Substitutional impurities and phonon density of states: a supercell study of Al-Mg alloys

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Abstract. The effect of Mg impurities on the FCC Al density of states in phonons is treated directly by introducing Mg in supercells of increasing size. A simple substitutional impurity is treated first, and the method is compared to the more usual Green function approach. Small clusters are then studied, and the additivity of pair effects on the lattice specific heat of the alloy is considered.

1. Introduction

When impurities are substituted into a host lattice, the density of states (DOS) in phonons $N(\omega^2)$ is modified and consequently so are the lattice specific heat and other thermodynamic properties [1–4]. The method widely used in the literature to obtain the change $\Delta N(\omega^2)$ in the DOS is that of the Green function, as explained in detail by Tiwari and coworkers [5]. The main steps in implementing this method are summarized below.

For an isolated impurity or cluster of impurities

$$\Delta N(\omega^2) = -(1/\pi)\,\mathrm{Im}\{(\mathrm{d}/\mathrm{d}\omega^2)\log[D(z)]\}$$

with $D(z) = \det|\mathbf{I} + G_0(z)\mathbf{P}(\omega^2)|$ where $\mathbf{P}(\omega^2)$ is the perturbation matrix, $G_0(z)$ the host lattice Green function and $z = \omega^2 + i\epsilon\mathbf{P}(\omega^2)$ and $D(z)$ are of dimension $3n$ if n is the number perturbed host sites.

In practice one introduces phase shifts and takes advantage of symmetry by writing

$$\Delta N(\omega^2) = \sum_{\nu} \Delta N_{\nu}(\omega^2)$$

where ν is an irreducible representation of the point group of the system and

$$\Delta N_{\nu}(\omega^2) = (l_{\nu}/\pi)\,\mathrm{d}\delta_{\nu}/\mathrm{d}\omega^2 \tag{1}$$

where the phase shift δ_{ν} is defined by

$$\tan\delta_{\nu} = -\,\mathrm{Im}\,D(z)/\,\mathrm{Re}\,D(z)$$
$$D(z) = \prod_{\nu} D_{\nu}(z).$$

The necessary independent elements $g_a(z)$ of $G_0(z)$ are computed in two steps. First the host lattice phonon spectrum is obtained in a given force constant model by sampling in the Brillouin zone (BZ) and thus the DOS of the host lattice and the imaginary part of $g_a(z)$ is easily obtained as a histogram by

$$\operatorname{Im} g_a(z) = \pi S_a(\omega)/2\omega \qquad S_a(\omega) = \sum_{k,s} j_a(k,s)\delta(\omega_{k,s} - \omega)$$

where k is in the (reduced) BZ, s is a branch index, and $j_a(k,s)$ is real.
   Then one obtains the real part of $g_a(z)$ by

$$\operatorname{Re} g_a(z) = \int_0^{\omega_m} \frac{S(\omega') - S(\omega)}{\omega'^2 - \omega^2} \, d\omega' + \frac{S(\omega)}{2\omega} \log \frac{\omega_m - \omega}{\omega_m + \omega}$$

with ω_m the maximum frequency. This last step is numerically delicate. Another not very reliable step would be taking the derivative in (1), but in the process of calculating a thermodynamic property such as the change in the lattice specific heat for one mole $\Delta C_v = k_b \int_0^\infty X^2 \Delta N(\omega) \operatorname{cosech}^2(X) \, d\omega$, with k_B the Boltzmann constant, $X = \hbar\omega/2k_B T$, $\Delta N(\omega) = 2\omega\Delta N(\omega^2)$, this may be avoided by first integrating by parts. Note that one has to include in $\Delta N(\omega^2)$ the out-of-band contributions $\sum_l \delta(\omega^2 - \omega_l^2)$, the sum covering the local modes ω_l.
   This Green function method requires several numerical steps, which may induce a lack of precision in the final results. It is also demanding when one wishes to include several interacting impurities [6, 7] or changes in the force constants: these latter changes are usually included to no more than the second neighbours of the impurities even in recent calculations [8].
   An alternative to the above method is the supercell one. The supercell idea is currently [9] being applied to electronic problems. Few applications have been made to phonons [10–12] and it seems that in this context it has not been fully appreciated. It is shown here for cubic crystals that it can be used easily with reliable accuracy and more power than the Green function.

