PREDICTING THE PROPERTIES OF PARTICULATE COMPOSITES - THEORY AND EXPERIMENTAL VERIFICATION

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ABSTRACT

Explicit formulae for the thermo-mechanical properties of isotropic composites in terms of the properties of the two – or more − constituents are lacking. Bounds are available but the upper and lower limits to properties defined by these are often wide apart and in some cases the bounds given in the literature are not consistent. We have recently re-examined the Maxwell formulation in detail and have shown that it is capable of giving accurate predictions for all the thermoelastic properties of a particulate composite without restriction to volume fraction and is capable of predicting the properties for a composite containing inclusions of more than one kind and of more than one size. By experimental measurement we have validated the theory of the thermal expansion coefficients (CTEs) of a number of systems and shown that the Maxwell formulation and method is capable of predicting accurately the measured CTE of silicon in silver, diamond and silica in copper and of aluminium containing both diamond and silicon.

1. INTRODUCTION

Maxwell [1] in 1873, in what is probably the very first discussion of composite properties, considered the effect on the electrical conduction of a homogeneous medium of the introduction of a set of spherical inclusions having an electrical conductivity different from that of the matrix. We have recently re-examined the Maxwell formulation in detail [2] and have shown that it is capable of giving accurate predictions for all the thermoelastic properties of a particulate composite without restriction to volume fraction and is capable of predicting the properties for a composite containing inclusions of more than one kind and of more than one size. The assertion that Maxwell's method is valid and equal or superior to other methods not involving the use of bounds may be "proven" by comparison with other theoretical models and with exact calculations of which there are rather few. We know from, as yet unpublished work, that predictions, using Maxwell's methodology, of the properties of multi-phase composites reinforced with transversely isotropic spheroidal inclusions, are identical to those predicted by Mori-Tanaka theory [3, 4], which is believed to take account of particle interactions, albeit approximately, and is expected to be reasonably accurate for all volume fractions of practical interest.

