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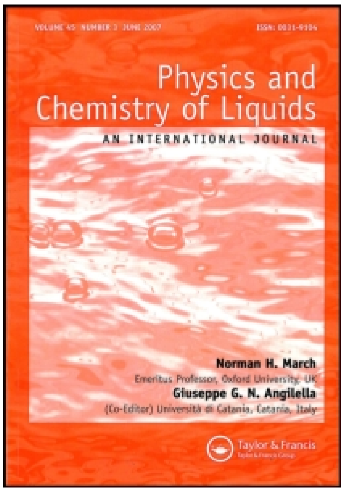

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ELECTRICAL RESISTIVITY OF LIQUID Sb-Te SOLUTIONS

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The specific resistivity of liquid antimony-tellurium alloys was determined by the DC four probe method. The cell with the capillary was used to measure potential drops in the temperature range 820–1150 K for pure antimony and six alloy compositions up to $X_{\mathrm{Te}} = 0.6$. Using experimental results obtained in the present study the resistivity change with the alloy composition at constant temperature was derived. It was demonstrated that depending on local ordering in the liquid state there is a interdependence between oxygen activity coefficient, diffusivity and the alloy conductivity measured in Sb-Te binary system.

Keywords: Resistivity; liquid solution; oxygen

1. INTRODUCTION

Specific electrical resistivity, ρ, is one of the few physical properties of materials that can give direct information about the structure, electron transport properties and electromagnetic phenomena in metals and their alloys. In practice, determination of this physical property can be used in the field of materials processing as a good indicator of phase changes. For instance, resistivity-temperature and resistivity-composition data can be used for monitoring composition change, in binary alloys. First studies [1] of liquid alloys along the lines of this technique have shown a general relationship between the resistivity-concentration curve and the phase diagram.

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Since the electron states in the condensed matter are responsible for the resistivity, ρ, measurements of this parameter can also be a good measure of the extent to which electrons are free in the liquid. Deviations from nearly free electrons behaviour (observed in pure liquid metals) due to the addition of alloying element speaks for the vanishing of the free Fermi surface for electrons as indicated by the increase in resistivity of the alloy. Consequently, it seems interesting to compare resistivity changes due to alloying with oxygen activity and mobility in the solution.

A dissolution reaction of oxygen in the liquid metal is frequently written as:

$$\frac{1}{2}O_2 \Leftrightarrow O \tag{1}$$

The equilibrium constant of this reaction can be determined by using various experimental techniques of studying gas-liquid equilibria. This approach does not require the knowledge about the state of oxygen entering the liquid in order to derive the solubility data. However, if reasonable assumptions have to be made about the model aiming at the prediction of the solubility data, this information is necessary to suggest a reasonable picture of interatomic interactions.

Unfortunately, experimental evidence does not carry a clear picture of what's going on in the metallic solution when non-metal enters it. Studies of Hall effect in liquid cesium [2] showed that free electron behaviour of pure cesium is disturbed by the addition of oxygen, which apparently removes free electrons from the conduction band. However, it is not clear if the removal of free electrons can be caused by O^{-2} or Cs_2O formation in the liquid state. Single resonance pattern observed by Host *et al.* [3], who carried out NMR studies of Cs^{133} in the Cs-O liquid solution, speaks for the presence of $O^{\ 2}$ ions. In a number of systems however, mixed states of the type: $\{\text{metal-O}\}^-$ $\{\text{metal}\}^+$ are more likely to be present. In both cases the availability of free electrons from the conduction band seems to be a necessary condition for oxygen to dissolve in the liquid metal.

Recently we have determined oxygen solubility, activity and diffusivity in the liquid Sb-Te solutions [4–6]. Liquid tellurium exhibits the variation of structure with temperature, while addition of antimony results in the compound-forming tendency in the liquid alloy. There is an experimental evidence that Sb_2Te_3 structure is retained after melting. This behaviour must reflect respective changes in the electron states in the liquid. Thus, it is interesting to see if there exists a correlation between the electrical resistivity of the liquid Sb-Te solutions and our results referring to oxygen behaviour in this melt.