2. The method and an example of application: isolated Mg in Al

The three cubic Bravais lattices with parameter a are treated as simple cubic (SC) with a basis. When the basis supercell (BSC) is taken to be of size na, the number of atoms to be included in the basis is n^3 for SC, $2n^3$ for BCC and $4n^3$ for FCC.
   The DOS $N(\omega)$ is computed by regular sampling in the reduced BZ. Satisfying results are obtained with 50 000 points, plus a few points near the origin in k space in order to increase the precision for small ω.
   The thermodynamic functions of the host lattice are calculated first and then one impurity is substituted in the BSC; n is increased until the variation of the thermodynamic functions, as normalized to a single impurity per mole, is stable. The overall precision for the specific heat C_v is better than 0.1 mJ mol^{-1} K^{-1}. For an FCC lattice and one impurity in the BSC, two impurities are at worse in the respective positions of eighth neighbours for $n = 2$ and 17th neighbours for $n = 3$. For a BCC lattice, the figures are sixth neighbours for $n = 2$, 13th neighbours for $n = 3$, 22nd neighbours for $n = 4$. For all actual applications it will not be necessary to go beyond the above numbers, so that the most unfavourable case will be a dynamical matrix of dimension 3×128 ($n = 4$, BCC), which is quite tractable on a

Table 1. First (') and second ('') derivatives of the pair potentials for nth neighbours. $n = 1$–10. R is the distance. Units are au.

	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$n=9$	$n=10$
(Al–Al)'/R	−0.0327	−0.0168	0.0055	−0.0032	0.0013	0.0004	−0.0009	0.0002	0.0005	−0.0002
(Al–Al)''	1.2574	0.2169	−0.0711	0.0099	0.0267	−0.0307	0.0036	0.0181	−0.0084	−0.0111
(Al–Mg)'/R	−0.0326	−0.0184	0.0061	−0.0032	0.0010	0.0006	−0.0009	0.0001	0.0005	0.0001
(Al–Mg)''	1.4648	0.1601	−0.0532	−0.0011	0.0334	−0.0308	0.0014	0.0189	−0.0064	−0.0126
(Mg–Mg)'/R	−0.0418	−0.0187	0.0064	−0.0031	0.0008	0.0008	−0.0009	0.0000	0.0006	−0.0001
(Mg–Mg)''	1.6284	0.0983	−0.0304	−0.0153	0.0391	0.0294	0.0031	0.0208	0.0046	0.0138

Table 2. The lattice specific heat of Al (cal mol^{-1} K^{-1}).

	10 K	20 K	30 K	40 K	50 K	100 K
Calculated	0.007	0.054	0.197	0.487	0.899	3.080
Experimental [15]	0.006	0.048	0.196	0.484	0.902	3.078
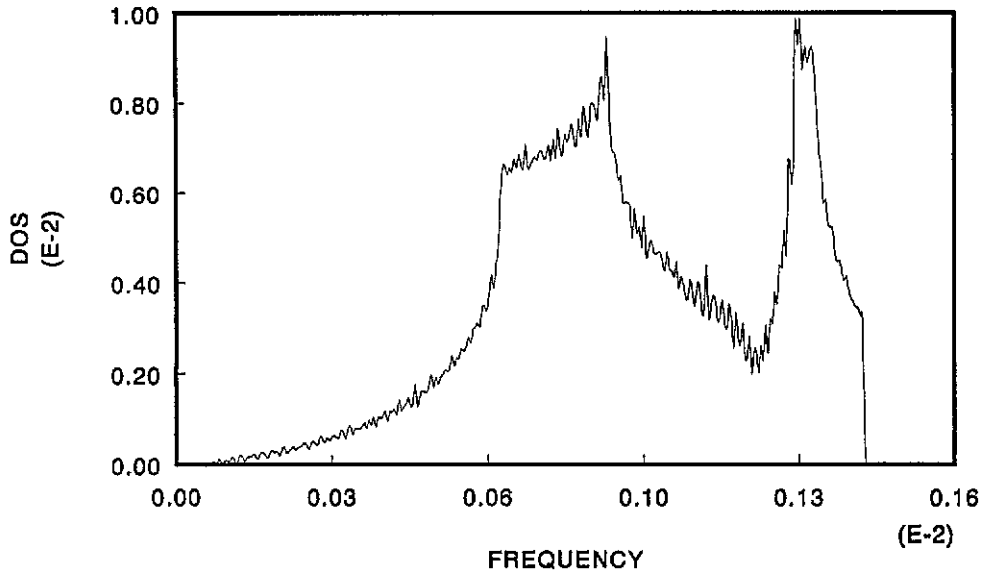
Figure 1. The DOS $N(\omega)$, for pure Al, as a function of frequency ω. ω is in au.

