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Determination of the thermodynamic properties of liquid Ag-Sb-Sn system by equilibrium saturation method

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Properties

ABSTRACT

Purpose: The interaction of lead-free solders with a copper substrate is an essential issue for the reliability of solder joints. In order to understand this interaction, the knowledge of thermodynamic and other physical properties of several ternary systems such as Ag-Sb-Sn system is necessary. The aim of this work was to determine the activities of all components in Ag-Sb-Sn alloy.
Design/methodology/approach: The investigation of this system was carried out using the equilibrium saturation (ES) method. The ES measurements were performed at 1273, 1373 and 1473 K. As the latter method is a comparative one, a Sn-Sb alloy was accepted as a reference alloy, where a formula for the Sb activity proposed by Jönsson and verified by Vassiliev was accepted.
Findings: In the frame of the presented experiments the activity of Sb was determined by ES method.
Research limitations/implications: The activity of Sb was obtained by ES and fitted to the Redlich-Kister-Muggianu (RKM) model.
Practical implications: A knowledge of multi-component phase equilibrium can provide the alloy developer with specific data enabling finding alloys that meet certain criteria. Phase diagrams are built on the basis of experimental data and the reliability of phase diagrams depends on the reliability of the experimental data used for the optimisation. Hence it is advantageous to use various source of data obtained by several methods and when the data of different source agree (like the ones presented in this paper) it proves their reliability. Data presented in this paper will be used for Ag-Sb-Sn phase diagram optimisation in the frame of the COST Action MP0602.
Originality/value: Sb activity values in Ag-Sb-Sn alloys obtained by ES and activity values of Sb, Ag and Sn calculated using the RKM model.
Keywords: Ag-Sb-Sn system; Equilibrium saturation; Liquid alloys

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1. Introduction

Many Sn-Sb-based alloys have been developed as high-temperature solders in compliance with recent Pb-free requirements for electronic products [1-4]. Chemical thermodynamics can provide a fundamental basis for understanding a material's microstructure and hence, properties. A knowledge of multi-component phase equilibria can provide the alloy developer with specific data enabling finding alloys which meet certain criteria. When binary sub-systems are known, it is possible to calculate higher order systems (ternary, quaternary, etc.) For a ternary system, thermodynamic models consistent with the experimental data are first obtained, than a thermodynamic extrapolation method is used to calculate a ternary system. From the calculated phase diagram, the melting temperature range, the solidification path as well as the susceptibility to inter-metallic formation can be estimated. [5, 6]. Knowledge of the phase equilibria of the Sn-Sb-Ag ternary system is essential for the applications and development of the solders. Masson and Kirkpatrick [7] experimentally determined the Sn-Sb-Ag liquidus projection. Oh *et.al*. [8] modelled this system on the basis of literature data whereas Gierlotka *et.al* [9] used the CALPHAD approach for modelling. An obvious requirement is that calculated phase equilibria data reproduce the experimental data within the limits of the experimental accuracy. Therefore, a sufficient number of experiments must be carried on (although they are time consuming) to establish the phase diagrams reasonably well.

In this paper, there are presented results of antimony activity determination by ES method and fitting these data to Redlich-Kister-Muggianu (RKM) model.

2. Experiments

2.1. Equilibrium saturation (ES) technique

The vapour pressures of the components of Ag-Sb-Sn alloy are at 1373 K: $p^*_{Sn} = 1.6 \cdot 10^{-1}$ Pa, $p^*_{Ag} = 6.69 \cdot 10^{-2}$ Pa, $p^*_{Sb} = 1103$ Pa [10]. Since the vapour pressure of Sb is much higher than that of the other two elements, the determination of the activity of Sb were carried out by the comparative method of equilibrium vapour saturation (ES). This method has already been successfully applied for alloys with only one volatile component [11, 12, 13]. The studied Ag-Sn-Sb mixture and the reference Sn-Sb mixture were placed inside a closed crucible under a reduced argon pressure and saturated with the vapour of Sb until equilibrium was reached (Fig. 1). At equilibrium state, the activity of Sb is the same in all samples inside a closed system.

The temperature was measured with a {Ni-(Ni-Cr)} thermocouple. The accuracy of temperature measurements was 5 K. The pressure in the furnace was measured with a vacuum meter APG-010, manufactured by Balzers. The accuracy of pressure measurements was 10 Pa. Alloys were prepared from elements of purity at least 99.98 mass fraction purchased from Aldrich.

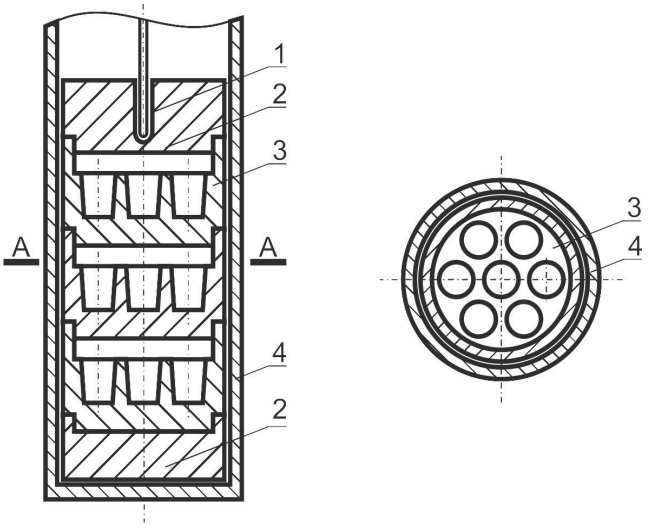

Fig. 1. Apparatus for the equilibrium saturation with metal-vapour: 1 − thermocouple and alundum sheets for thermocouple, 2 − graphite cover, 3 − graphite blocks with grooves for alloys, 4 − vacuum chamber

Graphite elements were made of EK-412 type graphite purchased from Ringsdorf. The reference and the studied solutions of appropriate composition were prepared by melting carefully weighed masses of metals at an argon pressure of 0.1 Pa. The compositions of the alloys were determined by the weighing method. The accuracy of weighing was 10^{-5} g. The quantities were determined experimentally, *i.e.* the argon pressure and the equilibration time were meant to ensure the attainment of equilibrium between Sb(g) in the reference and the studied solution. In preliminary tests, in five grooves were Sn-Sb alloys of different compositions and pure Sn in two groves. The equilibrium state was attained when the mole fraction of Sb was the same in all solutions. The value of argon pressure was specially chosen to be higher than the vapour pressure of Sb in order to limit the evaporation process to that of antimony only with a sufficiently high rate. It was established, that for the temperature 1373 K, the necessary time to reach the equilibrium was 2 hours and the necessary argon pressure was 2.2 kPa.

