

Coefficient of thermal expansion for solder alloys based on cluster expansion method

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Theoretical calculations of the thermal expansion coefficients of the solder alloy systems Sn–Pb and Sn–Ag were attempted by using a cluster expansion method. Five ordered fcc phases for each system were employed to perform the matrix inversion and to determine the correlation coefficients in cluster expansion formalism. The coefficients of thermal expansion of the ordered alloys were obtained through first-principles electronic structure calculations coupled with a Debye treatment of the vibrating lattice. The correlation functions for disordered alloys were derived through Monte-Carlo simulations. The calculated results are in very good agreement with experiments, indicating the feasibility of using cluster expansion theory for thermal expansion coefficient calculations. This study may provide a simple approach to estimating thermal expansion coefficients of disordered structures.

1. Introduction

In the microelectronics industry, solder alloy plays an important role as a joint material. It provides the electrical and mechanical connection between a silicon die and the bonding pad.¹ Therefore, the performance and quality of solder are crucial to the overall functioning of the assembly. Sn–Pb solder alloys, which are well developed with many years of experience, are commonly used in electronic packaging due to their unique combination of electrical, chemical, physical, thermal and mechanical properties.¹ However, the use of Pb will be banned due to environmental considerations, and the search for suitable lead-free solders has become an important issue for the electronics industry.

In the search for a “drop in” alternative to the Sn–Pb solders, some performance specifications, such as the melting temperature, surface tension and thermal expansion coefficient, must be met. Estimation of melting temperature has been extensively reported by thermodynamic calculations of phase equilibria in multi-component systems.^{2–5} Theoretical investigations on the surface tension of Sn-based alloys have also been attempted,^{6–7} and these have led to simple methods for surface tension prediction. However, no theoretical calculations of coefficients of thermal expansion (hereafter CTE) have been performed so far, due to the disordered structure of solder alloys. In addition, even for ordered structures, theoretical calculations of CTEs, by methods such as phonon dispersion curve calculations⁸ and *ab initio* constant pressure dynamics,⁹ as well as *ab initio* lattice dynamics in the quasi-harmonic approximation,^{10–11} still remain challenging. Hence, it is desirable to develop a simple but reliable CTE calculational approach that can be applied to disordered systems. With this in mind, an attempt is made in this paper to explore the possibility of CTE calculations for solder alloys by using the cluster expansion method, which has been well developed and extensively used in phase stability calculations.^{12–18}

2. Cluster expansion method

The basic idea of the cluster expansion method is that any quantity (Q), which is related to atomic configuration, can be

expanded as the sum of terms which involves the series of correlation functions¹⁹

$$Q = \sum_n q_n \zeta_n \quad (1)$$

where q_n is the coefficient of correlation functions, and is assumed to be transferable from one phase to another once the alloy system is fixed. ζ_n is the multisite correlation function for the subcluster ($n = 0$ refers to empty, $n = 1$ to point, $n = 2$ to pair, $n = 3$ to triangle clusters *etc.*), and is defined as follows:

$$\zeta_n = \frac{1}{N_n} \sum_{p_i} \sigma_{p1} \sigma_{p2} \dots \sigma_{pn} \quad (2)$$

where σ_{pn} is a spin-like operator that takes the value of +1 or –1, depending on whether the lattice point p is occupied by an A or B atom. N_n is the total number of lattice subset-like points, pairs, triangles, tetrahedrons in a crystal, in which n equals 1, 2, 3, 4, ..., respectively.

Suppose quantity Q is the thermal expansion coefficient (α). If q_n and ζ_n are known, eqn. (1) can be applied to obtain α . For q_n , there are several ways to derive it, and the simplest one is to use a method due to Connolly and Williams.²⁰ In Connolly and Williams’s scheme, it is assumed that only those clusters consisting of entirely nearest neighbors are important, so that the cluster sum of eqn. (1) is truncated at the fourth order, *i.e.* there are five q_n ($n = 0, 1, 2, 3, 4$) terms to be determined. Five ordered compounds with easily derived correlation functions were employed and inverted to derive the five coefficients terms. The derived coefficient terms then can be applied to the disordered alloy of the same system. For ζ_n , it can be derived through either the cluster variation method or Monte-Carlo simulation,²¹ and the latter is used in this study.