Two 'exact' predictions, known to the authors, are the calculation due to Arridge [5] for the bulk modulus and thermal expansion coefficient and that due to Sangani and Acrivos [6] for the thermal conductivity. Figures 1 and 2 show that the Maxwell formulation agrees very well with the 'exact' results for volume loadings well above 50% which is the highest loading obtainable in practice with particles of a single size.
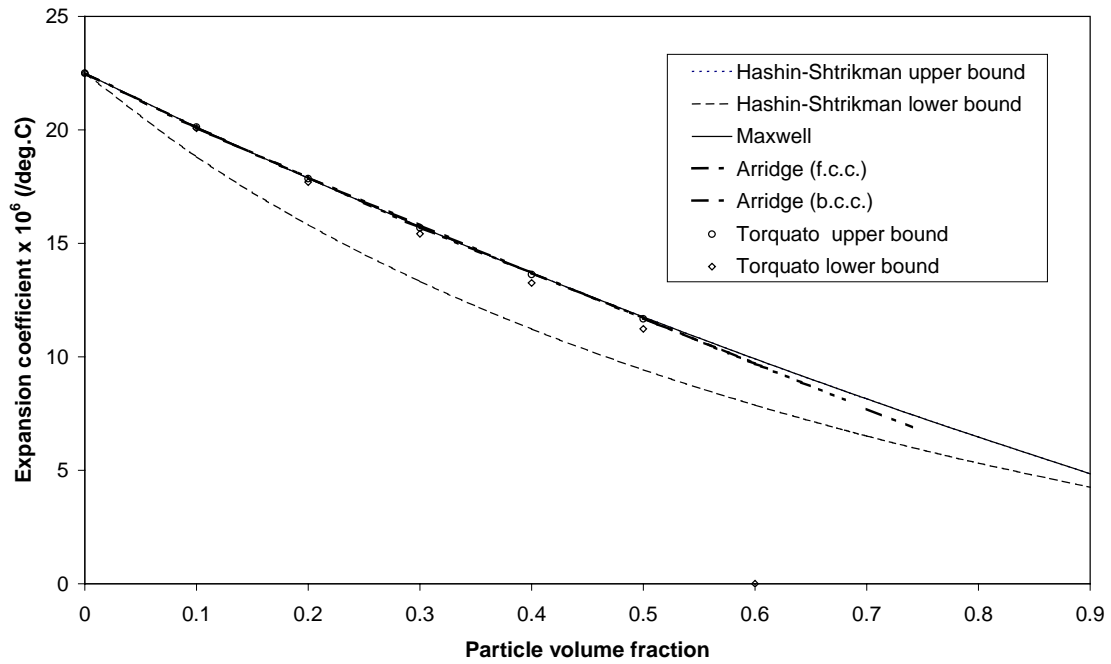
Figure 1: Dependence of effective thermal expansion coefficient for a two-phase composite on particulate volume fraction. For references see [2].
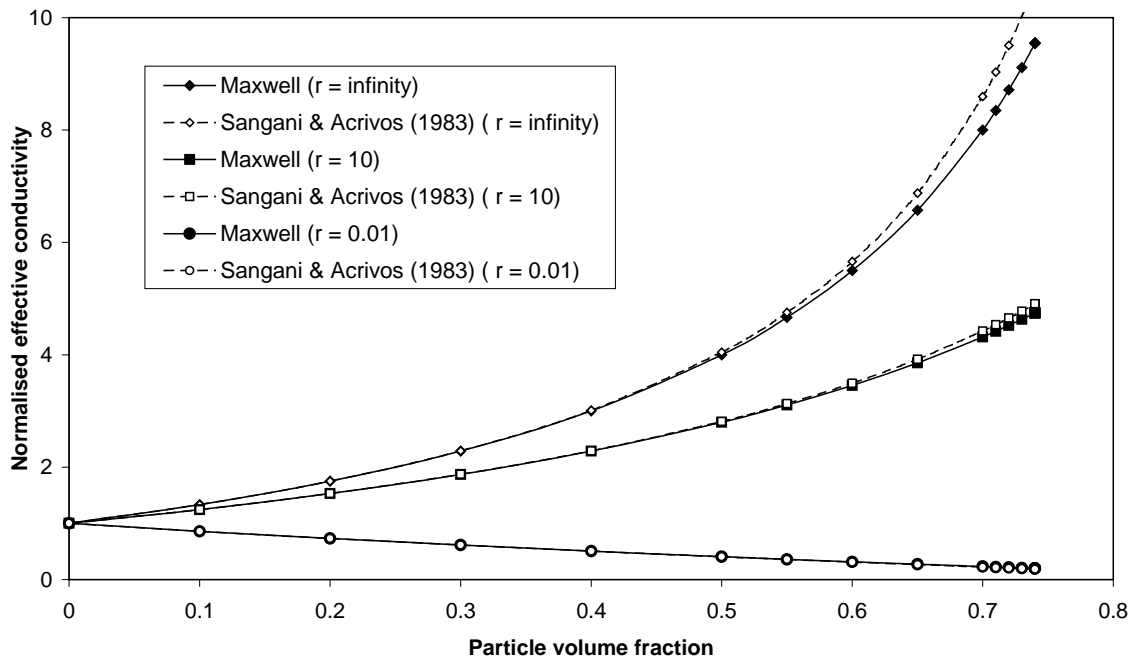

Figure 2: Dependence of ratio of effective thermal conductivity to the matrix thermal conductivity versus particulate volume fraction for a face centred cubic array of spherical particles, at various phase contrasts r. (r is the ratio of the value of the conductivity of the included material to that of the matrix). [2].

The aim of this paper is to show that the Maxwell formulation agrees well with experimental results. Measurements of the bulk modulus of composites are rarely made − experimenters usually reporting values of Young's modulus − neither is there much data on measurements of thermal conductivity. Accurate experimental data are more easily provided by measurements of the thermal expansion coefficient (CTE).