modern computer. The same computer code is used for the three cubic lattices; if A is the host lattice atom and B the impurity atom, the code reads A–A, A–B and B–B force constants, and including force constant changes or small B clusters requires no extra work.

As an example of application we have considered again the low-temperature lattice specific heat of Al–Mg FCC alloys previously obtained [13] with the Green function formalism and force constants from the pseudopotential of Dagens and coworkers with the standard parameters for Al: $r_s = 2.069$ au; $k_F = 0.9276$ au and $a = 4.033$ Å [14]. The first and second derivatives of the pair potential as used to generate the force constants involved throughout this work are given in table 1, for the first ten distances. Atomic masses are 26.928 for Al and 24.321 for Mg. C_v for pure Al as a function of temperature is given in table 2 for force constants up to 20th neighbours and compared with experiment [15]. The agreement is very good.

The DOS $N(\omega)$ for Al and Al–Mg with one Mg at the origin of the BSC, changes in force constants for first and second neighbours, are given in figures 1–4.

In figure 4 when the Mg atoms are practically independent we notice in particular the peak at high frequency that corresponds to the out-of-band local frequency in the Green function method.

Figure 5 gives ΔC_v, the variation of C_v normalized to one Mg per mole of Al as computed from the above DOS. Curves 2 and 3, which correspond respectively to 32 and 108 atoms in the BSC, are close enough to assert that the process has converged.

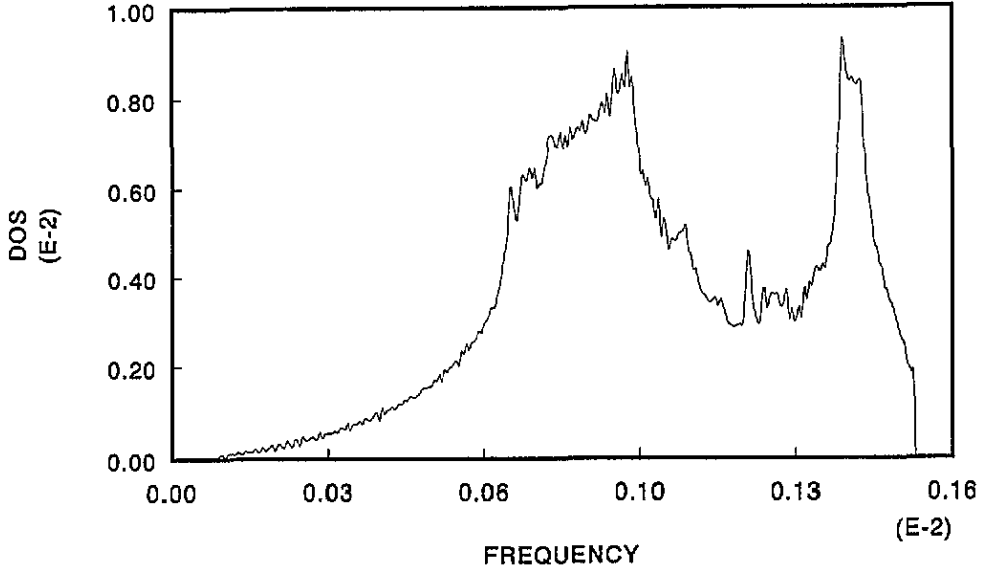Finally figure 6 gives the converged ΔC_v for different models of force constant changes.