At equilibrium state, the activity of Sb is the same in all samples inside a closed system. Unless the activity of Sb in the reference Sb-Sn is known, it is possible to calculate the activity of Sb in the Ag-Sb-Sn (l):

$$a_{Sb(Ag\text{-}Sb\text{-}Sn\text{-})} = a_{Sb(Sn\text{-}Sb)} \tag{1}$$

$$\gamma_{Sb(Ag\text{-}Sb\text{-}Sn)} = X_{Sb(Sn\text{-}Sb)} * \gamma_{Sb(Sn\text{-}Sb)} / X_{Sb(Ag\text{-}Sb\text{-}Sn)} \tag{2}$$

where $X_{Sb(Sn\text{-}Sb)}$ and $X_{Sb(Cu\text{-}Sn\text{-}Sb)}$ denote the equilibrium mole fractions of Sb in Sb-Sn and Ag-Sb-Sn, respectively, and $\gamma_{Sb(Sn\text{-}Sb)}$ and $\gamma_{Sb(Ag\text{-}Sn\text{-}Sb)}$ are the corresponding activity coefficients of Sb.

To present the activity coefficient of Sb (γ_{Sb}) in the reference Sn-Sb solution Eqn. (3), proposed by Jönsson [14] and verified by Vassiliev [15], with the following Redlich-Kister parameters were used:

$$
\begin{aligned}
&{}^{E}G^{L}_{Sb,Sn} = X_{Sb}X_{Sn}\left[\sum_{m=0}^{n} {}^{(m)}L^{L}_{Sb,Sn}\left(X_{Sb}-X_{Sn}\right)^{m}\right]\\
&{}^{(0)}L^{L}_{Sb,Sn} = -5695.14 - 1.7090 * T \qquad \text{[J/mol]}\\
&{}^{(1)}L^{L}_{Sb,Sn} = 782.595 \qquad \text{[J/mol]}\\
&{}^{(2)}L^{L}_{Sb,Sn} = 1840.01 \qquad \text{[J/mol]}
\end{aligned}
\tag{3}
$$

where ${}^{(m)}L^{\varphi}_{Sb,Sn}$, T and ${}^{E}G^{L}_{Sb,Sn}$ denote the binary $L-$parameter, the temperature and the excess Gibbs energy, respectively. The symbol L represents the state of the mixed phase which is liquid for the used reference Sb-Sn binary alloy. The number of the Redlich-Kister (RK) polynomials (n) necessary for the precise thermodynamic description of the Sb-Sn alloy is 3 ($m = 0.1$ and 2) according to Refs. [14] and [15].

3. Results

Tables 1 and 2 present values of Sb activity coefficients determined by ES technique. The reference state for the activities is pure liquid Sb.

Since many ternary liquid alloys satisfy the Redlich-Kister-Muggianu (RKM) model [13, 16, 17] the obtained a_{Sb} data were used to fit them to this model using a mathematical regression procedure. The excess Gibbs energy of ternary solution, assumed as random mixture of components A, B and ,C taking both binary and ternary interactions into account, can be described by a sub-regular-solution type model after Muggianu [17] as follows (Eqn. 4):

$$
\begin{aligned}
{}^{E}G^{L}_{ABC} &= X_A X_B \sum_{m=0}^{n_{AB}} {}^{(m)}L^{L}_{AB}(X_A - X_B)^m + X_A X_C \sum_{m=0}^{n_{AC}} {}^{(m)}L^{L}_{AC}(X_A - X_C)^m +\\
&+ X_B X_C \sum_{m=0}^{n_{BC}} {}^{(m)}L^{L}_{BC}(X_B - X_C)^m + X_A X_B X_C\left[{}^{(0)}L^{L}_{ABC}X_A + {}^{(1)}L^{L}_{ABC}X_B + {}^{(2)}L^{L}_{ABC}X_C\right]
\end{aligned}
\tag{4}
$$

where X_A, X_B and X_C are the mole fractions of the components in alphabetic order (Ag, Sb, Sn) and L's are the so-called binary (${}^{(m)}L^{L}_{AB}$, ${}^{(m)}L^{L}_{AC}$, ${}^{(m)}L^{L}_{BC}$) and the ternary (${}^{(0)}L^{L}_{ABC}$, ${}^{(1)}L^{L}_{ABC}$, ${}^{(2)}L^{L}_{ABC}$) interaction parameters. Using the regression on the measured activities of Sb at limited number of compositions and temperatures, not only the activity of Sb, but that of Sn and Cu could also be obtained as a function of temperature and composition in an equation form. If the ternary interaction parameters are equal or very near to each other (${}^{(0)}L^{L}_{ABC} = {}^{(1)}L^{L}_{ABC} = {}^{(2)}L^{L}_{ABC} = L^{L}_{ABC}$), Eqn (4) turns to a simpler form (Eqn. (5)) as follows:

$$
\begin{aligned}
{}^{E}G^{L}_{ABC} &= X_A X_B \sum_{m=0}^{n_{AB}} {}^{(m)}L^{L}_{AB}(X_A - X_B)^m + X_A X_C \sum_{m=0}^{n_{AC}} {}^{(m)}L^{L}_{AC}(X_A - X_C)^m +\\
&+ X_B X_C \sum_{m=0}^{n_{BC}} {}^{(m)}L^{L}_{BC}(X_B - X_C)^m + X_A X_B X_C L^{L}_{ABC}
\end{aligned}
\tag{5}
$$

Because of the relatively small number of experimental (ES) data and the relatively low Sb-concentration difference between the compositions having equal Sb-activity, a multiple regression resulting in all the three ternary interaction parameters (${}^{(0)}L^{L}_{ABC}$, ${}^{(1)}L^{L}_{ABC}$ and ${}^{(2)}L^{L}_{ABC}$) was not possible with the necessary accuracy. Therefore, assuming the equality of these parameters, the single parameter L^{L}_{ABC} was determined using a single regression. The regressions were performed separately at each temperature. The binary interaction parameters of liquid Ag-Sb and Ag-Sn alloys were taken from [15, 18, 19].