2. ACCURACY OF PREDICTION FOR A SINGLE TYPE OF INCLUSION

We consider first the accuracy of prediction for the case of a single type of inclusion. A convenient form of the relationship for thermal expansion coefficient given by the Maxwell methodology is

$$\alpha_c = \alpha_m V_m + \alpha_p V_p + \frac{4G_m\left(K_m - K_p\right)\left(\alpha_m - \alpha_p\right)V_m V_p}{3K_m K_p + 4G_m\left(K_m V_m + K_p V_p\right)} \ , \tag{1}$$

where the subscripts m and p refer to matrix and particulate and c to the composite, and where V = volume fraction, K = bulk modulus, G = shear modulus and α = CTE.

We have experimented very carefully with the system pure silver containing 3wt% (11at%) silicon. This system is a suitable matrix for enabling the incorporation into silver of particles of diamond or of carbon fibres of very high thermal conductivity. Silver has the highest thermal conductance at room temperature of the noble metals and since it does not readily form a carbide, fails to wet diamond or graphite. Silicon is therefore added and the binary system Ag-Si forms a eutectic at 3wt.% silicon melting at 840°C. At temperatures less than this, the silver may all be precipitated from solution following a suitably long term anneal − the condition we have examined. The measurement of the volume fraction of silicon has been made through careful measurement of the density by the Archimedean method of measuring the weight of a sample in air and in a fluid of known density − in this case Flutec PP9 (perfluoro-1-methyl decalin) of density 1.95 Mgm^{-3}.

The measured density of two samples of the material were 9.519$_8$ and 9.524$_5$ Mgm^{-3} and those of silver 10.492 Mgm^{-3} and of silicon 2.335 Mgm^{-3} respectively. This yields a volume fraction of 0.119, which is very close to that expected of the eutectic composition. We have measured carefully the expansivity of the silver silicon alloy at room temperature and that of pure silver and that of silicon. The method used was to take the specimens through a temperature cycle. After measuring the length of each specimen it was placed in a Netzsch 420 dilatometer and the extension as a function of temperature measured through the following temperature cycle. Starting from 25°C the specimen was cooled to –15°C or so and then heated at a constant rate of heating of 1°C/minute to about 75-80°C and then cooled to room temperature. The results reported here refer to the heating part of the cycle between 0°C and 70°C. Each specimen was taken through the same cycle twice and the results are shown in Table 1.

The Netzsch automatically evaluates from the expansion curve the values of such quantities as the physical CTE defined as $1/l(dl/dT)$ and the technical CTE defined as $1/l_0(\Delta l/\Delta T)$, denoted respectively in Tables by 'Phys α' and 'Tech α'.

Table 1

Specimen	Tech α 0-70°C	Phys α 25°C	Tech α 20-30°C	Tech α 10-40°C	Average
EPFL 5 1	18.22	18.14	18.23	18.34	18.23
EPFL 5 1 rep	17.78	17.21	17.32	17.54	17.46
EPFL 5 4	17.34	17.18	17.20	17.25	17.24
Silicon	2.36	2.54	2.53	2.41	2.46

The average value from the three thermal expansion measurements was 17.64 ppm/K. The results of a number of measurements of silver and of silicon give average values shown in the second column in Table 2.

Table 2

Material	Expansivity ppm/K measured	Expansivity ppm/K predicted
Silver	18.26±0.5	19 Hbook
Silicon	2.46±0.14	2.6 Hbook
Silver + 12% silicon	17.64±0.6	17.3

In order to test the prediction of equation (1) values are required of the shear and bulk moduli. We have used the measured single crystal elastic constants at room temperature and the following relationships: $K = 1/3(C_{11} + 2C_{12})$ and for G we have taken the mean of C_{44} and $\frac{1}{2}(C_{11} - C_{12})$. The values derived for Ag and Silicon are shown in Table 3:

