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July 19, 2004

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# Thermal Expansion of AuIn<sub>2</sub>

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## **Abstract:**

The thermal expansion of AuIn<sub>2</sub> gold is of great interest in soldering technology. Indium containing solders have been used to make gold wire interconnects at low soldering temperature and over time, AuIn<sub>2</sub> is formed between the gold wire and the solder due to the high heat of formation and the high inter-metallic diffusion of indium. Hence, the thermal expansion of AuIn<sub>2</sub> alloy in comparison with that of the gold wire and the indium-containing solder is critical in determining the integrity of the connection. We present the results of x-ray diffraction measurement of the coefficient of linear expansion of AuIn<sub>2</sub> as well as the bulk expansion and density changes over the temperature range of 30 to 500 °C.

Keywords: *Thermal Expansion, CTE, Gold Indide-AuIn<sub>2</sub>, X-ray diffraction*

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## **1. Introduction**

The physical behavior of gold indide (AuIn<sub>2</sub>) is of great interest in the application of soldering technology, because over time the AuIn<sub>2</sub> compound will be formed at the soldered junction of gold and an indium containing solder due to the high heat of formation [1]. The phase diagram of Au-In has also been reported [2, 3] and recalculated [4] by several authors. The rate of formation and the behavior of this material as a function of time and temperature are of great concern in evaluating the integrity of the solder joints or inter-connects. Cracks can occur due to stresses exerted by the formation of this compound, and due to difference in the thermal expansion coefficients (CTE) of gold, gold-indide, and the indium containing solder.

In this paper we use x-ray diffraction to measure crystallographic changes as a function of temperature and extract from these changes the CTE, which has not been reported in the literature. The CTE of AuIn<sub>2</sub> is found to be  $1.14 \times 10^{-5}$  /°C. This result also revealed that the thermal expansion of AuIn<sub>2</sub> is lower than that of gold and indium and clearly does not follow the rule of mixtures.

## **2. Experimental**

The sample was prepared by mixing stoichiometric quantities of gold and indium, melting the mixture in high vacuum to 900°C and then cooling to room temperature. The sample is then ground to fine powder using conventional ball milling method. It is then examined

by X-ray diffraction, which shows that the sample is indeed single-phase cubic structure  $\text{AuIn}_2$  having a lattice parameter of  $a=6.517 \text{ \AA}$  [5]. As indicated in the phase diagram,  $\text{AuIn}_2$  is a line compound. Composition changes are not allowed and the elemental composition was also confirmed by EDX. The powder sample is then loaded onto an aluminum holder and placed in a temperature-controlled furnace inside the X-ray spectrometer. The furnace consists of a thermally insulated copper block heated by cartridge heaters. The block is enclosed in a chamber with opening for the x-ray beam probe. A thin Kapton film is used as the x-ray window. During the experiment, helium gas flows through the chamber to avoid significant oxidation.

The experiment is carried out using the INEL CPS120 curved position sensitive detector system utilizing copper  $K_\alpha$  radiation. The data acquisition and the furnace's temperature controller (Omega 2400 series) are software-controlled, resulting in a fully automated system. A few heating and cooling cycles are performed on the sample to determine structural changes, if any. The temperature range is set from 30 to 500 °C for this experiment. As pointed out in the phase diagram the material melts above 540 °C.

### 3. Results and Discussion

Figure 1 shows the resulting diffraction spectra of  $\text{AuIn}_2$  as a function of temperature. Data sequence starts at the bottom of the graph and ends at the top. The data are also plotted in the shifted square root scale on the vertical axis. The peaks can be indexed to a cubic structure. The miller indices of the cubic structure are labeled in the plot.  $\text{AuIn}_2$  has the  $\text{CaF}_2$  crystal structure with 4 gold atoms at the (0,0,0) positions and 8 indium atoms in the (1/4,1/4,1/4) positions. Clearly, the diffraction peaks are shifted as a function of temperature. In order to avoid changing the phase, the temperature range chosen is from 30 to 500 °C, which is slightly below the melting temperature. There is also no obvious change in peak widths indicating that the crystallite size remains the same. No crystal growth can be observed in the temperature range of the measurement. Differences in peaks intensity can be observed between the first heating and cooling spectra. The results are essentially similar indicating that the atoms re-organized themselves only in the first heating and cooling cycle. The experiment is repeated for the 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> heating cycle. For the sake of simplicity, these results will not be presented.

