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## A calculation of the low-temperature lattice specific heat of very dilute Al–Li alloys

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**Abstract.** The low-temperature lattice specific heat of very dilute FCC Al–Li alloys has been studied by applying the Green function method to an isolated substitutional Li impurity. The specific heat is very sensitive to force constant changes induced by the defect. It is observed that the contribution of the  $T_{1u}$  mode is not preponderant. We include the effect of the second neighbours of the Li atom.

### 1. Introduction

In recent years, several quantitative studies have been made of the Al–Li alloys using various pseudopotential theories [1–3] or the KKR method [4]. Although many characteristic properties, such as heat of formation, volume change and elastic moduli, have been calculated, it seems that no attempt has been made so far to determine the change  $\Delta C_v$  in the lattice specific heat for Al due to the introduction of an isolated substitutional Li atom. It is the object of this paper to report this change, for the Al–Li FCC phase (stable to about 5 at. % Li at room temperature).

### 2. Method

$\Delta C_v$  and the change in other thermodynamic properties of Al are easily determined once we know  $\Delta N(\omega^2)$ , the change in the density of states in phonons as a function of the squared frequency  $\omega^2$  [5].

The method used to calculate  $\Delta N(\omega^2)$  has been explained in detail by Tiwari *et al* [6] and will only be briefly recalled here.

If  $G_0(\omega^2)$  is the Green function matrix of the host crystal, then  $\Delta N(\omega^2)$  depends only on the complex determinant  $D(z) = \det[\mathbf{I} + G_0(z)\mathbf{P}(\omega^2)]$ , where  $\mathbf{P}(\omega^2)$  represents the perturbation matrix and  $z = \omega^2 + i\varepsilon$ :  $\Delta N(\omega^2) = -(1/\pi) \text{Im}\{(d/d\omega^2)\log[D(z)]\}$ . Call  $n$  the number of host sites perturbed by the impurity;  $\mathbf{P}(\omega^2)$  is only of dimension  $3n$ . Here  $3n$  will be equal to 39 when we include in  $\mathbf{P}(\omega^2)$  the change in mass and the change in force constants between the impurity site and its nearest neighbours (model 1); it will be 57 when we take the next-nearest neighbours into account (model 2). For a light impurity such as Li in Al, one finds out-of-band modes from the condition  $\text{Re}[D(z)] = 0$ . Group theory allows a further reduction in the dimension of the problem;

here the symmetry is  $O_h$  and the representation  $\Gamma$  of  $\mathbf{P}(\omega^2)$  is:

$$\Gamma = A_{1g} + A_{2g} + A_{2u} + E_u + 2(E_g + T_{1g} + T_{2g} + T_{2u}) + 4T_{1u} \quad \text{for model 1}$$

$$\Gamma = 2A_{1g} + A_{2g} + A_{2u} + E_u + 3(E_g + T_{1g} + T_{2g} + T_{2u}) + 6T_{1u} \quad \text{for model 2.}$$

Then

$$D(z) = \pi_\nu D_\nu(z)$$

$$\Delta N(\omega^2) = \sum_\nu \Delta N_\nu(\omega^2) \quad \Delta N_\nu(\omega^2) = -(1/\pi) \text{Im}\{(d/d\omega^2) \log[D_\nu(z)]\}$$

where  $\nu$  is an irreducible representation.

For model 1 (nearest neighbours only) the independent elements  $g_\mu(\omega^2)$  ( $\mu = 1-13$ ) of  $G_0(\omega^2)$  may be found from [7] and have been used in [6]; it is easily found that for model 2 there are 19 independent  $g_\mu$ .

To calculate the perturbation matrix  $\mathbf{P}(\omega^2)$  we need the radial force constants  $K_r$  and the tangential force constants  $K_t$  for Al-Al and for Al-Li. We derive them from the corresponding pair potentials computed with the model semilocal pseudopotential of Rasolt and Taylor [8].

The Al-Al pair potential has been given before and found to generate phonon frequencies in very good agreement with the experimental values [9], although other pair potentials differing from this in a quite significant manner, particularly in the first minimum region, may be found in the literature [2, 10, 11].

