

Electrical resistivity of In–Sb liquid system and its relation to thermodynamic behaviour

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The electrical resistivity of liquid alloys in the system In–Sb has been determined using a.d.c. four probe method. The resistivities range from 40 to 120 $\mu\Omega$ cm and show a positive temperature dependence. A maximum in electrical resistivity is observed at compositions close to that of the inter-metallic compound InSb. Such a compound behaves as a semiconductor in the solid state and as a metal in the liquid state. Maxima are found in the reduced resistivity and in the excess thermodynamic stability at about 50 at% Sb.

1. Introduction

There has been great interest in studying the electrical properties and thermodynamic characteristics of III–V semiconductor alloys [1, 2]. Such quantities provide information regarding interatomic interaction and their effects upon structure. Generally, the 1:1 intermetallic compounds in the A^{III}–B^V systems dominate the binary phase diagrams. At such compositions these alloys present properties which characterize conventional solid semiconductors. This makes such systems potentially useful as electronic devices since a large range of conditions, essential to an electronic device, can be varied while the compounds are stable.

The measurement of the electrical properties of the In–Sb system has been partially accomplished previously [3, 6]. Related binary alloy systems are also encountered in the literature [7, 10]. InSb is a semiconductor but on melting its electrical conductivity exhibits metallic behaviour. It is expected that the whole alloy system behaves as a simple metallic component in the liquid state [6]. Here we present the electrical resistivity, ρ , of the In–Sb system in a range between 650 and 750°C and its correlation with the thermodyn-

amic excess stability. From the experimental results the residual resistivity, $\Delta\rho$, can be evaluated by using [11].

$$\Delta\rho = \rho - (x_{\text{In}}\rho_{\text{In}} + y_{\text{Sb}}\rho_{\text{Sb}}) \quad (1)$$

where x_{In} and y_{Sb} are the atomic fractions of indium and antimony, respectively; ρ_{In} and ρ_{Sb} are the resistivities of indium and antimony, respectively, at the temperature of measurement. The calculation of thermodynamic quantities for liquid alloys were based on published data [12], with the thermodynamic stability as defined for an A–B alloy by Darken [13]. Darken defined the second derivative of the molal free energy with respect to the mole fraction as “stability” of a solution. In order to evaluate the stability we need first to differentiate the general (isobaric, isothermal) thermodynamic relation of the partial molal for one of the components, B, for instance:

$$G_{\text{B}} = G + (1 - y) \frac{dG}{dy} \quad (2)$$

where y is the molar fraction of component B, and G is the molal free energy of the solution:

$$G = \bar{G}_{\text{A}}x + \bar{G}_{\text{B}}y \quad (3)$$

Equation 2 in turn is obtained by differentiating Equation 3 and using the Gibbs–Duhem relation:

$$x dG_A + y dG_B = 0 \quad (4)$$

Differentiating Equation 2 and using $d\bar{G}_B = RT d \ln a_B$ immediately gives:

$$\text{Stability:} \quad \frac{d^2 G}{dy^2} = -2RT \frac{d \ln a_B}{dx^2} \quad (5)$$

$$\text{Excess stability:} \quad \frac{d^2 G^{xs}}{dy^2} = -2RT \frac{d \ln \gamma_B}{dx^2} \quad (6)$$

$$\text{Ideal stability:} \quad \frac{d^2 G^{id}}{dy^2} = -2RT \frac{d \ln x}{dx^2} \quad (7)$$

where a is the chemical activity, γ is the activity coefficient, x and y represent the atomic fractions of components A and B respectively. The superscripts xs and id mean excess and ideal quantities. The excess stability is an indication of the deviation of thermodynamic quantities of the actual solution from those quantities in an ideal solution. That is, if we consider the change in partial molal free energy of the component i in solution

$$\begin{aligned} \Delta \bar{G}_i &= \bar{G}_i - G_i^0 \\ &= RT \ln a_i \\ &= RT \ln \gamma_i + RT \ln x_i \end{aligned} \quad (8)$$

where G_i^0 is the free energy of the pure component i , a_i is the chemical activity of component i , γ_i is its activity coefficient and x_i is the molar fraction for an ideal solution

$$(\Delta \bar{G}_i)_{ideal} = RT \ln x_i \quad (9)$$

since $\gamma_i = 1$ for an ideal solution, then the excess free energy is defined as

$$\Delta \bar{G}_i^{xs} = \Delta \bar{G}_i - (\Delta \bar{G}_i)_{ideal} \quad (10)$$

or

$$\Delta \bar{G}_i^{xs} = RT \ln \gamma_i \quad (11)$$

The excess stability is usually thought of as an indication of the extent to which electrons are tied up in bonding as the maxima in the excess stability function are associated with maxima in the electrical resistivity for some binary mixtures of liquid metals [10].