Table 3

Material	K (GPa)	G (GPa)	CTE (ppm/K)
Silver	103	30.8	18.3 meas.
Silicon	97.2	65.1	2.46 meas.
Silica	35.4	31	0.5
Copper	137	49.3	17.2
Diamond	442	526	0.8
Aluminium	77	26.0	See text

The measured and predicted values for the three materials are compared in Table 2 – agreement with the predicted value for the expansivity of Ag-12at.%Si from equation (1) is good. The predicted value of 17.3, arises from use of the measured value of the CTEs of silver and of silicon in these experiments. If the Handbook value for silver is used the predicted value is 18.1ppm/K – just within our experimental error. We show below that in other cases, particularly for multiple inclusions, the result is sensitive to the input value of the CTE of the matrix.

It is worth noting that if we assumed a linear variation of CTE for the composite with volume fraction of the second phase we should predict an expansivity of 0.12 x 2.46 + 0.88 x 18.26 = 16.36 ppm/K, which is outside the experimental error. The non-linearity, while not large, arises, of course, from the differences in elastic moduli, most importantly the difference in bulk modulus, between that of the two constituents. We have investigated in some detail the departure from linearity by comparing results for a copper matrix containing diamond and one containing fused silica (see Figure 3).

3. HARD AND SOFT INCLUSIONS IN A GIVEN MATRIX

Equation (1) shows that if the CTE of the matrix is greater than that of the inclusion, any deviation from linearity will be positive or negative depending on whether the bulk modulus of the matrix is larger or smaller than that of the inclusion. Diamond and fused silica have very small and conveniently close (quoted) values of the CTE at room temperature. When particles of each are incorporated into a copper matrix the bulk modulus of the matrix will be less than that of the inclusion in the case of diamond, and greater than that of the inclusion in the case of fused silica-Table 3. Specimens of four 9s copper containing silica have been prepared using the pressure infiltration method and specimens of copper boron containing diamond by the same method, both preparations being carried out at EPFL. It is not possible to fabricate useful specimens of pure copper containing diamond by the pressure infiltration method since copper does not wet diamond.

Measurements have been made of the expansivity of copper containing fused silica-specimens. After measuring the length of each specimen it was placed in a Netzsch 420 dilatometer and the extension as a function of temperature measured through the following temperature cycle. Starting from 25°C the specimen was cooled to –10°C or so and then heated at a constant rate of heating of 2°C/minute to about 80°C and after a short hold at 80°C cooled to at the same rate to –10°C. It was then heated at the same rate of heating as before back to room temperature. In this way values for the CTE are obtained both on heating through a given temperature range and cooling through the same range. The values reported here are for temperatures centred upon 25°C. In all cases except one, both for specimens containing silica and those containing copper, the values obtained on heating are slightly larger than those measured on cooling.

The Netzsch automatically evaluates from the expansion curve the values of such quantities as the physical CTE defined as $1/l(dl/dT)$ and the technical CTE defined as $1/l_0(\Delta l/\Delta T)$. The measured values obtained on heating are shown in Table 4.

Table 4

Sample	V_f SiO$_2$-EPFL	Tech α 5-70°C	Phys α 25°C	Tech α 20-30°C	Tech α 10-40°C	Ave. Heat	Ave. Heat & Cool
EPFL5 0	0.53	11.19	11.54	11.52	11.37	11.41	11.08
EPFL5 1	0.61	9.5	9.93	9.77	9.61	9.70	9.34
EPFL5 2	0.65	9.76	9.89	9.88	9.75	9.82	9.76
EPFL5 3	0.67	11.61	11.34	11.41	11.36	11.43	11.38
EPFL5 4	0.71	8.62	8.83	8.82	8.67	8.74	8.53
EPFL5 5	0.74	6.93	7.04	7.05	6.94	6.99	6.82
EPFL5 F5	0.7	8.01	7.80	7.83	7.93	7.89	8.17
OFHC Cu	0	Heat only	17.25	17.22	17.33	17.27	

The specimens containing diamond were taken through a precisely similar temperature cycle curves were obtained both for heating and cooling as before. We report here in Table 5 only the values obtained on heating.