Figure 1 also shows a peak at about 34° and also probably a weak one at 42° (2 $\theta$ ) which appear at high temperature and upon cooling. We believe that these peaks are due to oxidation of small impurities, namely indium manganese iron oxide ( $\text{InMnFeO}_4$ ). The plots are given in relative square root scale on the vertical axis which tends to enhance small peaks. The formation of this impurity phase does not interfere with the thermal expansion behavior of  $\text{AuIn}_2$ . As indicated in the literature [1, 4], the heat of formation is highest for  $\text{AuIn}_2$  indicating that this cubic phase is most preferred. This preference of  $\text{AuIn}_2$  has also been reported by both Kubota et. al. [6] and Simic et. al. [7] in their gold-indium thin film studies.

Data analysis is first performed by appropriately converting the x-axis from channel number from the ADC (analog to digital converter) to  $2\theta$  angles and thereafter feeding

the data into commercial analysis software [8]. The peak positions are extracted, the lattice parameter  $a$ - is refined and the results are listed in Table I. Table I also lists the error bar in  $\Delta a$ , volume ( $\text{\AA}^3$ ), and the density (gm/cc) as a function of temperature. The initial room temperature lattice refinement of  $a$ - = 6.5107(10)  $\text{\AA}$  is consistent and within experimental error of the published result of 6.517  $\text{\AA}$  for AuIn<sub>2</sub>. Figures 2a-c plot the changes in lattice parameter, volume, and density with temperature. The CTE is defined as,

$$\alpha = \frac{1}{L} \frac{dL}{dT}$$

where  $L$  is the original length and  $dL/dT$  describes the change in length over temperature; a value of  $\alpha = 1.141 (\pm 0.045) \times 10^{-5} / ^\circ\text{C}$  is calculated from the data. Since the material has a cubic structure, the bulk CTE is just  $3\alpha$  which is  $3.442 (\pm 0.122) \times 10^{-5} / ^\circ\text{C}$ . Similarly, the coefficient of volume and density expansion can also be calculated and the results are tabulated and compared to the neat gold and indium metals in Table II. The numbers in brackets are the estimated errors. Over the range of 30-500  $^\circ\text{C}$ , there is a 1.7 % increase in volume and consequently, also 1.7 % decrease in density. The extracted properties appear to be linear over the range of the measurements.

It is interesting to note from Table II, the density and the melting point of AuIn<sub>2</sub> follow the rule of mixture of Au and In. That is, the density and the melting point of AuIn<sub>2</sub> have values between the densities and melting points of neat gold and indium. However, the thermal expansion of AuIn<sub>2</sub> falls out the bound of the thermal expansion of neat gold and indium, and consequently, the coefficients of volume expansion and/or density contraction do not obey the rule of mixtures. This significant mismatch the CTE's of AuIn<sub>2</sub>, and Au and In could probably causes cracks within the joints and interconnects over aging time and temperature fluctuations. To avoid CTE mismatches, it is proposed that AuIn<sub>2</sub> itself can be used as the soldering agent. So and Lee [9] pointed out that AuIn<sub>2</sub> can be used as bonding agent with copper substrate since AuIn<sub>2</sub> is a stable compound, good barrier for oxygen penetration, good thickness and composition control and void-free.