Table 1.
Experimental activity values of Sb, obtained by the ES method at 1473 K, 1373 K and 1273 K. The last column presents the activity of Sb which is the same for both ternary and the reference binary alloys

1473 K						
Ag-Sb-Sn				Sb-Sn (REF.)		
X_{Ag}	X_{Sn}	X_{Sb}	γ_{Sb}	X_{Sb}	γ_{Sb}	a_{Sb}
0.8199	0.0413	0.1387	1.2170	0.2511	0.6722	0.1688
0.8013	0.0894	0.1093	1.5446	0.2511	0.6722	0.1688
0.7701	0.1346	0.0953	1.7713	0.2511	0.6722	0.1688
0.6730	0.1662	0.1608	1.0497	0.2511	0.6722	0.1688
0.6426	0.2174	0.1400	1.2056	0.2511	0.6722	0.1688
0.3819	0.4646	0.1535	1.1063	0.2524	0.6731	0.1699
0.3537	0.5263	0.1200	1.4151	0.2524	0.6731	0.1699
0.3080	0.5663	0.1257	1.3511	0.2524	0.6731	0.1699
0.2578	0.6087	0.1335	1.2722	0.2524	0.6731	0.1699
0.2105	0.6304	0.1592	1.0673	0.2524	0.6731	0.1699
0.5771	0.2454	0.1775	1.0389	0.2692	0.6850	0.1844
0.5714	0.3063	0.1222	1.5090	0.2692	0.6850	0.1844

1473 K						
Ag-Sb-Sn				Sb-Sn (REF.)		
X_{Ag}	X_{Sn}	X_{Sb}	γ_{Sb}	X_{Sb}	γ_{Sb}	a_{Sb}
0.5246	0.3606	0.1148	1.6064	0.2692	0.6850	0.1844
0.4834	0.3925	0.1240	1.4871	0.2692	0.6850	0.1844
0.4214	0.4163	0.1623	1.1366	0.2692	0.6850	0.1844
0.1664	0.6614	0.1723	1.0758	0.2702	0.6858	0.1853
0.1320	0.7461	0.1219	1.5204	0.2702	0.6858	0.1853
0.0894	0.7894	0.1211	1.5298	0.2702	0.6858	0.1853
0.0436	0.8312	0.1252	1.4800	0.2702	0.6858	0.1853
0.0264	0.7976	0.1760	1.0530	0.2702	0.6858	0.1853
1373 K						
0.8840	0.0446	0.0714	3.4249	0.3377	0.7246	0.2447
0.8432	0.0941	0.0627	3.9035	0.3377	0.7246	0.2447
0.8099	0.1415	0.0486	5.0334	0.3377	0.7246	0.2447
0.7321	0.1808	0.0870	2.8110	0.3377	0.7246	0.2447
0.6910	0.2337	0.0752	3.2531	0.3377	0.7246	0.2447
0.4132	0.5026	0.0842	3.0708	0.3513	0.7356	0.2584
0.3782	0.5628	0.0590	4.3831	0.3513	0.7356	0.2584
0.3261	0.5995	0.0744	3.4715	0.3513	0.7356	0.2584
0.2745	0.6481	0.0773	3.3417	0.3513	0.7356	0.2584
0.2298	0.6884	0.0818	3.1588	0.3513	0.7356	0.2584
0.6270	0.2666	0.1064	2.6602	0.3751	0.7547	0.2831
0.6173	0.3309	0.0518	5.4602	0.3751	0.7547	0.2831
0.5637	0.3874	0.0489	5.7878	0.3751	0.7547	0.2831
0.5221	0.4239	0.0540	5.2409	0.3751	0.7547	0.2831
0.4636	0.4581	0.0783	3.6167	0.3751	0.7547	0.2831
0.1828	0.7266	0.0906	3.2974	0.3898	0.7666	0.2988
0.1429	0.8074	0.0497	6.0072	0.3898	0.7666	0.2988
0.0966	0.8531	0.0503	5.9428	0.3898	0.7666	0.2988
0.0472	0.9011	0.0517	5.7775	0.3898	0.7666	0.2988
0.0293	0.8849	0.0858	3.4836	0.3898	0.7666	0.2988
1273 K						
Ag-Sb-Sn				Sb-Sn (REF.)		
X_{Ag}	X_{Sn}	X_{Sb}	γ_{Sb}	X_{Sb}	γ_{Sb}	a_{Sb}
0.7984	0.0403	0.1614	1.2888	0.3040	0.6840	0.2079
0.7807	0.0871	0.1322	1.5731	0.3040	0.6840	0.2079
0.7508	0.1312	0.1180	1.7623	0.3040	0.6840	0.2079
0.6601	0.1630	0.1769	1.1752	0.3040	0.6840	0.2079
0.6269	0.2121	0.1610	1.2915	0.3040	0.6840	0.2079
0.3711	0.4514	0.1775	1.2018	0.3098	0.6887	0.2134
0.3430	0.5104	0.1466	1.4553	0.3098	0.6887	0.2134
0.2992	0.5501	0.1506	1.4165	0.3098	0.6887	0.2134
0.2502	0.5907	0.1592	1.3406	0.3098	0.6887	0.2134
0.2039	0.6107	0.1854	1.1512	0.3098	0.6887	0.2134
0.5624	0.2391	0.1985	1.1137	0.3179	0.6953	0.2211
0.5542	0.2971	0.1487	1.4864	0.3179	0.6953	0.2211
0.5089	0.3497	0.1414	1.5639	0.3179	0.6953	0.2211
0.4657	0.3781	0.1562	1.4153	0.3179	0.6953	0.2211
0.4088	0.4039	0.1873	1.1806	0.3179	0.6953	0.2211
0.1611	0.6406	0.1983	1.1354	0.3222	0.6988	0.2251
0.1276	0.7210	0.1514	1.4869	0.3222	0.6988	0.2251
0.0862	0.7608	0.1531	1.4709	0.3222	0.6988	0.2251
0.0421	0.8039	0.1540	1.4619	0.3222	0.6988	0.2251
0.0255	0.7704	0.2041	1.1028	0.3222	0.6988	0.2251