Figure 1 displays both the Al-Al and the Al-Li pair potentials computed with the standard parameters in [9] ( $r_s = 2.069$  a.u.;  $a = 4.033$  Å). This Al-Li pair potential has not been reported before and, because of the strong variations in electronic density around Li, it is not obvious that the second-order theory used here is adequate. Lu and Carlsson [2] have recently proposed a method to take the local-density variations into account; their local-density correction is found to be weak and smooth for Al-Li as well as Al-Al so that our pair potentials may be expected to give reasonable force constants.

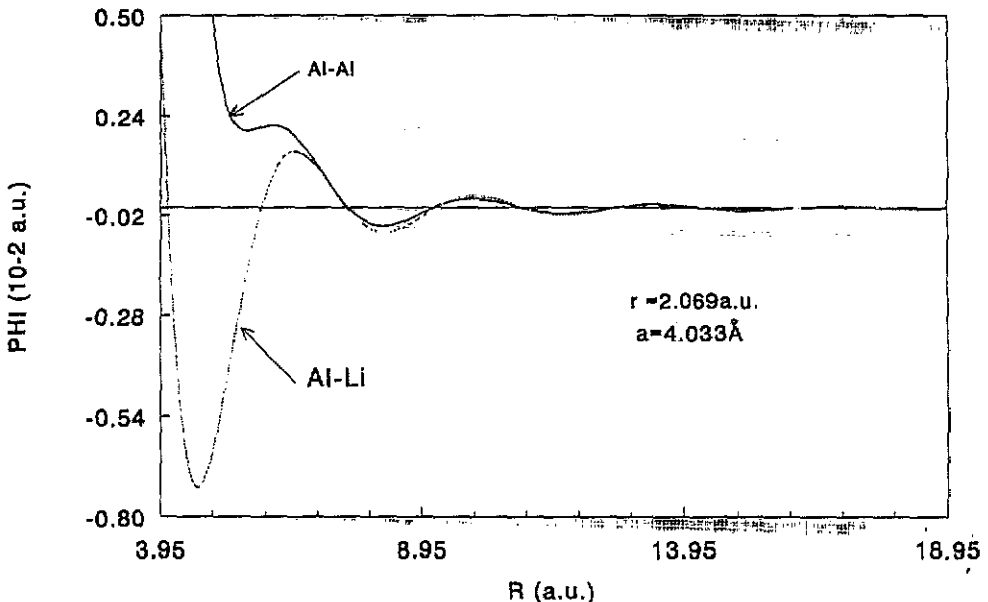


Figure 1. Interatomic pair potentials.

### 3. Computations and results

To obtain the density of states (DOS) of pure Al, the total in-band frequency range (maximum frequency  $\omega_m = 311 \text{ cm}^{-1}$ ) is divided into 600 equal bins for the computation of the Green functions  $g$ . The DOS of Al in the middle of these bins converges slowly with increasing number of sampling  $k$ -points in the first Brillouin zone, and with the number  $K_r$  and  $K_i$  of included force constants. The final calculations were carried out with 20 neighbouring shells and 43 860 points uniformly distributed (with appropriate weights) in the irreducible Brillouin zone.

The distortion induced by the defect is assumed to be restricted to the first-neighbour shell. We compute the change in the potential energy of a set of 20 neighbouring shells around the defect when we relax the first Al-Li distance. The minimum is found for a  $\Delta R/R = -1.25\%$  shrinkage in good agreement with other estimations [1, 12].

Figure 2 shows  $\Delta C_v$  as a function of temperature for model 1 (one perturbed shell) and model 2 (two perturbed shells). We neglect the global change in volume (less than 0.3% for a Li concentration of up to 15%) and keep the same pair potential for Al-Li. The results for  $\Delta R/R = 0\%$  are displayed in figure 3, and those for  $\Delta R/R = -2\%$  in figure 4 to show the influence of the relaxation in our model. We present in figure 3 the results for the mass-defect-only model; we see that this latter model is inadequate, while the first two models give very close numbers. In figure 4, owing to strong variations in  $K_r$  and  $K_i$  for the interactions between the first and second Al shells, the results for case 1 and case 2 now deviate strongly. We assess that the parameters used in this computation give rise to an error of 1% in  $\Delta C_v$  in each model since the force constants are sensitive to changes in the pseudopotential.