Of interest, are some of the typical non-lead commercially available binary soldering alloys of Au/Sn (gold/tin), Au/Si (gold/silicon), Au/Ge (gold germanium) used in soldering. Table III lists the CTE's of these alloys and are compared in Figure 3. As listed in the literature for Au/Sn depending on the composition, the CTE's ranges from  $1.36$ - $1.75 \times 10^{-5} / ^\circ\text{C}$ , for Au/Si ranges from  $1.2$ - $1.49 \times 10^{-5} / ^\circ\text{C}$  and for Au/Ge ranges  $1.2$ - $1.31 \times 10^{-5} / ^\circ\text{C}$ . The CTE's for neat Au, Sn, Si, Ge and In are 1.42, 2.35, 0.5, 0.6 and  $2.48 \times 10^{-5} / ^\circ\text{C}$ , respectively. Interestingly, when Au is added to either Si or Ge, the CTE remains high, that is, closer to the CTE of Au than Si or Ge. However, when Au is added to Sn, the resulting CTE's are closer to Au and they obey the rule of mixing.

In the case of Au/In, the CTE is lower than that of Au and outside the bound of both Au and In. This result can be explained by crystallographic packing. Gold is fcc with  $a$ - = 4.0786  $\text{\AA}$  and the closest possible gold-gold distance is 2.884  $\text{\AA}$  while indium is fct

(face` center tetragonal) and the closest indium-indium distance is calculated to be 3.244 Å. However, in AuIn<sub>2</sub>, the closest gold-indium distance is 2.822 Å. Hence, the bonding for gold-indium is significantly stronger than for indium-indium and gold-gold. Also from the published data, the heat of formation for AuIn<sub>2</sub> from indium and gold is about -5.2 kcal/gm-atom [1]. This also suggests that AuIn<sub>2</sub> atoms are more tightly bound, thus resulting in a smaller CTE.

#### **4. Conclusions**

X-ray diffraction technique is used to determine the CTE of AuIn<sub>2</sub>. The CTE of AuIn<sub>2</sub> is found to be  $1.141 \times 10^{-5}/^{\circ}\text{C}$ . Interestingly, unlike most binary materials, this value does not follow the rule of mixture. It is smaller than that of Au which is smaller than In. The result is explained by the changes in packing from In and Au to the CaF<sub>2</sub> structure of AuIn<sub>2</sub> and also the drastic change in the heat of formation. Because of the low CTE, oxidation resistance and stability, it is suggested that AuIn<sub>2</sub> will be an improved soldering material.

In the temperature range of 30-500 °C, AuIn<sub>2</sub> is found to expand in volume by 1.7 % with a reduction in density also of 1.7 %. The CTE is lower than that of indium and gold. Hence, it can be concluded that the thermal expansion of AuIn<sub>2</sub> does not follow the rule of mixtures of gold and indium. Consequently, the volume expansion/contraction over temperature also does not obey the rule of mixtures. This significant change in thermal expansion is explained by the high heat of formation of AuIn<sub>2</sub> as well as the reduction of Au-In bond distance in AuIn<sub>2</sub> when compared to Au-Au and In-In distances.

#### **Acknowledgement**

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. The authors will like to acknowledge technical support of Martin P. Stratman and the financial support from C. Hrousis of LLNL.

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Table I: X-ray extracted parameters.

Temperature C	a- (Å)	$\Delta a$ - (Å)	Volume Å <sup>3</sup>	Density gm/cc
30	6.5107	0.0010	275.99	10.266
50	6.5118	0.0011	276.12	10.261
100	6.5179	0.0015	276.90	10.233
150	6.5210	0.0017	277.29	10.218
200	6.5234	0.0019	277.61	10.207
250	6.5283	0.0016	278.23	10.184
300	6.5300	0.0017	278.44	10.176
350	6.5362	0.0016	279.24	10.147
400	6.5390	0.0014	279.60	10.134
450	6.5432	0.0018	280.14	10.114
500	6.5448	0.0025	280.34	10.107
500	6.5432	0.0026	280.14	10.114
450	6.5434	0.0011	280.17	10.113
400	6.5393	0.0015	279.64	10.132
350	6.5360	0.0014	279.21	10.148
300	6.5333	0.0015	278.86	10.161
250	6.5291	0.0004	278.33	10.180
200	6.5240	0.0007	277.68	10.204
150	6.5191	0.0010	277.05	10.227
100	6.5161	0.0015	276.67	10.241
50	6.5123	0.0014	276.19	10.259
30	6.5092	0.0019	275.80	10.274

Table II: Comparison of coefficients of Thermal Expansions  
The error bars are indicated by brackets.