Table 2.
Additional values for 1373 K (second run)

1373 K						
Ag-Sb-Sn				Sb-Sn (REF.)		
X_{Ag}	X_{Sn}	X_{Sb}	γ_{Sb}	X_{Sb}	γ_{Sb}	a_{Sb}
0.0234	0.7064	0.2702	0.6738	0.2706	0.6728	0.1821
0.0364	0.6952	0.2684	0.6783	0.2706	0.6728	0.1821
0.0749	0.6615	0.2636	0.6907	0.2706	0.6728	0.1821
0.1111	0.6282	0.2607	0.6984	0.2706	0.6728	0.1821
0.1493	0.5936	0.2571	0.7081	0.2706	0.6728	0.1821
0.1845	0.5526	0.2629	0.7099	0.2758	0.6767	0.1866
0.3351	0.4077	0.2572	0.7257	0.2758	0.6767	0.1866
0.3012	0.4482	0.2506	0.7447	0.2758	0.6767	0.1866
0.2239	0.5285	0.2476	0.7539	0.2758	0.6767	0.1866
0.2669	0.4907	0.2423	0.7703	0.2758	0.6767	0.1866
0.7188	0.0362	0.2450	0.7828	0.2816	0.6810	0.1918
0.6850	0.0764	0.2386	0.8038	0.2816	0.6810	0.1918
0.6556	0.1145	0.2299	0.8343	0.2816	0.6810	0.1918
0.6216	0.1535	0.2249	0.8527	0.2816	0.6810	0.1918
0.5806	0.1964	0.2231	0.8597	0.2816	0.6810	0.1918
0.4640	0.3189	0.2172	0.8712	0.2787	0.6788	0.1892
0.4332	0.3517	0.2151	0.8797	0.2787	0.6788	0.1892
0.5163	0.2768	0.2069	0.9144	0.2787	0.6788	0.1892
0.4010	0.3962	0.2029	0.9325	0.2787	0.6788	0.1892
0.5665	0.2409	0.1926	0.9824	0.2787	0.6788	0.1892

The excess chemical potential of Sb can be obtained using the following well-known thermodynamic relationship:

$$
\begin{aligned}
{}^{E}\mu^{L}_{Sb} &= RT\ \ln\gamma_{Sb} = RT\ \ln\left(\frac{a_{Sb}}{X_{Sb}}\right) = \\
&= {}^{E}G^{L}_{AgSbSn} - X_{Ag}\frac{\partial {}^{E}G^{L}_{AgSbSn}}{\partial X_{Ag}} - X_{Sn}\frac{\partial {}^{E}G^{L}_{AgSbSn}}{\partial X_{Sn}}
\end{aligned}
\qquad (6)
$$

Performing the mathematical operations of the right hand side of Eqn. (6) by means of the right hand side of Eqn. (4), we obtain the following equation:

$$
\begin{aligned}
{}^{E}\mu^{L}_{Sb} = {}^{(0)}L^{L}_{AgSbSn}\left(X_{Ag}\right)^2 X_{Sn}(1-3X_{Sb}) + {}^{(1)}L^{L}_{AgSbSn}\ X_{Ag}X_{Sb}X_{Sn}(2-3X_{Sb}) + \\
+ {}^{(2)}L^{L}_{AgSbSn}\ X_{Ag}\left(X_{Sn}\right)^2(1-3X_{Sb}) - \boldsymbol{Y}
\end{aligned}
\qquad (7)
$$

where Y includes terms having only binary L-parameters.

Adding Y to ${}^{E}\mu^{L}_{Sb}$ the three ternary L-parameters can be obtained by fitting as:

$$
\begin{aligned}
Ysumma = Y + {}^{E}\mu^{L}_{Sb} = {}^{(0)}L^{L}_{AgSbSn}\left(X_{Ag}\right)^2 X_{Sn}(1-3X_{Sb}) + \\
+ {}^{(1)}L^{L}_{AgSbSn}X_{Ag}X_{Sb}X_{Sn}(2-3X_{Sb}) + {}^{(2)}L^{L}_{AgSbSn}X_{Ag}\left(X_{Sn}\right)^2(1-3X_{Sb})
\end{aligned}
\qquad (8)
$$

By varying the composition the three ternary parameters can finally be obtained by solving a set of linear equations or by a multiple regression as:

$$
\begin{bmatrix}
\left(X_{Ag}\right)^2\cdot X_{Sn}(1-3X_{Sb})_1 & \left(X_{Ag}X_{Sb}X_{Sn}(2-3X_{Sb})\right)_1 & \left(X_{Ag}\left(X_{Sn}\right)^2(1-3X_{Sb})\right)_1 \\
\left(X_{Ag}\right)^2\cdot X_{Sn}(1-3X_{Sb})_2 & \left(X_{Ag}X_{Sb}X_{Sn}(2-3X_{Sb})\right)_2 & \left(X_{Ag}\left(X_{Sn}\right)^2(1-3X_{Sb})\right)_2 \\
. & . & . \\
\left(X_{Ag}\right)^2\cdot X_{Sn}(1-3X_{Sb})_n & \left(X_{Ag}X_{Sb}X_{Sn}(2-3X_{Sb})\right)_n & \left(X_{Ag}\left(X_{Sn}\right)^2(1-3X_{Sb})\right)_n
\end{bmatrix}
\mathbf{X}
\begin{bmatrix}
{}^{(0)}L^{L}_{AgSbSn} \\
{}^{(1)}L^{L}_{AgSbSn} \\
{}^{(2)}L^{L}_{AgSbSn}
\end{bmatrix}
=
\begin{bmatrix}
Ysumma_1 \\
Ysumma_2 \\
. \\
Ysumma_n
\end{bmatrix}
\qquad (9)
$$

where 'n' is the number of the considered compositions. If n>4 the solution of the linear equation system becomes a multiple regression problem. The more compositions are used the more accurate are fitted parameters.