2. Experimental details

Alloy samples were prepared from 99.999% pure elements (Inlab materials). Weighed portions were

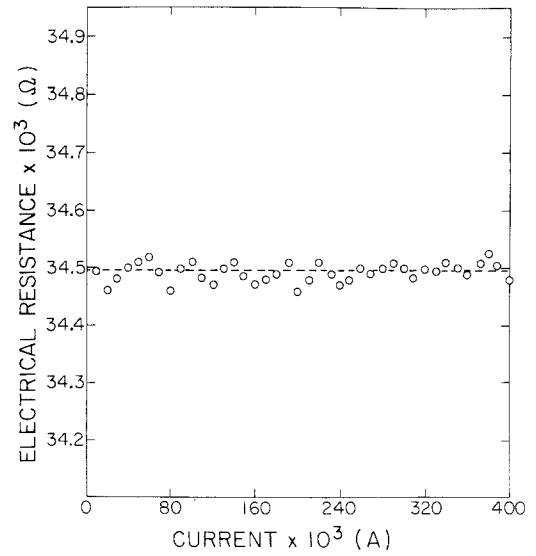


Figure 1 Calibration curve for measuring the resistivity of mercury at room temperature.

sealed inside evacuated quartz capsules, melted and homogenized before measurements. The experimental arrangement consisted of a capillary quartz tube (1 cm length, 0.05 cm diameter) inserted in a quartz crucible into which the alloys were melted under purified argon. The capillary tubes were calibrated previously with mercury at room temperature using a four-probe method [14] with tungsten wires as electrodes. Fig. 1 shows the effect of varying the current in the interval 0 to 400 mA on the electrical resistance of mercury. A constant value of 34.5 mΩ is observed. For determining the electrical resistivity of In–Sb alloys currents of 260, 300 and 320 mA were employed while cooling or heating in a temperature range between 650 and 750° C, at 20° C intervals. The resistivities could be calculated using

$$\rho_{In-Sb} = \left[\frac{V_{In-Sb}}{I_{In-Sb}} \frac{I_{Hg}}{V_{Hg}} \right] \rho_{Hg} \quad (12)$$

A least-squares program was used to analyse the resistivity temperature data.

3. Results

The electrical resistivity for the alloys as a function of temperature is shown in Fig. 2. A linear behaviour with a positive slope is found for all compositions in the liquid state. The reversed behaviour is observed for the intermetallic compound InSb in the solid state. Fig. 3 shows the

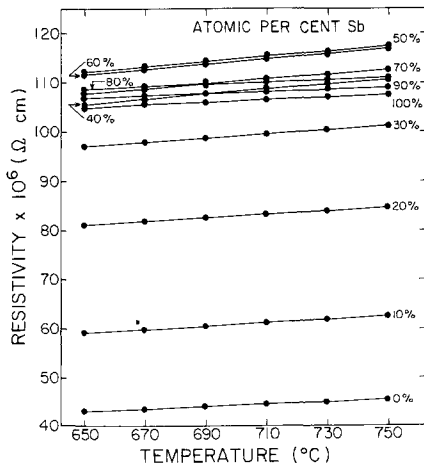


Figure 2 Temperature dependence of the resistivity of liquid InSb systems.

dependence of the resistivity with the reciprocal temperature for indium, antimony and InSb. The resistivity of antimony in the solid state is greater than in the liquid state, while the contrary is observed for indium. The dependence of the electrical resistivity with composition at 650, 690 and 750°C is shown in Fig. 4. A change in slope is observed at compositions close to that of the intermetallic compound InSb. The experimental results are compared with those of previous authors [5, 6]. No similar change in slope at 0.5 molar fraction antimony was observed before. The data listed by Hultgren *et al.* [12] was employed to calculate the thermodynamic excess stability of the liquid alloys at 900 K together with Equation 10 starting from chemical activity values in the In-Sb system and