	AuIn2	Au	In
$\alpha_a \times 10^{-5}/^{\circ}\text{C}$	1.141(45)	1.41	2.48
$\alpha_{\text{Volume A3}} \times 10^{-5}/^{\circ}\text{C}$	3.442(122)		
$\alpha_{\text{Density}} \times 10^{-5}/^{\circ}\text{C}$	-3.385(122)		
Structure	Fcc	Fcc	ft
a,c (Å)	6.517	4.079	3.252, 4.946
Volume (Å <sup>3</sup> )	275.99		
Density gm/cc	10.266	19.3	7.3
Melting point °C	540.7	1064.4	156.6

Note: Data for Au and In metals are taken from the tables of the Goodfellow Corporation.

Table III: Coefficient of thermal expansion.

Elements/alloys	Coefficient of thermal expansion $\times 10^{-5} / ^\circ\text{C}$	References
Au	1.41, 1.42	1, 2
Sn	2.35, 2.0	1,2
Au <sub>2</sub> Sn <sub>8</sub>	1.75	5
Au <sub>8</sub> Sn <sub>2</sub>	1.6	3
Au <sub>9</sub> Sn <sub>1</sub>	1.36	5
Si	0.5, 0.3	4, 2
Au <sub>32</sub> Si <sub>68</sub>	1.49	5
Au <sub>02</sub> Si <sub>98</sub>	1.39	5
Au <sub>97</sub> Si <sub>03</sub>	1.2	3
Ge	0.575	1
Au <sub>12</sub> Ge <sub>78</sub>	1.2	5
Au <sub>74</sub> Ge <sub>26</sub>	1.31	5
Au <sub>88</sub> Ge <sub>22</sub>	1.3	3
In	2.48, 2.9	1, 3
Au <sub>33</sub> In <sub>66</sub>	1.14	Present work