If the three ternary L-parameters are equal to each other, Eqn. (8) turns to a simpler equation as:

$$
Ysumma = Y + {}^{E}\mu^{L}_{Sb} = L^{L}_{AgSbSn}X_{Ag}X_{Sn}(1-2X_{Sb}) \qquad (10)
$$

Thus, plotting *Ysumma vs.* $X_{Ag}X_{Sn}(1-2X_{Sb})$ the unknown single-ternary parameter L^{L}_{AgSbSn} can be determined.

Performing the fit for the data at 1473 K and 1273 K the values of L^{L}_{AgSbSn} are as follows: at 1473 K L^{L}_{AgSbSn} =78760 J/mol (corr. coeff.: 0.889), at 1273 K L^{L}_{AgSbSn} = 70880 J/mol (corr coeff.: 0.868) taking the binary *L*-parameters of Ag-Sb, Ag-Sn and Sb-Sn systems from Refs. [18, 19, 15] respectively. Replacing the binary *L*-parameters of Ag-Sb, Ag-Sn systems of Refs. [18, 19] with those given in Ref. [8] the obtained L^{L}_{AgSbSn} .parameter changes at both 1473 K and 1273 K only slightly since the difference between the thermodynamic data of these databases is negligible. A larger change of L^{L}_{AgSbSn} was obtained if the data of Ref. [9] is used since the latter source deviates from other literature sources as for the binary liquid Sb-Sn system, as can be seen in Tables 3 and 4 and Fig. 2.

Table 3.
Values of *L*-parameters of Ag-Sb, Ag-Sn and Sb-Sn systems from Refs. [18, 19, 15] and from Ref. [8]

	Databases in Refs. [15, 18, 19]			COST 531 database [COST] including Ref. [8]		
	A	*B*	*C*	*A*	*B*	*C*
L^{0}_{AgSb} [18]	-3619.5	-8.2962	0	-821.8	-9.6561	0
L^{1}_{AgSb} [18]	-21732.2	8.4996	0	-19309	4.4239	0
L^{2}_{AgSb} [18]	-6345.2	3.2151	0	-10381.2	0	0
L^{3}_{AgSb} [18]	0	0	0	0	0	0
L^{0}_{AgSn} [19]	-6386.2	-5.6668	0	-5146.7	-5.0103	0
L^{1}_{AgSn} [19]	-14689	3.3398	0	-15799.3	3.3208	0
L^{2}_{AgSn} [19]	-5339.3	1.058	0	-6687.5	0	0
L^{3}_{AgSn} [19]	1943.6	-1.0001	0	0	0	0
L^{0}_{SbSn} [15]	-5695.1	-1.709	0	-5695.1	-1.709	0
L^{1}_{SbSn} [15]	782.6	0	0	782.6	0	0
L^{2}_{SbSn} [15]	1840.9	0	0	1840.9	0	0
L^{3}_{SbSn} [15]	0	0	0	0	0	0

Table 4.
Values of *L*-parameters of Ag-Sb, Ag-Sn and Sb-Sn systems from Ref. [9]

	Data of Ref. [9]			
	A	*B*	*C*	*L* at 1273 K
L^{0}_{AgSb}	768.717449	-11.7667104	0	-14210
L^{1}_{AgSb}	-20530.6877	5.90571777	0	-13010
L^{2}_{AgSb}	-9380.44465	0	0	-9380
L^{3}_{AgSb}	0	0	0	0
L^{0}_{AgSn}	-28.297	-34.5762	3.4526	-12620
L^{1}_{AgSn}	-17256.756	5.4247	0	-10350
L^{2}_{AgSn}	-10737.534	4.8577	0	-4554
L^{3}_{AgSn}	0	0	0	0
L^{0}_{SbSn}	-5536.588	1.5399	0	-3576
L^{1}_{SbSn}	177.931	0	0	177.931
L^{2}_{SbSn}	883.186	0	0	883.186
L^{3}_{SbSn}	0	0	0	0

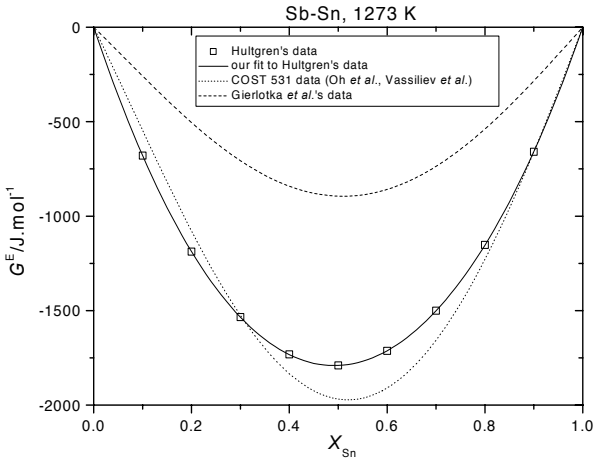

Fig. 2. The excess Gibbs energy of liquid Sb-Sn as a function of composition at 1273 K in various literature sources (Hultgren [20], COST 531 database [21], Gierlotka *et al*. [9])

The fit using the data at 1373 K was not satisfactory therefore the value of L^{L}_{AgSbSn} at 1373 K was estimated using the following linear equation obtained from the values of L^{L}_{AgSbSn} at 1273 K and 1473 K: $L^{L}_{AgSbSn}(T)/\text{J.mol}^{-1} = 20720 + 39.4 \cdot T$. Using the latter equation, L^{L}_{AgSbSn} = 74816 J/mol was obtained at 1373 K. In order to check the validity of the RKM model, the Sb activity data obtained by the model were compared to the measured activity data in Tables 3 and 4. Not all individual measured activity data in Table 1 were used for the fit to the model at 1273 K and 1473 K. Table 5 shows which individual measured data were selected in order to reach the best fit. It can be seen that the measured activity data at high and low Ag/Sn molar ratios were not taken for the fit (the values in italics). Concerning the intermediate Ag/Sn molar ratios a good agreement between the measured and modelled activity data was found.