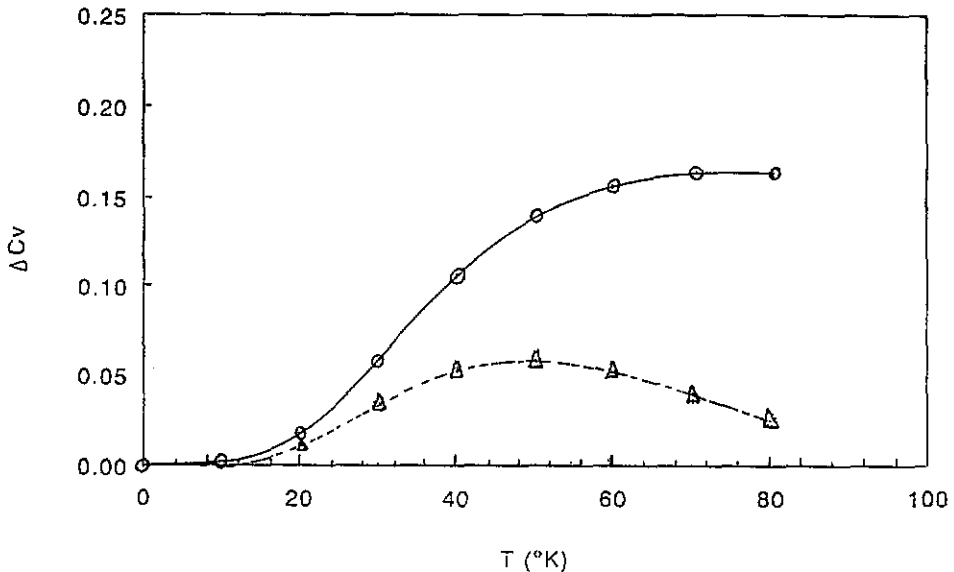


Figure 2. Enhanced lattice specific heat  $\Delta C_v$  for one Li impurity atom for  $\Delta R/R = -1.25\%$  in units of  $10^{-19}$  millijoules per kelvin per atom: ○, first-neighbour model; △, first- and second-neighbour model.

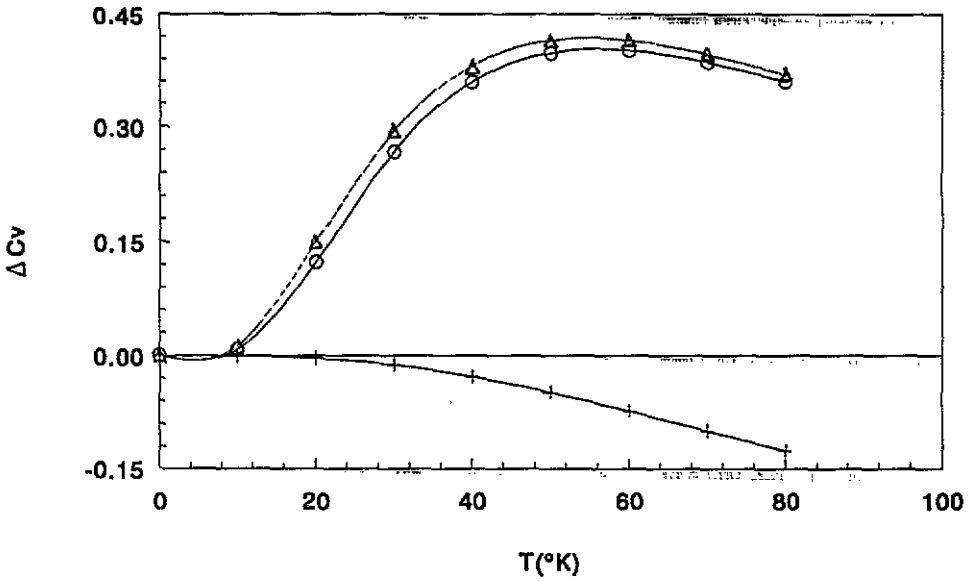


Figure 3.  $\Delta C_v$  for  $\Delta R/R = 0\%$  using the same conventions as in figure 2: +, defect-mass-only model.