2. EXPERIMENTAL

The scheme of the apparatus used for the conductivity measurements is shown in Figure 1. The cell construction is similar to that used in our previous work [7]. The cell with four electrodes (Fig. 2) was kept in a copper block in order to assure its vertical position inside the furnace as well as the constant temperature along capillary's length. The

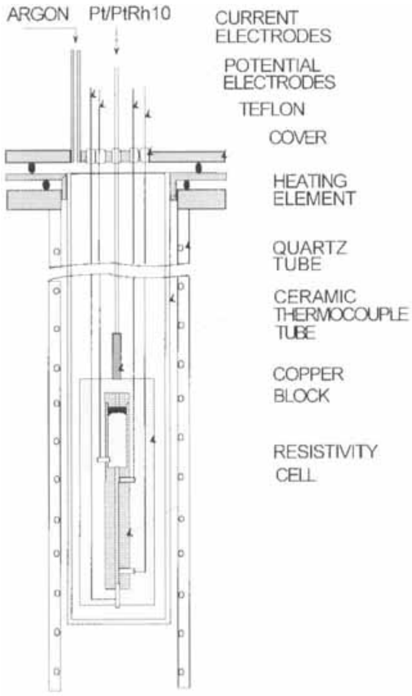

FIGURE 1 The scheme of the apparatus used for the resistivity measurements.

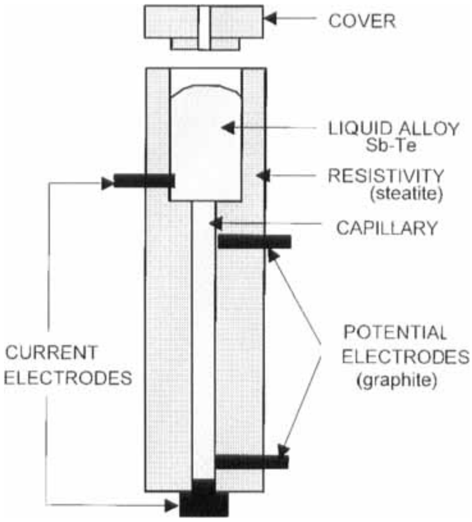

FIGURE 2 Schematic representation of a resistivity cell.

diameter of the capillary was ~1÷1.5 mm and its length was ~30 mm. Four electrodes made of graphite were connected with Pt paste with either gold or tungsten wires. A Pt/PtRh10 thermocouple inserted into copper block was used to measure temperature of the cell. The whole setup was placed inside the silica tube and closed with the brass head. The tube was kept inside the two-zone resistance furnace with maximum operating temperature 1400 K.

The antimony (99.999% pure) and tellurium (99.9999% pure) metals were obtained from Unitra Cemi Warszawa and ASARCO (USA), respectively. Sb-Te alloys of the chosen composition were prepared separately by melting of weighed amounts of metals in evacuated silica capsules, kept at 923 K for 12 h in the furnace and next quenched in liquid nitrogen.

The bulk of the liquid metal was contained in the reservoir of a cell made of either boron nitride or steatite. In order to introduce liquid metal into the capillary, the silica vessel was first evacuated with a vacuum system and then filled with purified argon in order to create the overpressure inside the vessel. The absolute pressure of argon of 1 bar was then applied over the liquid sample to push the liquid alloy into the capillary. Once the constant temperature was reached the potential drop due to the passing current between capillary's ends was measured with Keithley 197*A* multimeter and R3003 comparator. Direct current in the range 0.1÷0.15*A* was supplied by P317 Meratronic current source in time intervals of 5 s each. During this time interval the determination consisting of potential measurements of thermocouple, standard resistor and specimen were made. Thermoelectric e.m.f. was eliminated by inverting the current.

Specific resistivity, ρ, of the sample was calculated from the measured values by using the following relationship:

$$\rho = \frac{V}{IA}[\Omega m] \tag{2}$$

where A is a geometrical constant of the cell obtained from calibration, V is a potential across the specimen (between voltage electrodes) and I is a direct current passing through the cell.