Table 5.
Comparison of the directly measured and fitted activity values of Sb

1473 K				
X_{Ag}	X_{Sn}	X_{Sb}	a_{Sb} (meas.)	a_{Sb} (model.)
0.8199	0.0413	0.1387	*0.1688*	0.0560
0.8013	0.0894	0.1093	*0.1688*	0.0545
0.7701	0.1346	0.0953	*0.1688*	0.0602
0.6730	0.1662	0.1608	*0.1688*	0.1347
0.6426	0.2174	0.1400	*0.1688*	0.1378
0.3819	0.4646	0.1535	*0.1699*	0.2064
0.3537	0.5263	0.1200	*0.1699*	0.1711
0.3080	0.5663	0.1257	*0.1699*	0.1698
0.2578	0.6087	0.1335	*0.1699*	0.1661
0.2105	0.6304	0.1592	*0.1699*	0.1762
0.5771	0.2454	0.1775	*0.1844*	0.1901
0.5714	0.3063	0.1222	*0.1844*	0.1524
0.5246	0.3606	0.1148	*0.1844*	0.1583
0.4834	0.3925	0.1240	*0.1844*	0.1743
0.4214	0.4163	0.1623	*0.1844*	0.2146
0.1664	0.6614	0.1723	*0.1853*	0.1726
0.1320	0.7461	0.1219	*0.1853*	0.1165
0.0894	0.7894	0.1211	*0.1853*	0.1015
0.0436	0.8312	0.1252	*0.1853*	0.0892
0.0264	0.7976	0.1760	*0.1853*	0.1204
1273 K				
X_{Ag}	X_{Sn}	X_{Sb}	a_{Sb} (meas.)	a_{Sb} (model.)
0.7984	0.0403	0.1614	*0.2079*	0.0662
0.7807	0.0871	0.1322	*0.2079*	0.0652
0.7508	0.1312	0.1180	*0.2079*	0.0727
0.6601	0.1630	0.1769	*0.2079*	0.1488
0.6269	0.2121	0.1610	*0.2079*	0.1572
0.3711	0.4514	0.1775	*0.2134*	0.2274
0.3430	0.5104	0.1466	*0.2134*	0.1947
0.2992	0.5501	0.1506	*0.2134*	0.1901
0.2502	0.5907	0.1592	*0.2134*	0.1852

1273 K				
X_{Ag}	X_{Sn}	X_{Sb}	a_{Sb} (meas.)	a_{Sb} (model.)
0.2039	0.6107	0.1854	*0.2134*	0.1935
0.5624	0.2391	0.1985	*0.2211*	0.2131
0.5542	0.2971	0.1487	*0.2211*	0.1791
0.5089	0.3497	0.1414	*0.2211*	0.1856
0.4657	0.3781	0.1562	*0.2211*	0.2067
0.4088	0.4039	0.1873	*0.2211*	0.2379
0.1611	0.6406	0.1983	*0.2251*	0.1884
0.1276	0.7210	0.1514	*0.2251*	0.1358
0.0862	0.7608	0.1531	*0.2251*	0.1214
0.0421	0.8039	0.1540	*0.2251*	0.1051
0.0255	0.7704	0.2041	*0.2251*	0.1356
1373 K				
X_{Ag}	X_{Sn}	X_{Sb}	a_{Sb} (meas.)	a_{Sb} (model.)
0.8840	0.0446	0.0714	*0.2447*	0.0238
0.8432	0.0941	0.0627	*0.2447*	0.0378
0.8099	0.1415	0.0486	*0.2447*	0.0485
0.7321	0.1808	0.0870	*0.2447*	0.1290
0.6910	0.2337	0.0752	*0.2447*	0.1662
0.4132	0.5026	0.0842	*0.2584*	0.3758
0.3782	0.5628	0.0590	*0.2584*	0.3034
0.3261	0.5995	0.0744	*0.2584*	0.3078
0.2745	0.6481	0.0773	*0.2584*	0.2669
0.2298	0.6884	0.0818	*0.2584*	0.2299
0.6270	0.2666	0.1064	*0.2831*	0.2627
0.6173	0.3309	0.0518	*0.2831*	0.2115
0.5637	0.3874	0.0489	*0.2831*	0.2487
0.5221	0.4239	0.0540	*0.2831*	0.2890
0.4636	0.4581	0.0783	*0.2831*	0.3667
0.1828	0.7266	0.0906	*0.2988*	0.1944
0.1429	0.8074	0.0497	*0.2988*	0.0966
0.0966	0.8531	0.0503	*0.2988*	0.0687
0.0472	0.9011	0.0517	*0.2988*	0.0457
0.0293	0.8849	0.0858	*0.2988*	0.0633
second run at 1373 K				
0.0234	0.7064	0.2702	*0.1821*	0.1926
0.0364	0.6952	0.2684	*0.1821*	0.1970
0.0749	0.6615	0.2636	*0.1821*	0.2102
0.1111	0.6282	0.2607	*0.1821*	0.2234
0.1493	0.5936	0.2571	*0.1821*	0.2360
0.1845	0.5526	0.2629	*0.1866*	0.2543
0.3351	0.4077	0.2572	*0.1866*	0.2883
0.3012	0.4482	0.2506	*0.1866*	0.2777
0.2239	0.5285	0.2476	*0.1866*	0.2550
0.2669	0.4907	0.2423	*0.1866*	0.2632
0.7188	0.0362	0.2450	*0.1918*	0.1418
0.6850	0.0764	0.2386	*0.1918*	0.1624
0.6556	0.1145	0.2299	*0.1918*	0.1779
0.6216	0.1535	0.2249	*0.1918*	0.1963
0.5806	0.1964	0.2231	*0.1918*	0.2177
0.4640	0.3189	0.2172	*0.1892*	0.2547
0.4332	0.3517	0.2151	*0.1892*	0.2576
0.5163	0.2768	0.2069	*0.1892*	0.2341
0.4010	0.3962	0.2029	*0.1892*	0.2495
0.5665	0.2409	0.1926	*0.1892*	0.2055