In making the intended comparison we must bear in mind the matrix is not precisely the same in the two cases – the diamond containing specimens contain boron as well as

diamond whereas the silica containing specimens are of four 9s copper. The last column in both Tables 4 and 5 gives the overall average values obtained from the results from both heating and cooling. The graph in Figure 3 clearly indicates the deviation from a straight-line variation between the values of the individual components, and that for diamond and silicon the deviation occurs in an opposite sense.

Table 5: Cu(B) values on heating.

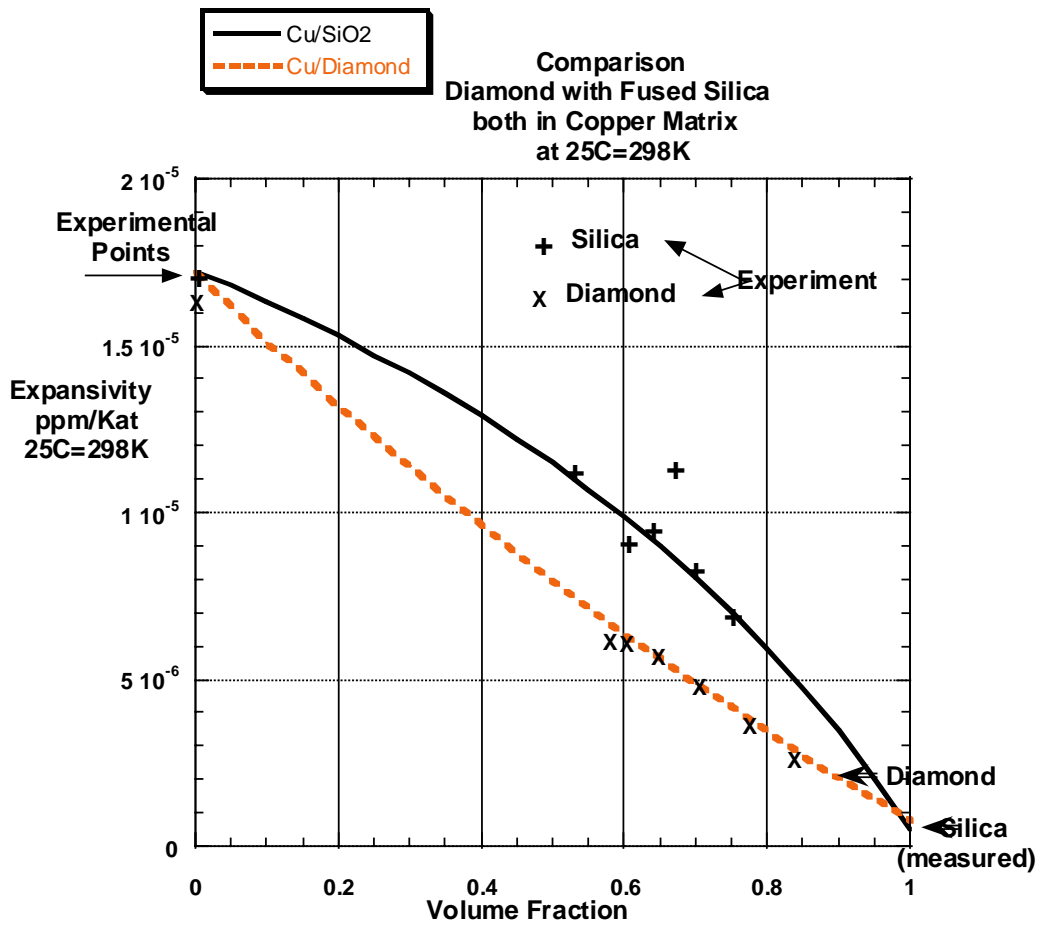| **Sample**	V_f diamond EPFL	Tech α 0-70°C	Phys α 25°C	Tech α 20-30°C	Tech α 10-40°C	Ave. Heat	Ave. Heat & Cool
CuB1	0.83	3.08	3.17	3.20	3.12	3.14	2.95
CuB2	0.77	3.50	3.76	3.68	3.52	3.61	3.36
#14	0.7	4.89	5.04	5.04	4.90	4.96	4.76
CuB3	0.6	5.80	6.09	6.00	5.67	6.09	5.68
CuB4	0.57	6.10	6.24	6.14	6.01	6.12	5.87
CuB5	0.64	5.83	6.02	5.98	5.80	5.90	5.64
CuB6	0	16.62	16.83	16.87	17.70	16.76	16.43
Silicon		2.84	3.09	3.07	2.86	2.96	2.70