Before experiments were started the cell was calibrated at room temperature with pure mercury, and consequently the calibration constant, A, of the cell was determined. The electrical resistivity of pure mercury has been obtained from the following equation at room temperature [8]:

$$\rho = \rho_{20}[1 + \alpha(t - 20^{\circ}\mathrm{C})] \tag{3}$$

where $\rho_{20} = 95.90$ $\mu\Omega$ cm, $\alpha = 0.00089\frac{\mu\Omega\,\mathrm{cm}}{\mathrm{C}}$ and t is temperature in centigrades.

It is important to calibrate the cell at the experiment's temperature. However, using materials with very low thermal expansion coefficient like alumina, *BN* or steatite in cell construction, it is also possible to calibrate the cell at room temperature.

3. RESULTS

The resistivity of liquid antimony and antimony-tellurium alloys was determined as a function of temperature in the 820–1150 K, depending on alloy composition, which varied between pure antimony and $X_{\mathrm{Te}} = 0.6$ (Sb_2Te_3 composition). The results of our measurements are shown in Figure 3. Also, in Figures 4 and 5, resistivity vs.

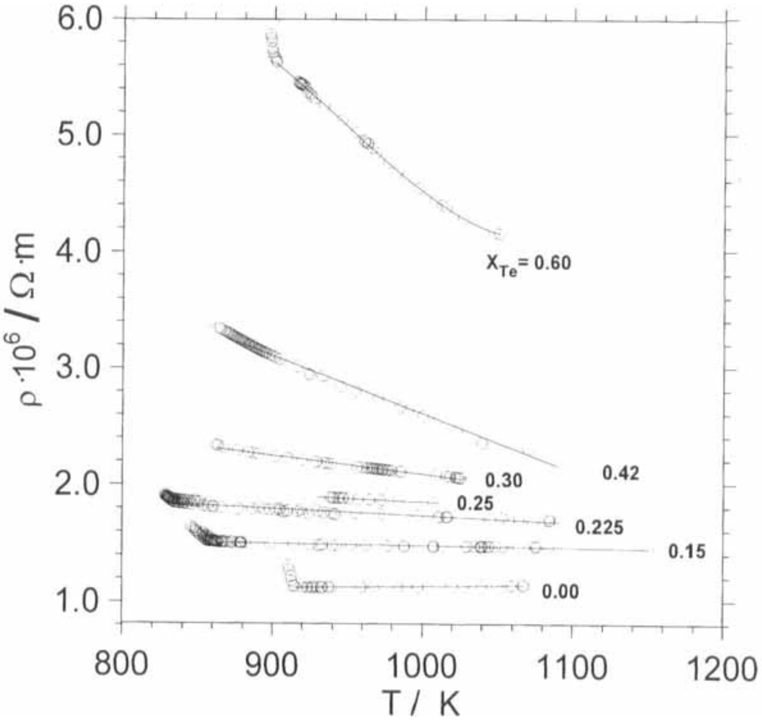

FIGURE 3 The resistivity of liquid antimony and antimony-tellurium alloys determined as a function of temperature and composition up to $X_{Te} = 0.6$.

temperature plots for pure antimony and $Sb_{0.4}Te_{0.6}$ alloy determined between room temperature and 1100 K are shown seperately.

The resistivity of liquid metals generally obeys the relation:

$$\rho = \mathbf{a} + \mathbf{b} \bullet T \quad [\Omega\text{m}] \tag{4}$$

where **a** and **b** ($\mathbf{b} = \frac{d\rho}{dT}$) are constants and T is the absolute temperature. The values of the parameters **a** and **b** are given in Table I. Obtained temperature coefficients **b** vs. composition are plotted in Figure 6. It indicates that the temperature coefficient $d\rho/dT$ changes its sign at $X_{Te} \approx 0.12$ and becomes negative for higher Te concentration.