A further possibility for comparison between the measured and modelled data is to calculate the isoactivity lines by means of the obtained model parameters and plot them together with the measured data in the ternary composition diagram. It can be seen in Tables 1 and 2 that measured compositions have the same measured activity in the experiments. Using the RKM model parameters it is possible to find the compositions having the same activity. Figure 3 shows the comparison of the measured and modelled data at 1473 K.

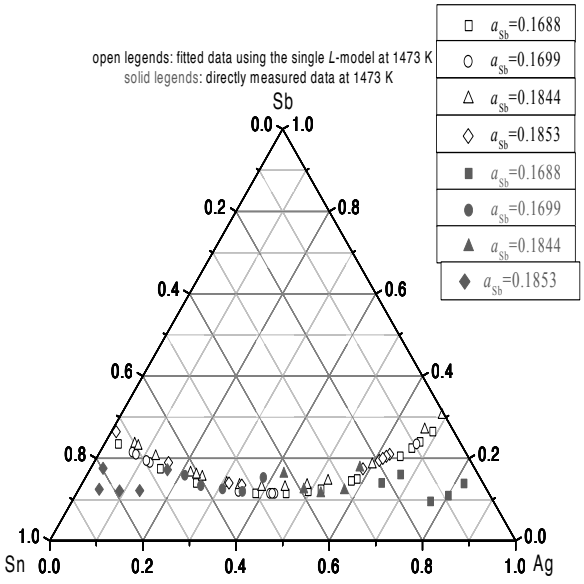

Fig. 3. The comparison of measured and modelled Sb-activity data

It can be seen that there are larger deviations between the measured and calculated results only for the sets at highest and at the lowest Ag/Sn molar ratios, i.e. for seven compositions of the total measured twenty compositions. The same feature, *i.e.* larger deviations only at high and low Ag/Sn molar ratios, can be seen at 1273 K and for the second run at 1373 K, whereas the deviation for the first run at 1373 K is larger.

As a further comparison, Figs. 4, 5 and 6 presents the activities of all the three components, using the ternary *L*-parameters obtained in this work and in Ref. [9] for three isothermal sections (X_{Ag}/X_{Sn}=1, 3 and 1/3) at 1273 K. In addition, the figure shows the case when no ternary interaction is taken into account, using the binary paramaters of Refs. [15, 18, 19]. It can be seen that in general the activities obtained using the assessed parameters of [9] are near to those with no ternary interaction whereas the data of this work deviate larger at certain compositions. In general, it can be stated that the activities obtained in the present work are somewhat higher than that obtained using the assessment parameters of [9] and when no ternary interaction is taken into account. Nevertheless, the assessment of the ternary liquid Ag-Sb-Sn system by Gierlotka *et al.*[9] is based so far on only one experimental source of mixing data at 980°C over the isothermal section X_{Sn}/X_{Sb}=1/4 in Ref. [22].

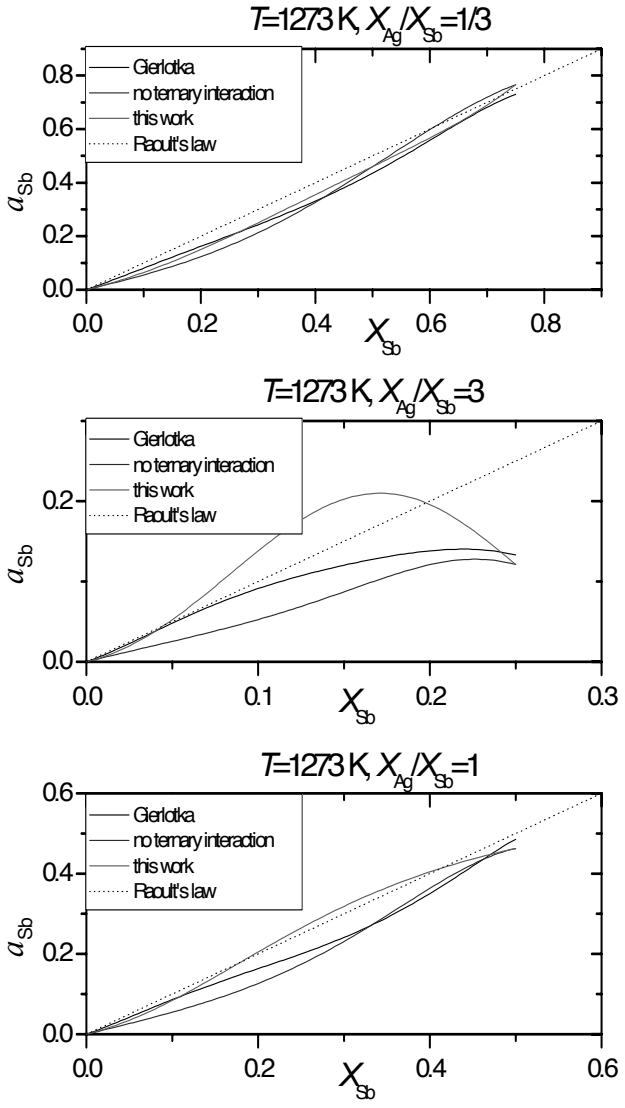

Fig. 4. Activity of Sb, using the ternary *L*-parameters obtained in this work and in Ref. [9], as well as taking no ternary interaction into account, for three isothermal sections (X_{Ag}/X_{Sn}=1, 3 and 1/3) at 1273 K

