si_{0.1}$ or $Al_{0.9}Ge_{0.1}$ they should be around 400 K. So, the contribution from anharmonicity is expected to be minimal for 200 K. Further investigations are in progress to refine the model for simulation and, to identify the exact mechanism behind such unusual variation in Al-Si and Al-Ge alloys.

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