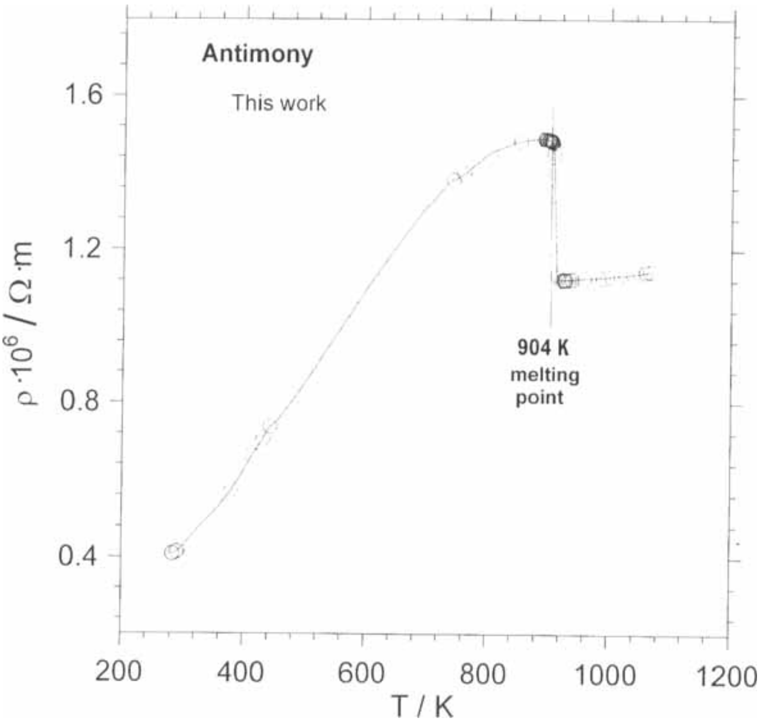

FIGURE 4 The resistivity vs. temperature plot for pure antimony determined between room temperature and temperature 1100 K.

Finally, the resistivity vs. composition plot derived at different temperatures is shown in Figure 7. The value of the resistivity for pure Te, shown in this plot for 940 K, is taken from Blakeway [10]. It is seen that in general, the addition of Te to liquid Sb increases the specific resistivity of the alloy. Once the composition of the compound is reached, Figure 5 shows that the specific resistivity of the liquid Sb_2Te_3 exhibits a typical semiconducting behaviour: it decreases rapidly with increasing temperature. It drops from $\sim 9.1 \cdot 10^{-6} \Omega$ m near the melting point determined in this work (890 K) to $4.15 \cdot 10^{-6} \Omega$ m at 1050 K.

The accuracy of the electrical resistivity measurements is estimated to 0.4%, that of the composition of the alloy to 0.3%. The main error arises from the uncertainty of the composition of the alloy in the capillary, which can be estimated to 0.5%.

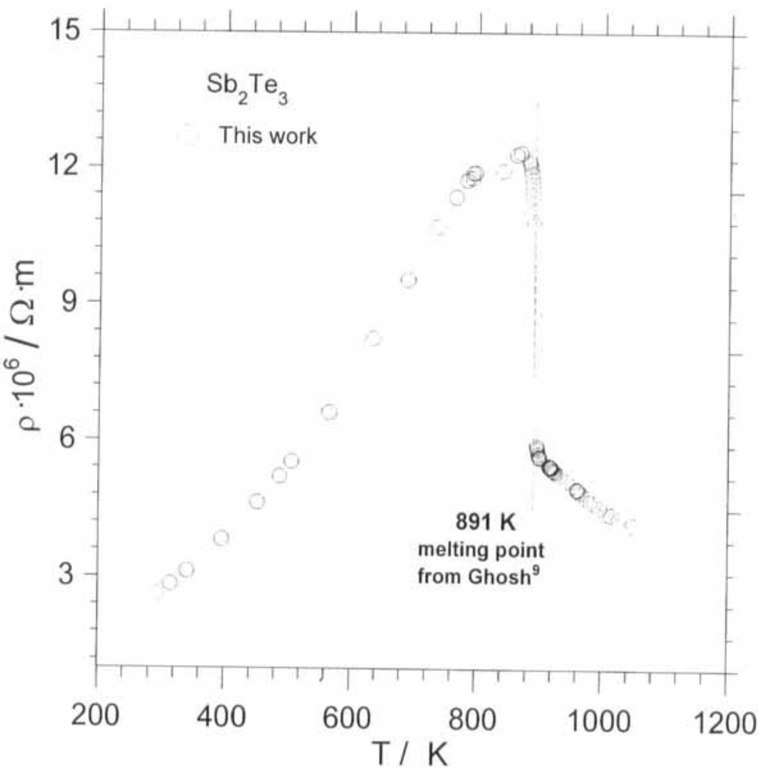

FIGURE 5 The resistivity vs. temperature plot for Sb_2Te_3 alloy determined between room temperature and temperature 1100 K.