4. Conclusions

The activity of antimony in Ag-Sb-Sn liquid alloy was determined using the ES method and obtained experimental

values were fitted to the Redlich-Kister-Muggianu (RKM) model. Antimony activities obtained in this work are somewhat higher than that obtained using the assessment parameters of [9] and when no ternary interaction is taken into account. Nevertheless, the assessment of the ternary liquid Ag-Sb-Sn system by Gierlotka *et al.*[9] is based on the so far only one experimental source of mixing data at 980 °C over the isothermal section X_{Sn}/X_{Sb}=1/4 in Ref. [22], not at direct measurements.

The results will be used for further work in the framework of COST Action MP0602 "High Temperature Solders".

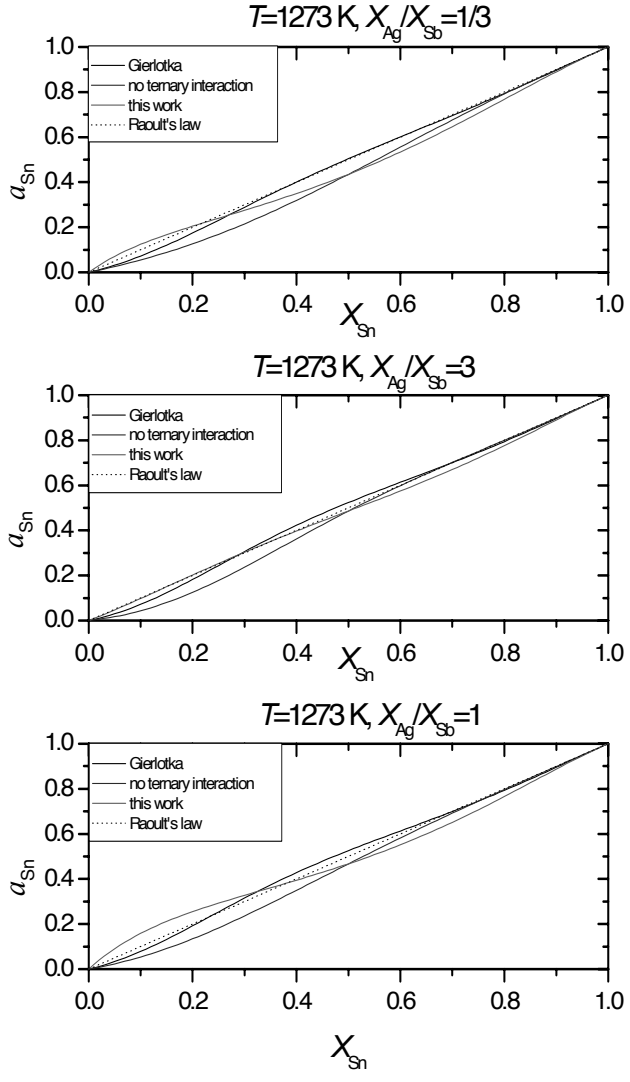

Fig. 5. Activity of Sn, using the ternary *L*-parameters obtained in this work and in Ref. [9], as well as taking no ternary interaction into account, for three isothermal sections (X_{Ag}/X_{Sn}=1, 3 and 1/3) at 1273 K

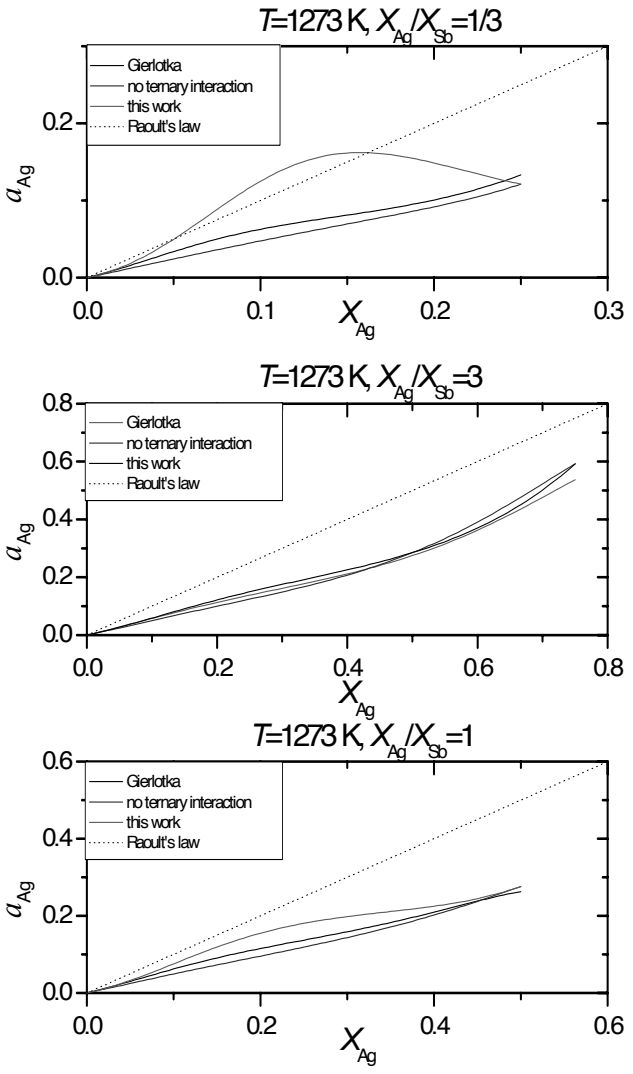

Fig. 6. Activity of Ag, using the ternary *L*-parameters obtained in this work and in Ref. [9], as well as taking no ternary interaction into account, for three isothermal sections (X_{Ag}/X_{Sn}=1, 3 and 1/3) at 1273 K

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