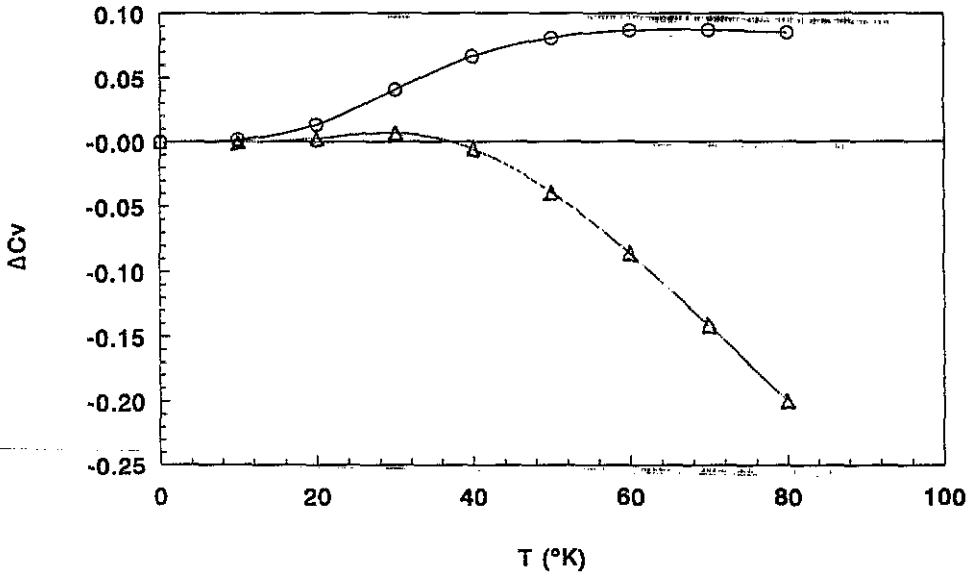


Figure 4.  $\Delta C_v$  for  $\Delta R/R = -2\%$  using the same conventions as in figure 2.

**Table 1.** Contribution of the irreducible representation to  $\Delta C_v$  for  $\Delta R/R = -1.25\%$  for the first- and second-neighbour model.

<i>T</i> (K)	Contribution to $\Delta C_v$ ( $10^{-19}$ mJ K <sup>-1</sup> /atom)					
	$T_{1u}$	$T_{2u}$	$T_{2g}$	$E_g$	$T_{1g}$	$A_{2u}$
10	-0.000 52	+0.000 10	+0.001 09	+0.000 70	-0.000 47	-0.000 02
20	-0.002 77	+0.003 86	+0.007 65	+0.004 49	-0.002 50	-0.000 34
30	-0.006 27	+0.019 43	+0.019 03	+0.013 71	-0.007 35	-0.001 33
40	-0.008 82	+0.036 89	+0.027 93	+0.023 08	-0.014 49	-0.003 01
50	-0.008 75	+0.047 01	+0.030 85	+0.028 20	-0.021 15	-0.005 75
60	-0.006 95	+0.050 09	+0.029 02	+0.029 21	-0.025 70	-0.010 11
70	-0.004 96	+0.048 89	+0.024 82	+0.027 74	-0.028 01	-0.016 17
80	-0.003 67	+0.045 64	+0.019 99	+0.025 17	-0.028 59	-0.023 52

#### 4. Conclusions

We may draw the following conclusions.

(1) The second neighbours should be included in the perturbation matrix, contrary to what has been done in previous similar studies. For the most reliable results (model 2;  $\Delta R/R = -1.25\%$ ; figure 3) we find all the irreducible representations to have comparable contributions to  $\Delta C_v$  (table 1), i.e.  $T_{1u}$ , the mode of the Li atom displacements, is not preponderant. Also we find one local mode to be of symmetry  $A_{2u}$ ; this local mode occurs at  $314 \text{ cm}^{-1}$ , very close to  $\omega_m$ , and vanishes into the continuum or shows up in other symmetries in the other cases treated here.

(2) The low-temperature Al lattice specific heat is enhanced by Li for a zero or 1.25% contraction but is almost unaffected ( $T < 40 \text{ K}$ ) and then decreased ( $T > 40 \text{ K}$ ) for a 2% contraction. This hopefully might help the interpretation of the at present lacking experimental measurements of  $\Delta C_v$  for very dilute alloys where the individual contributions of Li impurity atoms may be considered additive.

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