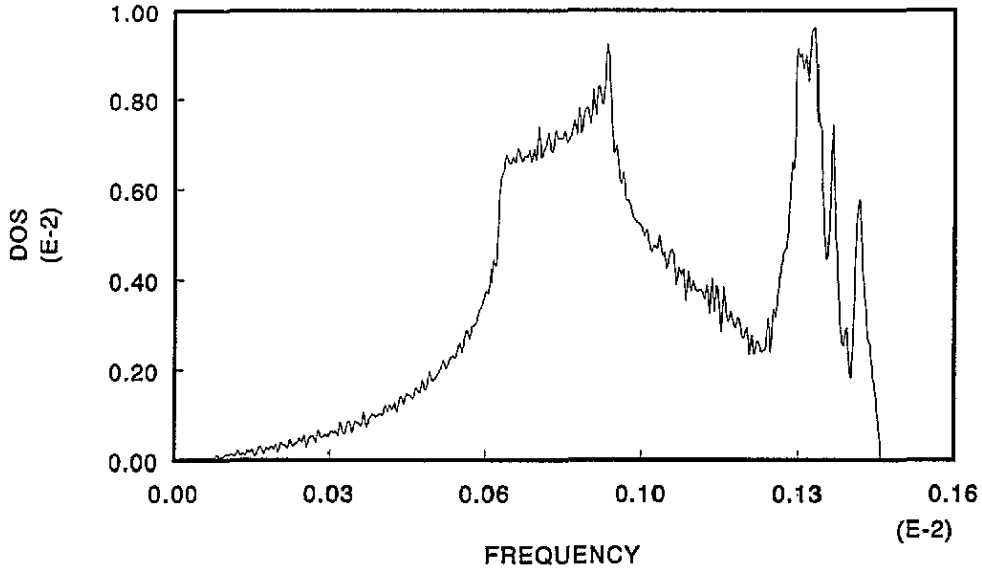Figure 2. The same conventions as figure 1. The atomic concentration of Mg is $\frac{1}{4}$.

Figure 3. The same conventions as figure 1. The atomic concentration of Mg is $\frac{1}{32}$.

The results corresponding to the models of curve 1 (change of mass only), curve 2 (mass + first neighbours) and curve 3 (mass + first and second neighbours) have already been published in [13]. The numbers here and in [14] are not quite the same and the disagreement increases with the complexity of the model (some 20% for the curve 3 model): we attribute these discrepancies to the numerical imprecisions of the Green function theory. We have
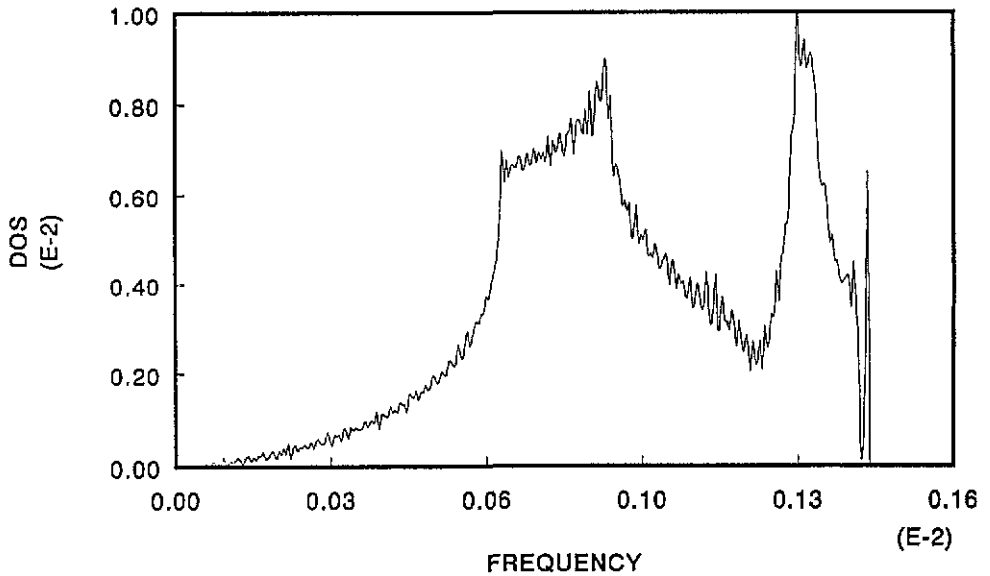
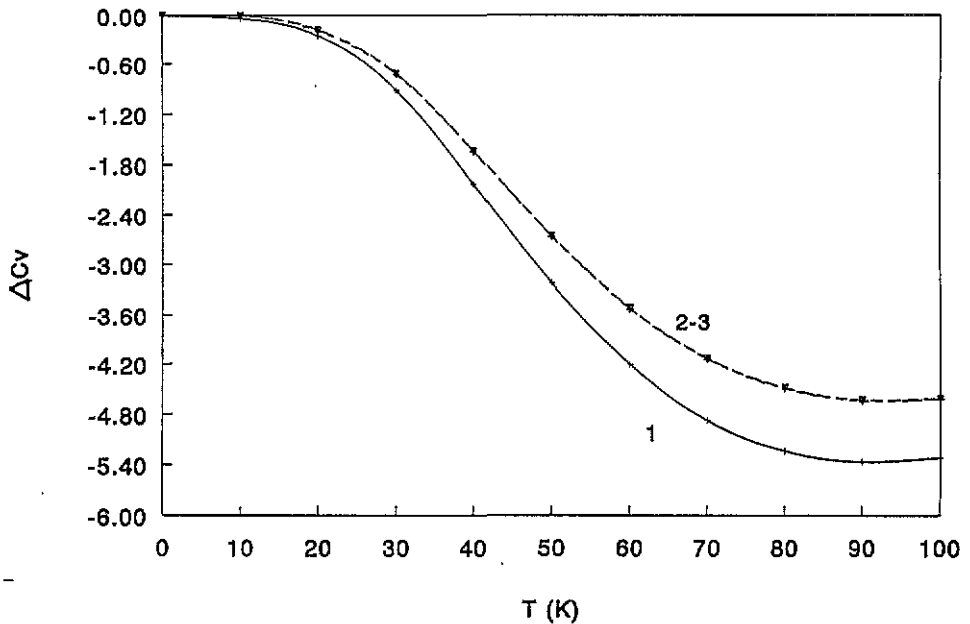**Figure 4.** The same conventions as figure 1. The atomic concentration of Mg is $\frac{1}{108}$.