In the work which follows, we attempt the cluster expansion method of CTE calculations for Sn–Pb and Sn–Ag systems. To apply the cluster expansion method, the CTEs of the following five ordered phases are used to derive the correlation coefficient q_n : A(fcc), B(fcc), AB in the L1₀ structure (AuCu) and A₃B, AB₃ in the L1₂ structure (Cu₃Au). Here A and B represent Sn and Pb(Ag), respectively. For pure metals (A and

B), the experimental CTE data²² are readily available, and therefore we use them directly. For the other three ordered phases AB, A₃B, AB₃, we obtain the CTE from first principles electronic structure calculations coupled with a Debye treatment of the vibrating lattice since their experimental data are not available.

3. Results and discussions

3.1 Thermal expansion coefficient for Sn–Pb system

3.1.1 Theoretical calculation of CTEs for three ordered alloys. To derive the CTEs for SnPb(L1₀), Sn₃Pb(L1₂), SnPb₃(L1₂), Morruzi, Janak and Schwarz's scheme²³ was adopted. This approach is applicable to cubic metals and has been applied to alloys by Mohri.¹⁷

The CASTEP program, as implemented with MSI's CERIUS2²⁴ package, was employed for the electronic structure calculation. The generalized gradient approximation (GGA) of exchange-correlation function to density functional theory is used to obtain the static energy. The pseudopotentials used are in Kleinman–Bylander separable form and are norm-conserving. The summation over the Brillouin zone (BZ) is performed on a 6 × 6 × 6 Monkhorst–Pack k-point mesh, which results in 18 k-points in the irreducible part of the Brillouin zone. A binding energy curve is obtained by fitting the static energy of volume per atom $E(r)$ and r into a Morse functional form

$$E(r) = A - 2De^{-\lambda(r-r_0)} + De^{-2\lambda(r-r_0)} \quad (3)$$

where A is a fitting parameter, D is the depth of the potential well, λ is the inverse line width of the potential and r is the Wigner–Seitz atomic radius, which is related to the volume per atom (Ω) by the relation $\Omega = (4\pi/3)r^3$. For the compound we use an average of the Wigner–Seitz radii of each element. The energy points on the binding curve are obtained by a spanning variable r , in the range of $\pm 10\%$ of the equilibrium Wigner–Seitz atomic radius (r_0).

Table 1 shows the results of a non-linear least square fit to the Morse function of eqn. (3) for the system considered. The theoretical bulk modulus B , Debye temperature ϑ_{D0} , and Grüneisen constant γ , are determined within the Debye–Grüneisen approximation following the method of ref.23. In the Debye–Grüneisen approximation, the free energy is given by

$$F(r, T) = \frac{9}{8} k_B \theta_D + E(r) - k_B T [D(\vartheta_D/T) - 3 \ln(1 - e^{-\frac{\vartheta_D}{T}})] \quad (4)$$

where k_B is Boltzmann's constant and $D(\vartheta_D/T)$ is the Debye function.

The calculated binding curve for the rigid lattice together with the Debye temperatures and the Grüneisen constant enable the calculation of the free energy of eqn. (4). A subsequent Morse fit at finite temperature can yield values of $r_0(T)$ and the coefficient of thermal expansion (α) can be calculated with

Table 1 Morse parameters of Sn₃Pb(L1₂), SnPb(L1₀) and SnPb₃(L1₂) and theoretical thermal expansion coefficients at 293 K

	Sn ₃ Pb	SnPb	SnPb ₃
r_0/au	3.4507	3.5349	3.6643
λ/au^{-1}	1.2234	1.2046	1.1515
A/Ry	-35.78	-64.37	-93.43
D/Ry	0.191	0.168	0.137
B/kbar	646.41	539.65	386.02
ϑ_D/K	157.0	145.2	125.0
γ	2.111	2.129	2.109
$\alpha \times 10^{-6}/\text{K}$	18.2061	20.6834	26.2250

