

## THERMAL EXPANSION OF BISMUTH-TIN AND BISMUTH-LEAD ALLOYS

### ABSTRACT

Thermal expansion coefficients of bismuth-tin and bismuth-lead alloys have been measured and it is observed that the simple rule of mixtures is applicable in the two phase region of these two alloy systems.

In a recent publication<sup>1</sup> the authors have pointed out that in the absence of complicating influences the simple rule of mixtures is applicable to coefficients of thermal expansion in the two-phase region of lead-tin and lead-cadmium alloys. In order to examine whether such a rule is applicable to other systems where the difference in coefficients of expansion of the two phases is high, the work has been extended to bismuth-tin and bismuth-cadmium as these two systems are also free from complicating influences affecting thermal expansion.

The alloys were made from chemically pure metals in pyrex tubes containing requisite amounts of component metals sealed in vacuum. The alloys were made by keeping the pyrex tube (with the component metals) in a furnace kept at 100° C above the liquidus temperature of the alloy and after the alloy was molten the pyrex tube was shaken for efficient mixing after which the tube containing the alloy was cooled in the furnace. The solidified alloys were homogenised at 50° C below the eutectic temperature for thirty-six hours and then cooled to room temperature. In each series about ten alloys were made to cover the entire range of composition.

Dilatometric samples were made from homogenised alloys and coefficients of thermal expansion were measured in the temperature range room temperature to 100° C in a dilatometer described in a previous publication<sup>2</sup>. Results of measurements along with the values calculated from the rule of mixtures are shown in Tables I and II. Thermal expansion coefficients of two-phase alloy have been calculated as follows. If  $E$  is the net coefficient of expansion of the two-phase alloy and  $E_1$  and  $E_2$  are the coefficients of expansion of bismuth and lead (or tin) rich phases respectively then  $E = a E_1 + b E_2$  where  $a$  and  $b$  are the volume percentages of bismuth and lead (or tin) rich phases in the alloy. As the solubility of tin in bismuth is very small, for purposes of calculation the expansion coefficients of pure

bismuth (tin) have been taken. For the bismuth-lead alloys, the coefficients of expansion of pure bismuth and that of  $\beta$  phase have been taken as results of  $\beta + \gamma$  phase region of the system are reported here.

TABLE I  
 Bismuth-lead alloys

Sl. No.	Wt. % Bi	Wt. % Pb	Coefficient of thermal expansion $\times 10^{-6}$	
			Experimental	Calculated
1	35	65	23.95	24.13
2	45	55	22.15	22.25
3	55	45	20.48	20.45
4	60	40	19.63	19.59
5	70	30	18.11	17.91
6	80	20	16.46	16.30
7	90	10	14.76	14.76

TABLE II  
 Bismuth-tin alloys

Sl. No.	Wt. % Bi	Wt. % Sn	Coefficient of thermal expansion $\times 10^{-6}$	
			Experimental	Calculated
1	5	95	21.98	21.96
2	10	90	21.65	21.61
3	15	85	21.26	21.25
4	20	80	20.90	20.89
5	30	70	20.14	20.12
6	40	60	19.32	19.33
7	50	50	18.52	18.46
8	60	40	17.49	17.55
9	70	30	16.57	16.59
10	80	20	15.55	15.56
11	90	10	14.47	14.47