TABLE I Resistivity data obtained for $Sb_{1-x}Te_x$ alloys

X_{Te}	$\mathbf{a}\cdot10^6[\Omega\cdot m]$	$\mathbf{b}\cdot10^{10}[\Omega\cdot m\cdot deg^{-1}]$
0.000	0.9909	1.4128
0.150	1.6400	−1.5849
0.225	2.3204	−5.8314
0.250	2.4222	−5.6857
0.300	3.6675	−15.7563
0.420	7.5496	−49.3956
0.600*	15.6485	−111.3691

*data fitted in temperature range (900−1020 K).

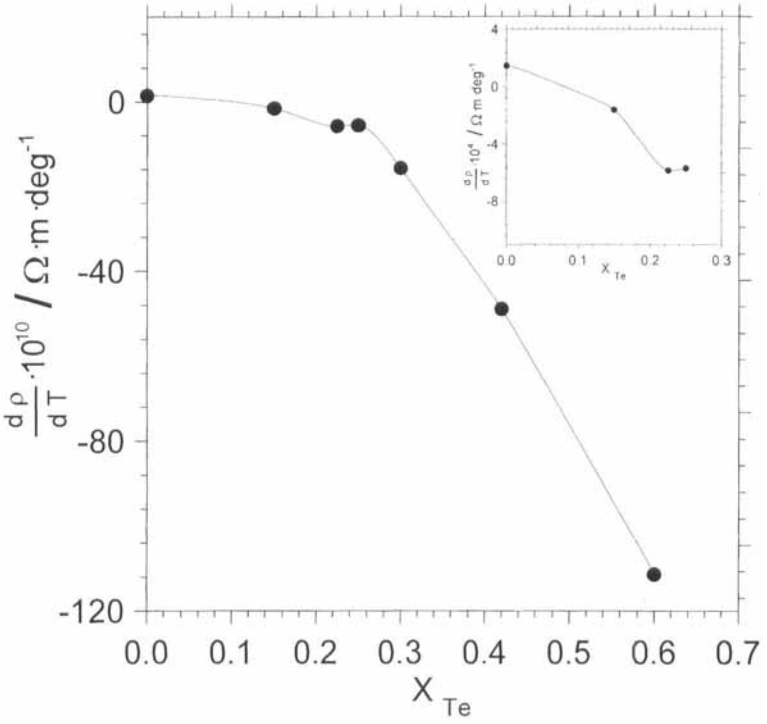

FIGURE 6 The $d\rho/dT$ vs. composition plot.

4. DISCUSSION

In his early works, Matuyama [1] discovered that in the case of antimony the specific resistivity of solid Sb, $\rho_S(T_m)$, is much larger at the melting temperature than specific resistivity of liquid Sb, $\rho_L(T_m)$. This metal exhibits also another abnormality-electrical resistance decreases during melting instead of increasing as it does in other metals (Fig. 4). In turn, in liquid tellurium the specific resistivity, is also smaller at the melting temperature than specific resistivity of solid Te [11 – 12]. Additionally the diffusion coefficient of oxygen [4] in liquid Te indicate the change of a structure [13] of liquid Te which becomes hard sphere mixture between 823 and 873 K. Influence of that residual structure on a specific resistivity was observed by Blakeway [10].