Table 2 Correlation functions for Sn(fcc), Sn₃Pb(L1₂), SnPb(L1₀), SnPb₃(L1₂) and Pb(fcc)

Phase	ζ_0	ζ_1	ζ_2	ζ_3	ζ_4
Sn(fcc)	1	1	1	1	1
Sn ₃ Pb(L1 ₂)	1	1/2	0	-1/2	-1
SnPb(L1 ₀)	1	0	-1/3	0	1
SnPb ₃ (L1 ₂)	1	-1/2	0	1/2	-1
Pb(fcc)	1	-1	1	-1	1

$$\alpha(T) = \frac{1}{r_0} \left(\frac{dr_0}{dT} \right) \quad (5)$$

Table 1 shows that the calculated thermal expansion coefficients (α) as well as the bulk modulus (B), Debye temperature (ϑ_D) and Grüneisen constant (γ) under room temperature (293 K).

3.1.2 Determination of correlation coefficient term q_n . For the five ordered alloys, the correlation function ζ_n (shown in Table 2¹⁵) can be easily derived from eqn. (2). The largest cluster in the present case is a tetrahedron formed by nearest-neighbor sites. In the tetrahedron approximation, eqn (1) can be expanded as:

$$\alpha(m) = q_0 + q_1 \zeta_1 + q_2 \zeta_2 + q_3 \zeta_3 + q_4 \zeta_4 \quad (6)$$

where m indexes the different phases to be used in obtaining q_n ; here it represents Sn(fcc), Pb(fcc), SnPb(L1₀), Sn₃Pb(L1₂) and SnPb₃(L1₂), respectively. $\alpha(m)$ is the thermal expansion coefficient for the corresponding phase. The series of eqn. (6) for five different phases can be solved for the five different coefficients q_n by matrix inversion.

$$q_n = \sum_m \{ \zeta_i \}^{-1} \cdot \alpha(m) \quad (7)$$

The matrix description of eqn. (7) is:

$$\begin{bmatrix} q_0 \\ q_1 \\ q_2 \\ q_3 \\ q_4 \end{bmatrix} = \begin{bmatrix} \zeta_{Sn} \\ \zeta_{Sn3Pb} \\ \zeta_{SnPb} \\ \zeta_{SnPb3} \\ \zeta_{Pb} \end{bmatrix} \begin{bmatrix} \zeta_1 \\ \zeta_2 \\ \zeta_3 \\ \zeta_4 \end{bmatrix}^{-1} \begin{bmatrix} \alpha(Sn) \\ \alpha(Sn_3Pb) \\ \alpha(SnPb) \\ \alpha(SnPb_3) \\ \alpha(Ag) \end{bmatrix} \quad (8)$$

Combining the data of Table 1 (CTE data of last row), the data of Table 2 as well as the experimental CTE of Sn and Pb, which are $23.8 \times 10^{-6} \text{ K}^{-1}$ ²² and $29.1 \times 10^{-6} \text{ K}^{-1}$ ²² respectively, the correlation coefficient terms are calculated through eqn. (8) and are listed in Table 3.

As mentioned earlier, the idea of the cluster expansion method is that the coefficient term derived from the ordered compound is applicable for any configuration, *i.e.*, for both ordered and disordered alloys. Therefore, the above coefficient terms can be used to calculate thermal expansion coefficients of disordered alloys once their correlation functions are determined.