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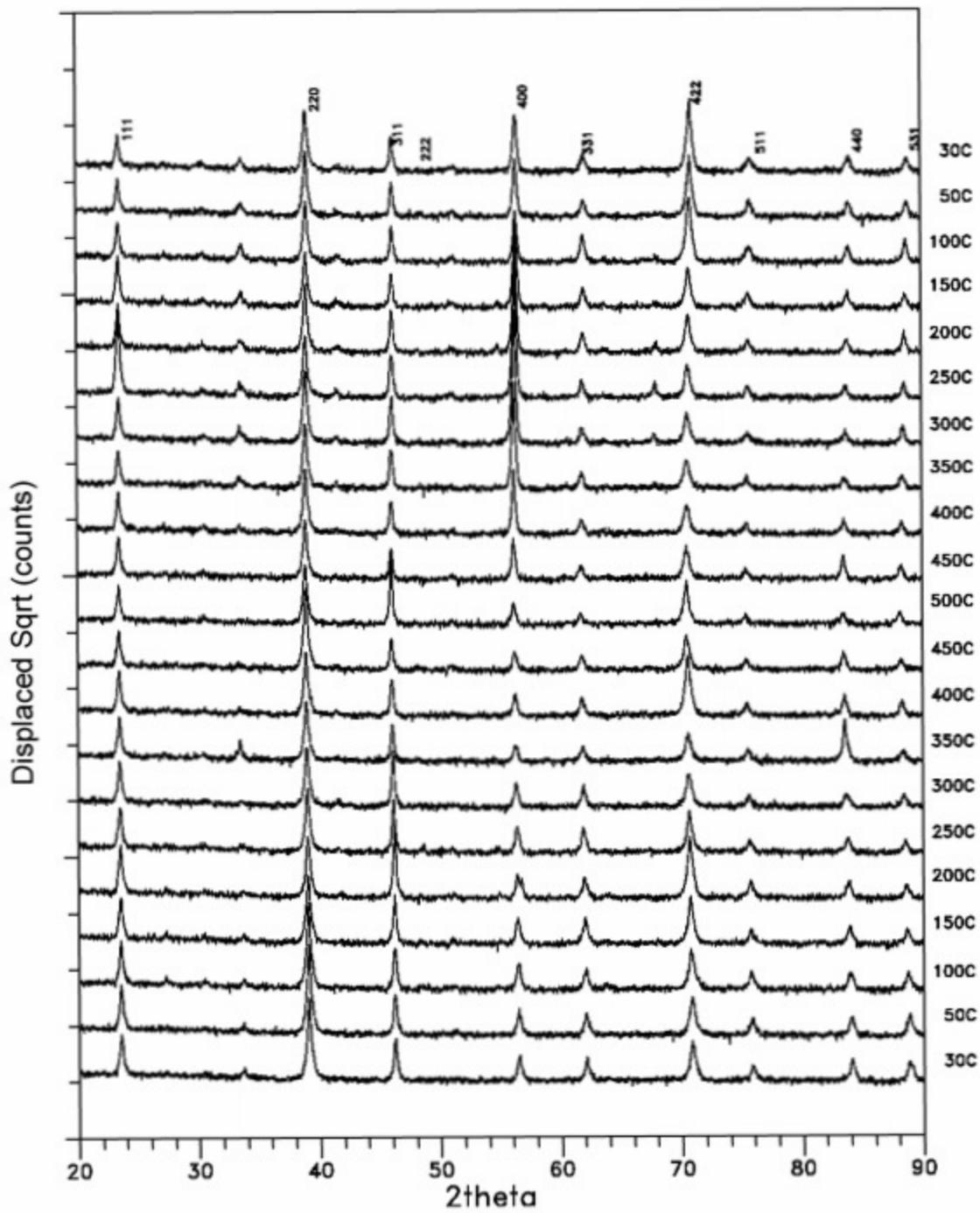
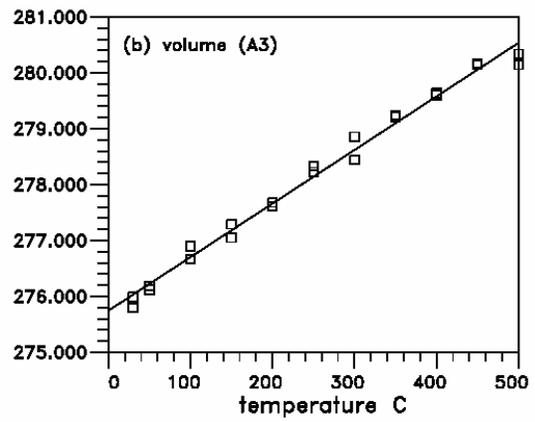
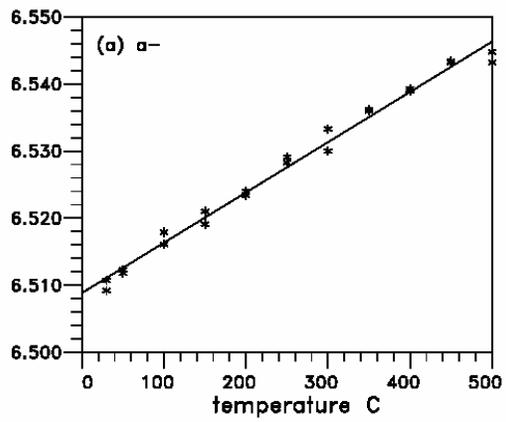
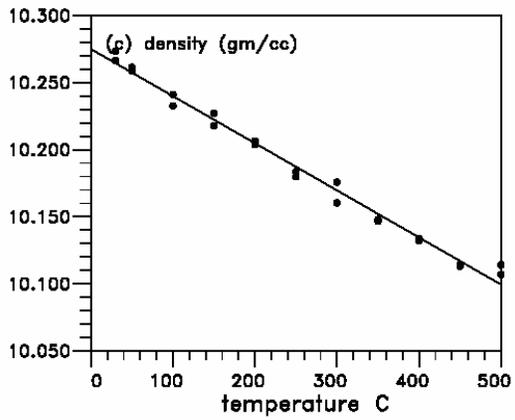