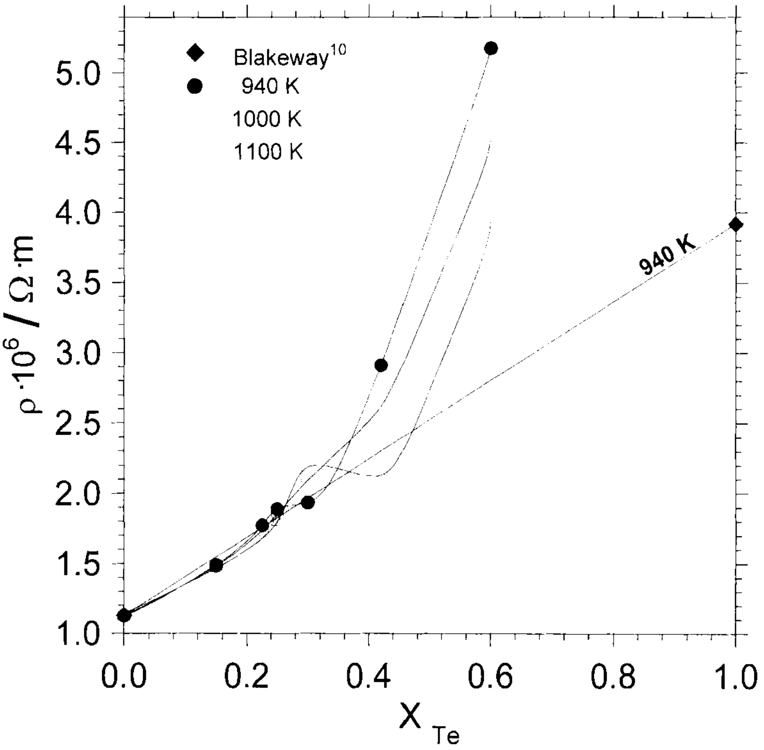

FIGURE 7 The specific resistivity vs. composition plot derived for different temperatures.

As far as liquid alloys are concerned, the resistivity-concentration isotherms for simple eutectic systems have been found to be smooth single-valued curves [1]. Only in these cases when molecular ordering persists after fusion irregularities were found at the resistivity-concentration isotherms. Antimony and tellurium are found to be miscible in all proportions in the liquid state [9]. So one would expect to find abnormal behaviour along resistivity-concentration isotherms for the Sb-Te system at Sb_2Te_3 concentration.

Since the work of Ioffe and Regel [14] it has been pointed out that the bonding nature between neighbouring atoms in liquid semiconductors (like Sb_2Te_3) significantly influences electron transport phenomena and the local order. However, the anomalies of the electronic properties of liquid Sb-Te solutions are less clear as compared with typical compound forming liquids.

Results of our measurements are in good agreement with those of Blakeway [10] and differ slightly from those of Zieliński [15], Mustiaca *et al.* [16] and El Bakkali [17]. At the antimony-rich side resistivity values reported by Mustiaca *et al.* are higher than those obtained in our work. We did not confirm the rapid change of the conductivity vs. composition plot observed in the vicinity of $X_{Te}=0.3$ reported by Gubskaya *et al.* [11]. However, our results shown in the resistivity vs. composition plot (Fig. 7) suggest not only large positive deviation from the linear dependence (broken line), assumed between resistivities of pure antimony and tellurium, but also small negative deviation from this dependence. The sudden rise in the resistivity of liquid alloys (conductivity drop) suggests a formation of complexes in the liquid with corresponding decrease in the number of free electrons due to their localisation. Small resistivity decrease (conductivity raise) in the range of concentration $X_{Te}=0.2 \div 0.3$ can not be simply explained.

Recently, Herwig and Wobst [13] measured the viscosity of liquid Sb-Te alloys in the whole concentration range. They observed a maximum of the viscosity vs. composition plot at the Sb_2Te_3 composition. This kind of positive deviation on the viscosity vs. composition plot speaks for the cluster formation in the liquid. These results taken together with our resistivity data vs. alloy composition indicate the formation of localized bands in the liquid state and suggest that Sb_2Te_3 structure is retained in the liquid state after melting.