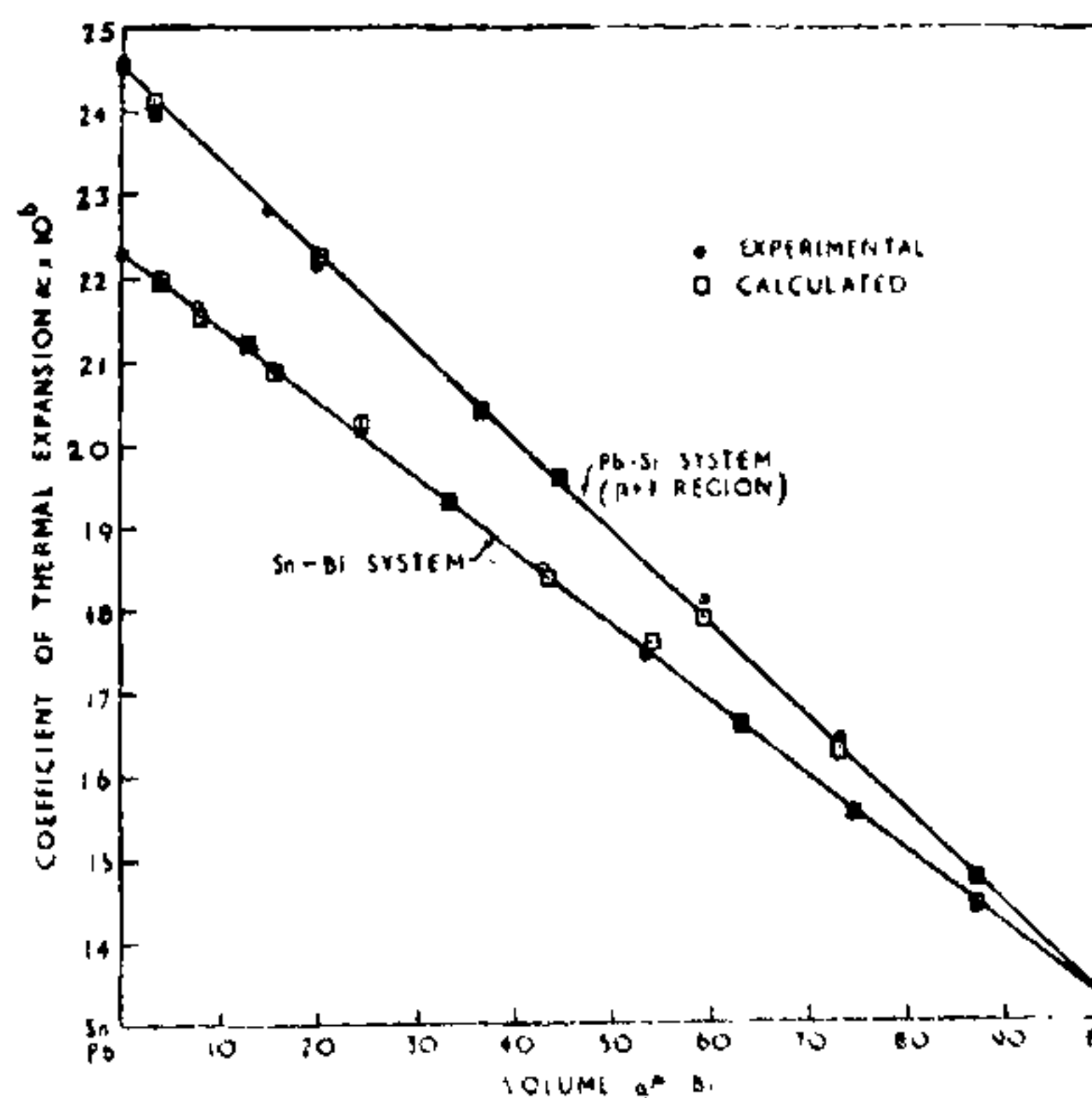


FIG. 1. Thermal expansion coefficients of Pb-Bi and Sn-Bi alloys.

As can be seen from Fig. 1, the coefficient of thermal expansion in the two-phase region of bismuth-tin and bismuth-lead ( $\beta + \gamma$  region)

alloys, the variation of expansion coefficients is proportional to the volume fraction of the two phases and there is close agreement between calculated and observed values, thereby suggesting that coefficients of expansion in the two-phase region of these alloys, follow the simple rule of mixtures.

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Physical Metallurgy L. J. BALASUNDARAM,  
Division, A. N. SINHA.

National Metallurgical  
Laboratory,  
Jamshedpur-7, December 9, 1971.

1. Balasundaram, L. J. and Sinha, A. N., Scheduled for publication in the *J. Appl. Physics*, Nov. 1971.
2. Sinha, A. N. and Balasundaram, L. J., *Trans. I.I.M.*, 1970, 23 (1), 5.