Figure 5. The variation ΔC_v of the lattice specific heat of Al for one Mg per mole. The unit is 10^{-21} mJ mol^{-1} K^{-1}. Curve 1 is from $N(\omega)$ of figure 2, curve 2 from figure 3 and curve 3 from figure 4.

included in figure 6 the results for the more complex model with changes in all the force constants (up to the 20th neighbours) (curve 4). Such a model would be quite untractable by
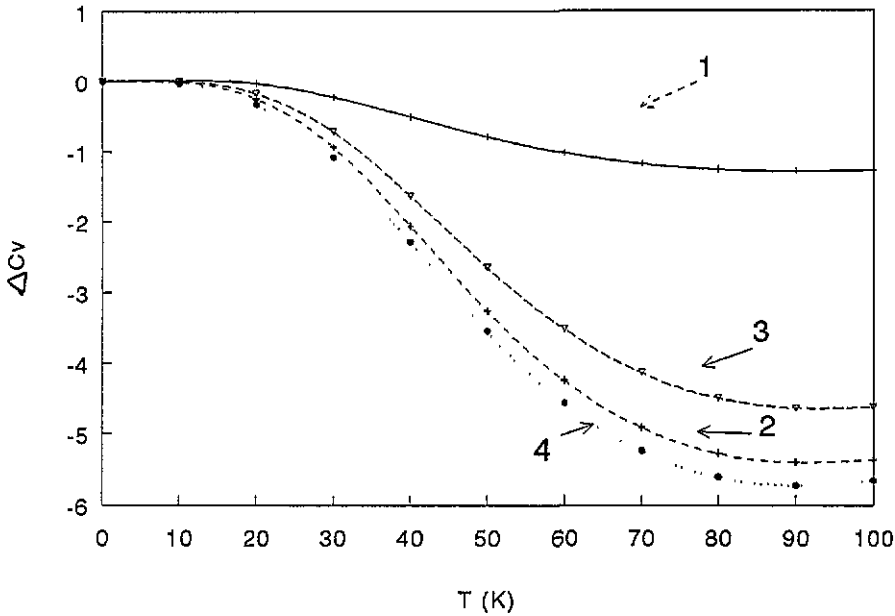
Figure 6. ΔC_v (the same conventions as figure 5) for different levels of force constant changes: curve 1, mass only; curve 2, first neighbours; curve 3, first and second neighbours; curve 4, first to 20th neighbours.

the Green function method; however, we see that curve 4 is notably different from curve 3, and this casts a doubt on the results usually obtained with force constant changes included only for the first layers, at least for metallic alloys where long-range forces are present.