Figure 1: XRD spectra of AuIn<sub>2</sub> as a function of temperature. Data sequence starts at the bottom of the graph and ends at the top.



Figures 2a-c: X-ray extracted parameters of  $a$ - ( $\text{\AA}$ ), volume ( $\text{\AA}^3$ ) and density (gm/cc) as a function of temperature.

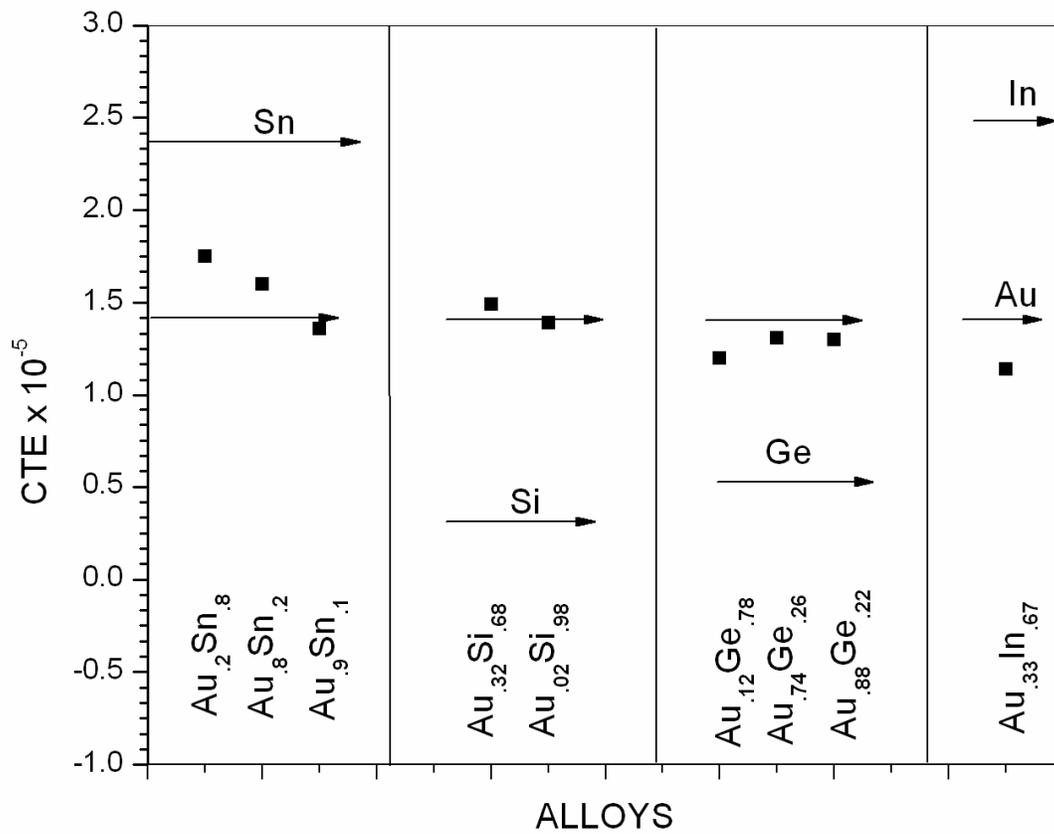


Figure 3: Comparison of the coefficient of thermal expansion of several common solders.