### PHASE STUDIES IN THE SYSTEM



VARIOUS workers<sup>1-6</sup> have studied the X-ray patterns of several spinel type of minerals, however the phase studies of the present system is not cited in the literature. The symmetry of crednerite ( $\text{CuMn}_2\text{O}_4$ ) is controversial<sup>7</sup> and the X-ray data is not available. Hence in order to assign the symmetry of crednerite and to correlate with gahnite we studied this system.

The samples were prepared by mixing the appropriate quantities of the component oxides and were fired at 1000° C for 8 hr and at 1150° C for 4 hr. The samples were finally quenched to room temperature in air. The X-ray patterns of these samples were obtained by the standard Philips diffractometer using MoK radiation. The patterns thus obtained were used to calculate the lattice parameters and to study the phases developed.

The results are given in Table I. It is observed that on introduction of  $\text{Cu}^{2+}$  in A

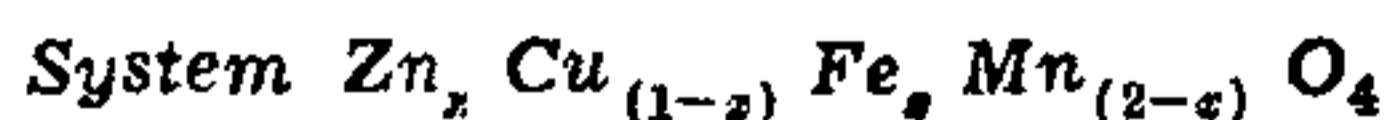
site and  $\text{Mn}^{3+}$  in B site of the gahnite lattice, the lattice parameters progressively decreased with a single phase of gahnite upto the addition of 60% of  $\text{Cu}^{2+}$  and  $\text{Mn}^{3+}$ . On introduction of 80% of  $\text{Cu}^{2+}$  and  $\text{Mn}^{3+}$  the crednerite phase developed with faint lines. In the last compound ( $\text{CuMn}_2\text{O}_4$ ), whose symmetry is still unknown, we indexed the pattern on the basis of tetragonal symmetry with the lattice parameters  $a = 7.81 \text{ \AA}$  and  $c = 8.71 \text{ \AA}$ . The X-ray data of this compound is given in Table II.

TABLE II

$d \text{ \AA}$	$I/I_0$	$hkl$
3.717	10	111
2.899	30	202
2.672	10	220
2.556	10	113
2.464	100	311
2.378	10	222
2.248	10	004
1.923	10	400
1.871	10	313
1.790	20	331
1.616	10	224
1.591	30	422
1.579	30	333
1.458	30	511
1.453	30	404
1.376	10	440
1.261	10	335
1.225	10	620
1.149	10	515
1.130	10	426
1.066	10	535

It is clear that the change in symmetry is caused by the distortion in the lattice resulted by the occupancy of smaller ions in the A site. However the arrangement of oxygen tetrahedra around the  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions and the oxygen octahedra around the  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$  ions in B site is not disturbed. Hence it is reasonable to assume that gahnite and crednerite are iso-structural minerals differing only in symmetry.

TABLE I



S. No.	Composition	Molecular weight	Colour	Density	Phases present
1	$\text{Zn}_{0.8}\text{Cu}_{0.2}\text{Fe}_{1.6}\text{Mn}_{0.4}\text{O}_4$	240.18	Black	5.58	Gahnite $a = 8.40 \text{ \AA}$
5	$\text{Zn}_{0.6}\text{Cu}_{0.4}\text{Fe}_{1.2}\text{Mn}_{0.8}\text{O}_4$	239.46	Black	5.44	Gahnite $a = 8.35 \text{ \AA}$
3	$\text{Zn}_{0.4}\text{Cu}_{0.6}\text{Fe}_{0.8}\text{Mn}_{1.2}\text{O}_4$	238.74	Black	5.34	Gahnite $a = 8.29 \text{ \AA}$
4	$\text{Zn}_{0.2}\text{Cu}_{0.8}\text{Fe}_{0.4}\text{Mn}_{1.6}\text{O}_4$	238.02	Vandy Ke Brown	5.22	Gahnite + Crednerite $a = 8.23$ $a = 7.81, c = 8.71 \text{ \AA}$
5	$\text{CuMn}_2\text{O}_4$	537.30	Burnt Umber	5.14	Crednerite $a = 7.81, c = 8.71 \text{ \AA}$