3. Small Mg clusters in Al

All calculations will now be made for 108 atoms in the supercell and all the force constants changed. The effect of Mg pairs on ΔC_v has been considered before by the Green function method [7] when the Mg atoms are first, second, third and fourth neighbours and then an extrapolation used when the atoms are farther apart. The effect has been recalculated directly here for the 10 first possible Mg pairs (again we have some quantitative disagreement). The DOS for Mg–Mg (first neighbours) is given in figure 7.

The pair interaction for ΔC_v, as defined by $\delta^{12} = \Delta C_v^{12} - 2\Delta C_v^1$, where ΔC_v^{12} is for the pair and ΔC_v^1 for the isolated impurity, is given in figure 8 for the four first Mg–Mg relative positions. Beyond the first Mg–Mg position, δ^{12} is found to be practically stable and very small.

We have next treated the four possible Mg triangles with two nearest neighbours, and the third pair, first to fourth neighbours. The DOS for the equilateral triangle is in figure 9.

In figure 10 we have ΔC_v for the equilateral triangle, together with ΔC_v obtained for these situations by $\Delta C_v = 3\Delta C_v^1 + \sum \delta^{12}$, that is, supposing the additivity of pair effects, δ^{12} being included only for first neighbours in view of the above results. This additivity of pair effects was tested for the regular tetrahedral cluster of four Mg atoms (DOS in figure 11), and the results are reported also in figure 10. The hypothesis seems quite satisfactory, and as a summary of the above computations, we will say that a good approximation for the
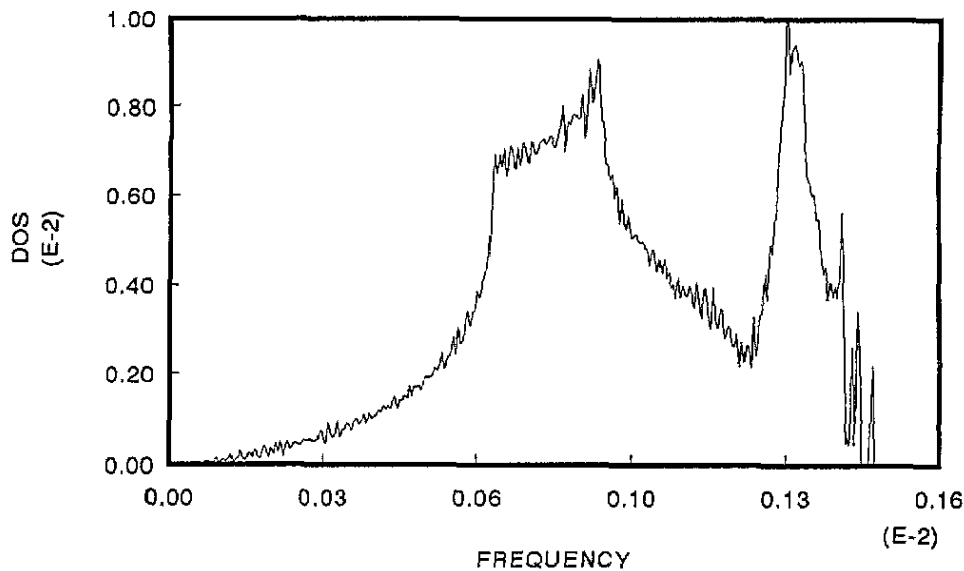
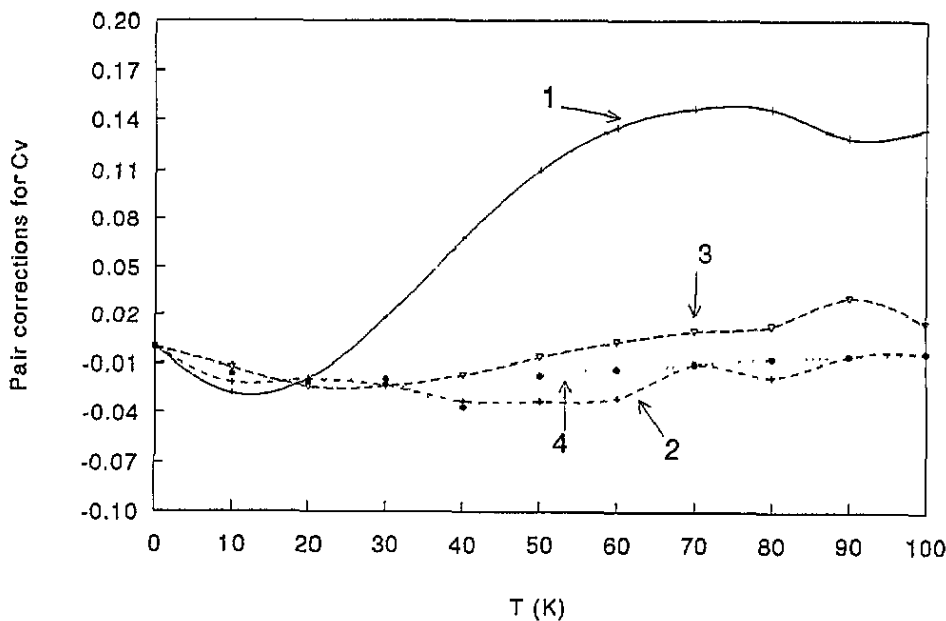**Figure 7.** The same conventions as figure 1, for one Mg pair (first neighbours).