In turn, temperature dependence of the resistivity measured for pure antimony and Sb_2Te_3 compound (Figs. 4 and 5) shows clearly that the resistivity of pure antimony increases with temperature after melting, while that of the compound decreases. The decrease in the resistivity with increasing temperature suggests that the liquid has semiconducting properties. This means that in the range of compositions between $X_{Te}=0$ and $X_{Te}=0.6$ the liquid changes its properties from metallic to semiconducting behaviour. If the conventional semiconductor theory is still valid in the liquid state it is highly probable that a positive Hall coefficient may be found. Enderby and Walsh [18] observed that Hall coefficient for Sb_2Te_3 compound is negative. In conclusion, the unusual composition dependence of the electronic properties observed

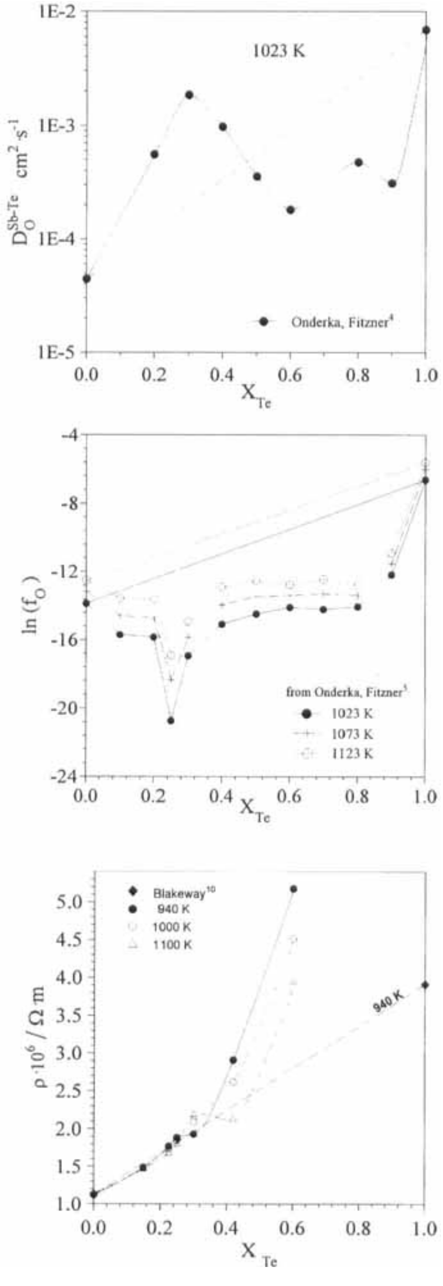

FIGURE 8 Comparison between resistivities measured in this work with the results of the oxygen diffusivity and oxygen activity coefficient measurements as a function of Sb_xTe_{1-x} composition.

in the present systems may be considered to be caused by the nonmetallic nature of Sb-Te bonds.

In Figure 8 we compared resistivities measured in this work with the results of the oxygen diffusivity and oxygen activity coefficient measurements [4–5] as a function of Sb_xTe_{1-x} composition. This comparison reveals that an unexpected D_0 and γ_0 behaviour with composition falls into the range where the suggested change metal → semiconductor took place. This change had to affect availability of "free" electrons in the liquid to oxygen entering the system.

Usually, the minimum in $d\rho/dT$ accompanying the maximum in ρ is a frequently observed phenomenon in compound-forming metallic alloys. Thus, it seems surprizing that in the range of concentrations up to $X_{Te} = 0.3$ $d\rho/dT$ almost does not change (Fig. 6). Since it is clear that metallic-semiconducting change takes place with tellurium addition, it seems unlikely that it may happen at one specific alloy composition. It is more likely that in the liquid state a gradual compensation takes place, and the composition range $X_{Te} = 0.1 \div 0.3$ is the one at which different contributions cancel each other. Therefore, it can be suggested that while observed maxima in $\ln\gamma_0$ and D_0 at $X_{Te} = 0.6$ take place for maximum of created covalent bonds, the unexpected behaviour of activity coefficient and diffusivity occurs at the composition at which there is a full compensation of metallic and semiconducting behaviour. More experimental data on concentration dependence of different physical properties in alloys are needed in order to gather enough information to support this point of view.

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