Figure 3: Experimental measurements of expansivity for diamond and silica reinforcements in a copper matrix.

Very accurate prediction of the variation with volume fraction requires accurate knowledge of the CTE and of the elastic moduli of both diamond and of silica as we have seen. The CTEs of both are very small (that is why they have been chosen) and hence difficult to measure.

In the case of copper plus boron the difficulty arises of the uncertainty of the thermo-mechanical properties of boron. Values of the CTE of boron found in the literature vary widely. We have been unable to find any reliable measurement of the single crystal stiffnesses of crystals of elemental boron. So this demonstration while qualitatively satisfying does not permit a rigorous quantitative test of theory. The theoretical curves in Figure 3 have been constructed using the values for copper, diamond and pure silica shown in Table 3.

Since the matrix in one case contains boron we can show that the effect of the boron is slight by estimating the effect of boron on the CTE of copper. We have measured the CTE of boron and find a mean value of 2.46ppm/K. The value of the bulk modulus taken from Wikipedia is 185GPa so, using these figures in equation (1) we find that even if the boron is present as particles of volume fraction as much 0.045 the effect on OHFC copper would be to change the CTE from 17.27 ppm/K to 16.6 ppm/K. Since in these experiments the matrix is never as much as 50% of the specimen, the effect of the presence of boron will be much less. And in effect this accounts well for the measured difference between the values for the matrix in Tables 4 and 5 respectively.

4. MULTIPLE INCLUSIONS

The variation of CTE with volume fraction of a single type of inclusion in a given matrix is quite close to a linear variation between the values for the two components even when the values of bulk and shear modulus differ by orders of magnitude, e.g. diamond particles in a weak polymer such as cyanate ester. When accurate matching of a particular value of CTE is sought this deviation from linearity is very important and we have just given examples of cases where the deviation from linearity occurs in opposite senses with single types of inclusion. The case of multiple inclusions would be very easily dealt with provided each inclusion in the given matrix showed a linear variation with volume fraction. In this case the effects of the two (or more) inclusions is simply

$$\alpha_{eff} = \alpha_m V_m + \alpha_p^1 V_p^1 + \alpha_p^2 V_p^2 + ... ,\tag{2}$$

which is easily shown to be the case or is apparent from a figure.

When the non-linearity of variation of CTE with volume fraction is important then we must use Maxwell's method of finding the effects of multiple inclusions. Prediction of the CTE for multiple inclusions according to the formulation of Maxwell requires first the computation of the bulk modulus of the composite K_{eff}

$$K_{eff} = \frac{1 + \Lambda}{\dfrac{1}{K_m} - \dfrac{3\Lambda}{4G_m}} ,\tag{3}$$

where Λ is obtained from the expression

$$\Lambda = \sum_{i=1}^{N} V_p^i \; \frac{1/K_m - 1/K_p^i}{1/K_p^i + 3/(4G_m)} = \frac{1/K_m - 1/K_{eff}}{1/K_{eff} + 3/(4G_m)} \quad , \tag{4}$$