3.1.3 Determination of correlation functions for disordered alloys by Monte-Carlo simulation. For the Sn–Pb system, one alloy composition we choose to study was Sn–37%Pb, this being a typical solder composition. As has been described, the

Table 3 Calculated coefficient terms for Sn–Pb system

$q_0 \times 10^{-6}$	22.1705
$q_1 \times 10^{-6}$	-5.33475
$q_2 \times 10^{-6}$	4.32495
$q_3 \times 10^{-6}$	2.68475
$q_4 \times 10^{-6}$	-0.0454

computation of the CTE for a disordered alloy is based on a cluster expansion of a set of ordered alloys. The particular choice of using several ordered alloys to perform matrix inversion may be regarded as a source of imprecision. It is therefore worthwhile to evaluate the accuracy of the inversion computation. With this aim, we used one more alloy with a composition of Sn-95%Pb in the Sn-Pb system for testing, since the experimental CTE of this composition is available.

To determine the correlation functions for the above two disordered alloys, we simulate a different fcc lattice with a 200*200*200 cell, using periodic boundary conditions. The total number of atoms is 4060301. For simulating the interdiffusion of atoms, Kawasaki (spin exchange) dynamics²¹ are applied, *i.e.* the exchange of pairs of neighboring Pb and Sn atoms in accordance with the algorithm of Metropolis *et al.*²¹ The goal of the simulation is to produce a series of atomic configurations such that the probability of a configuration being generated is proportional to the probability of the configuration occurring in the statistical ensemble. This is achieved through numerous repetitions of the following cycle. One starts with an initial atomic configuration. The state is then perturbed, by flipping the sign of the atoms to produce a new configuration. The interaction energy of the near neighbor pairs, which is needed for calculation of the energy of the different state, is determined by density functional theory calculations. If the energy of the new configuration, E_{new} , is smaller than the energy of the old configuration, E_{old} , transition occurs with probability 1. Otherwise, the transition probability is equal to $e^{(-\Delta E/k_B T)}$. Here, ΔE is the energy difference between two configurations, k_B is the Boltzman constant and T is the absolute temperature. A random number, w , is generated between 0 and 1 and if $w < e^{(-\Delta E/k_B T)}$, a transition is made, *i.e.* the new state is accepted. If $w > e^{(-\Delta E/k_B T)}$, no transition is made. In order to achieve a fully equilibrated state, each simulation runs up to 6×10^6 Monte-Carlo steps. After sufficient Monte-Carlo iterations, correlation functions for the disordered alloys Sn-37%Pb and Sn-95%Pb were calculated according to eqn. (2) and are listed in Table 4.

3.1.4 Thermal expansion coefficients for Sn-37%Pb and Sn-95%Pb. Once the correlation function and correlation coefficients are determined, the thermal expansion coefficient can be easily calculated with eqn. (6). The calculated CTEs for Sn-37%Pb and Sn-95%Pb are $20.5733 \times 10^{-6} \text{ K}^{-1}$ and $28.5479 \times 10^{-6} \text{ K}^{-1}$, respectively. On comparing these with the experimental CTEs for Sn-37%Pb ($21.0 \times 10^{-6} \text{ K}^{-125}$) and Sn-95%Pb ($29.0 \times 10^{-6} \text{ K}^{-126}$), it is obvious that excellent agreement is obtained, indicating the feasibility of using cluster expansion theory for CTE calculations on disordered alloys.

3.2 Thermal expansion coefficients for the Sn-Ag system

To further validate the general applicability of the cluster expansion of CTEs, we extend the method to the lead-free system Sn-Ag, due to the following considerations: (1) Sn-Ag is regarded as one of the most promising systems for new lead-free solder alloys, (2) we can use it to demonstrate an

Table 4 Correlation functions for Sn-37%Pb and Sn-95%Pb by using Monte-Carlo simulations

	Sn-37%Pb	Sn-95%Pb
ξ_0	1	1
ξ_1	0.26	-0.9
ξ_2	-0.013343	0.815676
ξ_3	-0.058374	-0.738271
ξ_4	-0.0194567	0.669935

Table 5 Morse parameters for Sn₃Ag (L1₂), SnAg (L1₀) and SnAg₃ (L1₂) and theoretical thermal expansion coefficients at 293 K