Figure 8. $\Delta C_v^{12} - 2\Delta C_v^{1}$ (the same conventions as figure 5). The two Mg atoms are first to fourth neighbours (curves 1–4, respectively).

computation of ΔC_v in Al–Mg alloys would be $\Delta C_v = N(c\Delta C_v^{1} + 6c^2(\Delta C_v^{12} - 2\Delta C_v^{1}))$, where we have only included the pair interaction for the first neighbours and c is the Mg atomic concentration and N the Avogadro number. In this expression ΔC_v^{1} and ΔC_v^{12} would have to be computed for each c to take into account the lattice expansion [16] but would
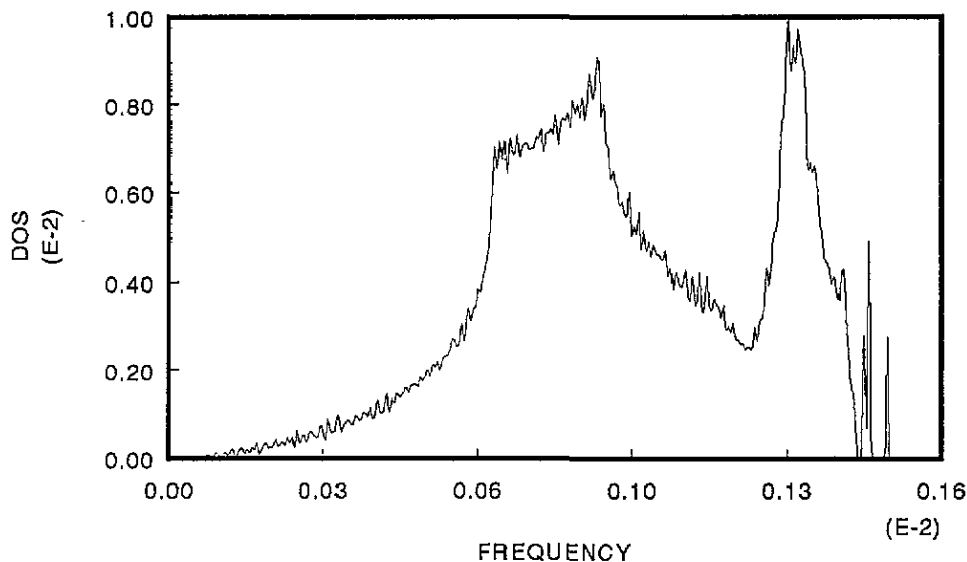
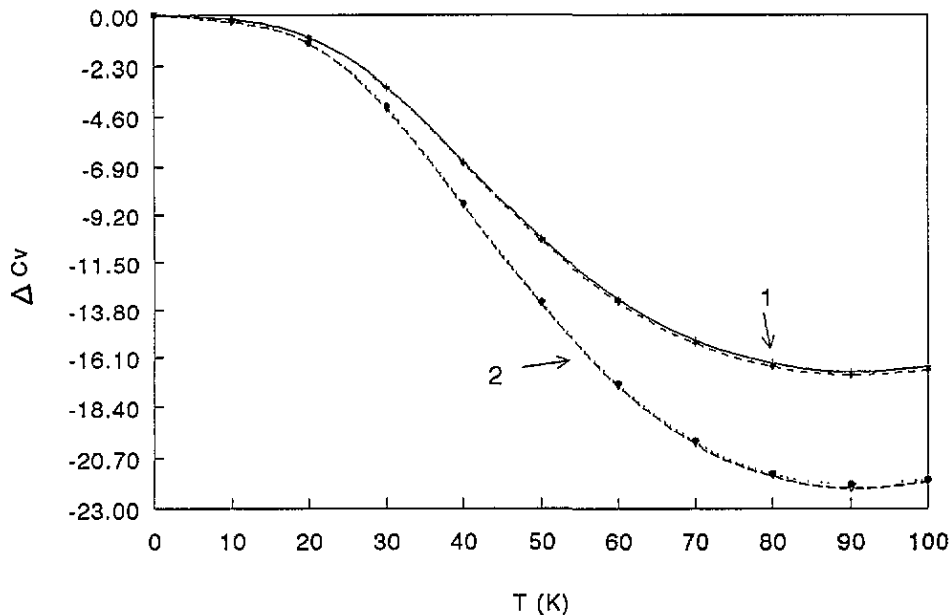**Figure 9.** The same conventions as figure 1, for an equilateral Mg triangle.