where the properties of each inclusion of N different types are designated by the superscript i. The effective CTE of the composite, α_{eff}, containing multiple inclusions is then obtained from the value of Ω given by

$$\Omega = \sum_{i=1}^{N} V_p^i \; \frac{\alpha_p^i - \alpha_m}{1/K_p^i + 3/(4G_m)} = \frac{\alpha_{eff} - \alpha_m}{1/K_{eff} + 3/(4G_m)} \quad . \tag{5}$$

or

$$\alpha_{eff} = \alpha_m + \Omega \left(\frac{1}{K_{eff}} + \frac{3}{4G_m} \right) . \tag{6}$$

For a system of **two** types of inclusion, the expression for Λ reads

$$\Lambda = \frac{\dfrac{1}{K_m} - \dfrac{1}{K_{p1}}}{\dfrac{1}{K_{p1}} + \dfrac{3}{4G_m}} \; V_{p1} \; + \; \frac{\dfrac{1}{K_m} - \dfrac{1}{K_{p2}}}{\dfrac{1}{K_{p2}} + \dfrac{3}{4G_m}} \; V_{p2} \quad . \tag{7}$$

Whence K_{eff} may be found via (4) and the relevant formula for the thermal expansion coefficient is

$$\alpha_{eff} = \alpha_m + \left(\frac{1}{K_{eff}} + \frac{3}{4G_m} \right) \left[\frac{\left(\alpha_{p1} - \alpha_m\right)V_{p1}}{1/K_{p1} + 3/(4G_m)} + \frac{\left(\alpha_{p2} - \alpha_m\right)V_{p2}}{1/K_{p2} + 3/(4G_m)} \right]. \tag{8}$$

We have attempted experimental verification of these formulae using aluminium containing particles of silicon and of diamond.

5. ALUMINIUM PLUS SILICON PLUS DIAMOND

Aluminium does not easily wet diamond so that specimens of the metal, which are to contain this type of inclusion, are prepared with an addition of silicon to the matrix. In this case the alloy used was of the eutectic composition containing 12 volume percent silicon and specimens were prepared at the EPFL by the pressure infiltration method and the heat treatment was such that all of the silicon was ex-solution.   Measurement of the CTE at room temperature was carried out in the same way as for the specimens of silver containing silicon described above. The results are shown in Table 6 and show the expected trend with the exception of Al Si 4, which is out of line. The measured values are compared with the predictions from equation (8).

Table 6 (1 = diamond, 2 = silicon)

Sample	V_{p1} EPFL	V_{p2} EPFL	V_m	Tech α 0-70°C	Phys α 25°C	Prediction α_m=21.5ppm/K	Prediction α_m=22ppm/K
Al Si 1	0.82	0.0216	0.158	3.34	3.63	3.38	3.44
Al Si 2	0.78	0.0264	0.194	3.66	3.40	3.99	4.07
Al Si 3	0.62	0.0456	0.334	6.68	6.58	6.56	6.69
Al Si 4	0.61	0.0468	0.343	8.04	7.89	6.72	6.86
Al Si 5	0.66	0.0408	0.299	5.97	5.97	5.89	6.01
Al Si 6		0.12	0.88	20.41	20.75	19.1	19.5

The Maxwell formulation quite correctly predicts the variation with increasing volume fraction of diamond, and with the exception of specimen Al Si 4 the agreement is satisfactory. Two quantitative predictions are shown assuming slightly different values for the CTE of aluminium viz: 21.5 or 22 ppm/K. The large relative difference emphasises that the prediction must depend importantly on the CTE of the matrix. Other uncertainties in prediction are in the assumed input values of the physical properties for diamond, silicon and aluminium.

6. CONCLUSION
We have demonstrated that Maxwell's method accurately predicts the thermal expansion coefficient of particulate composites, containing single or multiple inclusions having significant volume fractions, well within the uncertainty due to the lack of precise knowledge of the physical properties of the various components.

ACKNOWLEDGEMENT

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