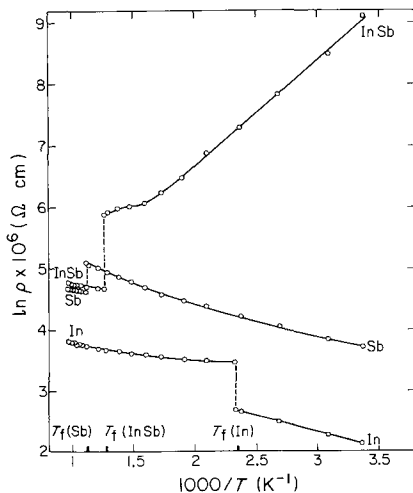


Figure 3 Dependence of $\ln \rho$ with the reciprocal temperature for indium, antimony and InSb.

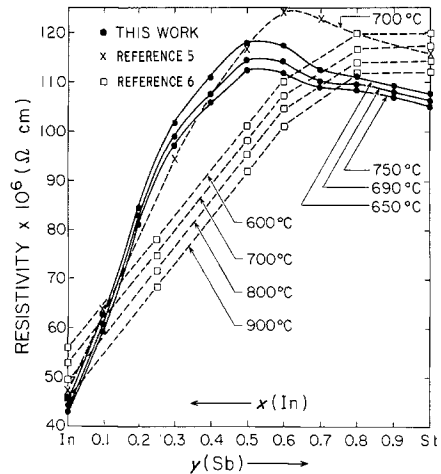


Figure 4 Composition dependence of the electrical resistivity of InSb alloys in the temperature range 650–750°C.

observing that if

$$\Delta \bar{G}_i = \bar{G}_i - G_i^0$$

then $d\Delta \bar{G}_i = d\bar{G}_i$, since G_i^0 is a constant. Such calculation indicates a maximum in the excess stability function at values close to $x_{Sb} \sim 0.5$.

4. Discussion and conclusions

A linear dependence of the electrical resistivity with temperature is observed for liquid alloys in the In–Sb system (see Fig. 2). The slope of such curves is positive and this is associated with metallic behaviour [14]. The temperature coefficients ($d\rho/dT$) of liquid indium, antimony and InSb are listed in Table I showing similar values to those reported by Cusak [15]. It is also observed that the intermetallic compound InSb behaves as a semiconductor in the solid state and as a metal in the liquid state (see Fig. 3) in agreement with Ioffe and Regal [16]. Fig. 4 shows the dependence of the electrical resistivity with composition at 650, 690 and 750°C. A change in slope is observed at compositions close to that of InSb. No such marked change of slope at 0.5 at% Sb is observed by previous authors, which we believe we were able to

TABLE I Temperature coefficients of, indium, antimony and InSb in the liquid state

Material	$d\rho/dT(\mu\Omega \text{ cm}^{-1} \text{ C}^{-1})$	
	Observed	Reference [15]
Indium	0.0247	0.0255
Antimony	0.0251	0.0251
InSb	0.0550	—

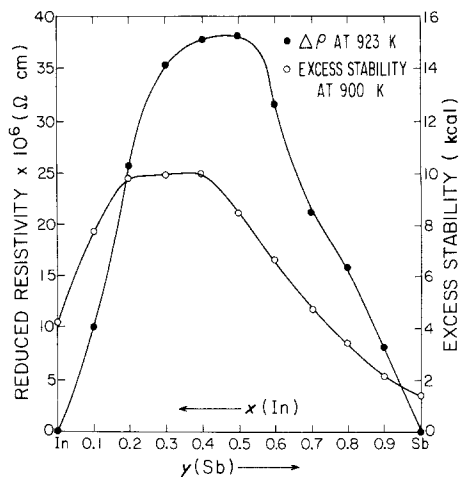


Figure 5 Composition dependence of the reduced resistivity and excess stability of InSb alloys at 923 and 900 K respectively.

detect due to the accuracy of our procedure (see calibration curve in Fig. 1).

Fig. 5 shows the residual resistivity, $\Delta\rho$, and the excess stability, as a function of composition. Maxima are observed at compositions around 50 at% Sb at which point an intermetallic compound forms. Such behaviour is usually taken as an indication of the magnitude of the binding of electrons in the valence shell. This in turn can be related to electrical properties by appropriate models [11].

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