Figure 10. ΔC_v for the equilateral triangle (curves 1) and regular tetrahedron (curves 2). The proper curve is practically superimposed on the one obtained by the pair approximation.

be valid at all c as long as the pair interactions were additive. Such computations were not carried out since the results will not be very different from those of [7], and because of the lack of experimental results.
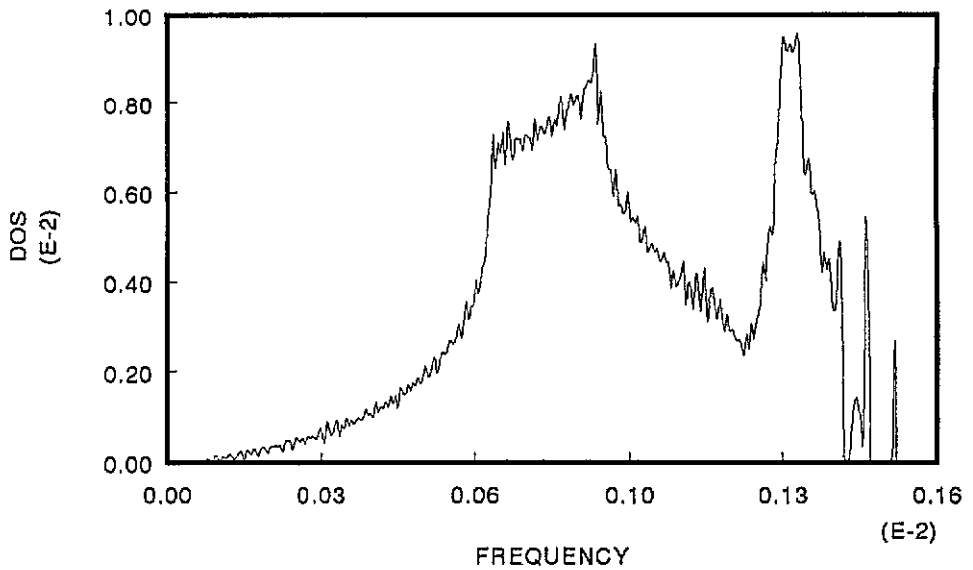
Figure 11. The same conventions as figure 1, for a regular Mg tetrahedron.

4. Conclusion

This paper is intended to show the flexibility and power of the supercell method for phonons, as opposed to the Green function method. It has been shown that many force constant changes can be treated as well as clusters. In any case n-atom clusters will provide results correct to c^n for the properties of the alloy, where c is the concentration of the solute, but further approximations may be studied with the help of clusters, such as here the additivity of pair interactions for the lattice specific heat.

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