	Sn ₃ Ag	SnAg	SnAg ₃
r_0/au	3.2905	3.1581	3.0740
λ/au^{-1}	1.3859	1.3618	1.7785
A/Ry	-24.12	-41.22	-58.56
D/Ry	0.165	0.201	0.126
B/kbar	751.29	921.19	1009.37
ρ_D/K	194.6	211.1	217.8
γ	2.280	2.150	2.734
$\alpha \times 10^{-6}/\text{K}$	19.8250	16.9369	22.0927

Table 6 Calculated coefficients terms for the Sn-Ag system

$10^{-6}q_0$	19.5058
$10^{-6}q_1$	0.06615
$10^{-6}q_2$	3.34732
$10^{-6}q_3$	2.33385
$10^{-6}q_4$	-1.45309

easy-to-apply approach for predicting CTEs of designed lead-free solder alloys.

In the Sn-Ag system, experimental CTEs for Sn-3.5Ag% and Sn-90%Ag alloys are available. Hence, we chose these two compositions to study. The procedure for calculating the theoretical CTEs for SnAg, Sn₃Ag and SnAg₃ is the same as that described in 3.1.1. Table 5 lists the calculated Morse parameters as well as the thermal expansion coefficients under room temperature (293 K).

To derive the correlation coefficient term q_n for the Sn-Ag system, the correlation functions shown in Table 2 can be applied to Sn-Ag ordered alloys since these values are dependent on the atomic configurations but not on the system. The experimental CTE of Ag which is $19.0 \times 10^{-6} \text{ K}^{-1}$ according to ref. 25 is used for the matrix inversion. By inserting the CTEs of five ordered alloys (Sn, Sn₃Ag, SnAg, SnAg₃, Ag) and the correlation functions of Table 2 into eqn. (1), the correlation coefficient terms q_n for the Sn-Ag system are derived and are listed in Table 6.

The correlation functions of the disordered alloys Sn-3.5%Ag and Sn-90%Ag are generated through Monte-Carlo simulation and are shown in Table 7. With the obtained coefficient terms and the correlation functions, the calculated CTEs of Sn-3.5%Ag and Sn-90%Ag are $23.2466 \times 10^{-6} \text{ K}^{-1}$ and $19.9577 \times 10^{-6} \text{ K}^{-1}$ corresponding to Sn-3.5%Ag and Sn-90%Ag, respectively. Comparing with experiment, which is $22.0 \times 10^{-6} \text{ K}^{-127}$ for Sn-3.5Ag and $20.0 \times 10^{-6} \text{ K}^{-128}$ for Sn-90%Ag, it can be seen that very good agreement is obtained, demonstrating the success of extending the model to lead-free solder alloys.

4. Conclusions

In this study, we explored the possibility of applying cluster expansion theory for CTE calculation of solder alloys. The exploration was started with currently used Sn-Pb solder compositions, and then extended to the potential lead-free solder composition Sn-Ag in order to further validate the

Table 7 Correlation functions for disordered alloys Sn-3.5%Ag and Sn-90%Ag by Monte-Carlo simulation

	Sn-3.5Ag%Pb	Sn-90%Ag
ξ_0	1	1
ξ_1	0.93	-0.9
ξ_2	0.861991	0.627889
ξ_3	0.795776	-0.473469
ξ_4	0.731731	0.338508

general applicability of the cluster expansion approach to CTE calculations. Five ordered phases in each system were considered to perform the cluster expansion. CTEs of ordered phases from experiments or theoretical prediction were employed to derive the correlation coefficients for disordered alloys. Monte-Carlo simulations were carried out to determine the correlation functions for the disordered alloys. With the derived correlation coefficients and correlation functions, the CTEs of Sn–37%Pb, Sn–95%Pb, Sn–3.5%Ag and Sn–90%Ag were calculated. Comparing with experiment, very good agreement was obtained, indicating the feasibility of using the cluster expansion approach for CTE calculation. As far as we know, this is the first example of using cluster expansion theory for CTE calculations. This study may provide an interesting approach to predicting CTEs of disordered structures.

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