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Electrical resistivity and absolute thermopower of liquid GaSb and InSb alloys

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Abstract. The electrical resistivity and absolute thermoelectric power of liquid GaSb and InSb alloys have been carefully measured as functions of temperature. A U-shaped quartz cell was used in the measurement and more accurate data than those reported by other authors were obtained. The resistivity of liquid InSb and that of GaSb are 106.49 $\mu\Omega$ cm and 93.16 $\mu\Omega$ cm at the melting points. It is also found that the temperature dependence of the resistivity (TDR) for liquid GaSb and InSb increases with increasing temperature near the melting point and then is independent of temperature above 786 and 617 °C, respectively. The TDR at higher temperature is 2.36 and 2.59×10^{-2} $\mu\Omega$ cm $^{\circ}$C^{-1} for liquid GaSb and InSb, respectively. The temperature dependence of the thermoelectric power also changes at about 786 and 617 °C for liquid GaSb and InSb, respectively

1. Introduction

Some covalent semiconductors (Ge, Si, GaSb, InSb, etc) show metallic properties upon melting, as is established by studying their resistivities [1–3]. Measurements of the Knight shift [4] and, recently, the density of electronic states in the melt [5] also confirm this conclusion. However, the coordination number of such a liquid is still less than those of normal liquid metals, and some anomalous behaviour has been observed in this kind of liquid.

For liquid InSb, the heat capacity rises abruptly, reaches a maximum at 580 °C, and then is independent of temperature above 597 °C [6, 7]. X-ray absorption near-edge-structure (XANES) study demonstrates that the density of states of liquid GaSb shows the same kind of features as that for the crystalline state [5]. It is concluded from extended x-ray absorption fine-structure (EXAFS) measurements that heterogeneous atomic coordination and some (about 15%) tetrahedral units remain in liquid GaSb and InSb near the melting temperature [8].

Knowledge of the electrical properties is helpful for understanding the behaviour of such liquids, so some experimental and theoretical studies of the electrical resistivity have been carried out in the last few decades [9–11]. However, the results obtained by different investigators do not agree with each other, and the data relating to the temperature dependence are widely dispersed. Hence, higher-quality measurements of the electrical resistivity and thermopower are necessary. In the present work, the electrical resistivity and thermoelectric power of liquid GaSb and InSb were carefully measured as functions of temperature. More accurate data than those from earlier investigations were obtained, and new phenomena in the resistivity and thermopower were also found.

2. Experimental procedure

The resistivities of high-purity liquid GaSb and InSb, which were prepared by melting single crystals (99.999 99 at.%), were measured using the DC four-probe method. The advantage of this method is that the influence of the contact thermopower of the electrode and liquid can be removed. To eliminate the thermoelectric effect in the liquid, the sample holder was maintained in a constant-temperature zone in the furnace and the voltages for both directions of current were measured using a Keithley 2182 nanovoltmeter. A stable constant current (20–50 mA) furnished by a Keithley 220 programmable current source was passed through the specimen for a short time to reduce the Joule heating. A U-shaped quartz cell, about 11 cm long and of diameter 0.4 cm, with Mo electrodes was used in the measurement. The geometrical constant for each cell was determined by measuring the resistivity of high-purity mercury at room temperature. The overall experimental error was of the order of 0.2%.

The thermoelectric power was obtained from the measured electromotive force produced by the temperature gradient ΔT. A suitable temperature gradient was achieved using a two-zone furnace. Thus, the thermoelectric power of the material investigated can be obtained through measuring two voltages and ΔT. A schematic diagram is shown in figure 1. This method is superior to that usually employed to determine ΔT by a separate measurement of T_1 and T_2. Chromel–alumel thermocouples were used for the measurement of temperatures and molybdenum wires were used as electrodes. The voltage ΔV between the two electrodes was measured by a digital voltmeter with the accuracy of 0.1 μV. The value of $\Delta V/\Delta T$ gives the thermopower of the sample relative to the Mo electrode. By subtracting the value of the thermopower of Mo given by Cusack and Kendall [12], the absolute thermopower of the sample was obtained.

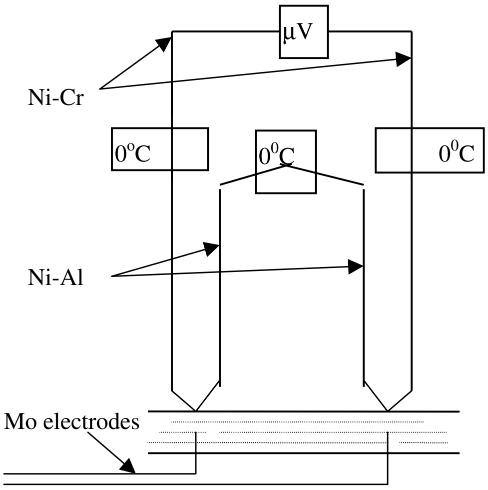

Figure 1. A schematic diagram of the method used to measure the temperature difference between the two Mo electrodes.

The system was evacuated to 10^{-6} Torr while heating; measurements were then performed at atmospheric pressure under high-purity argon gas to prevent oxidation and reduce vaporization of the liquid alloys. In order to measure the melting point precisely, the heating rate was controlled at under 2 °C min^{-1}. The melting temperatures of GaSb and InSb measured in the present work are 712 and 525 °C, respectively. Before the measurements were begun, each sample was heated to about 10 °C above its melting point and held at this temperature for 4–5 h to guarantee that the sample melted completely.

3. Results and discussion

To confirm the results measured in our experimental system, the electrical resistivity of liquid indium (99.9999 at.%) was measured. Figure 2 shows the results from the present work and the data reported by other authors [13–17]. Our value of 2.42×10^{-2} $\mu\Omega$ cm °C^{-1} of the temperature dependence of the resistivity (TDR) is in satisfactory agreement with published values of 2.39 [13], 2.48 [14], and 2.45×10^{-2} $\mu\Omega$ cm °C^{-1} [15].

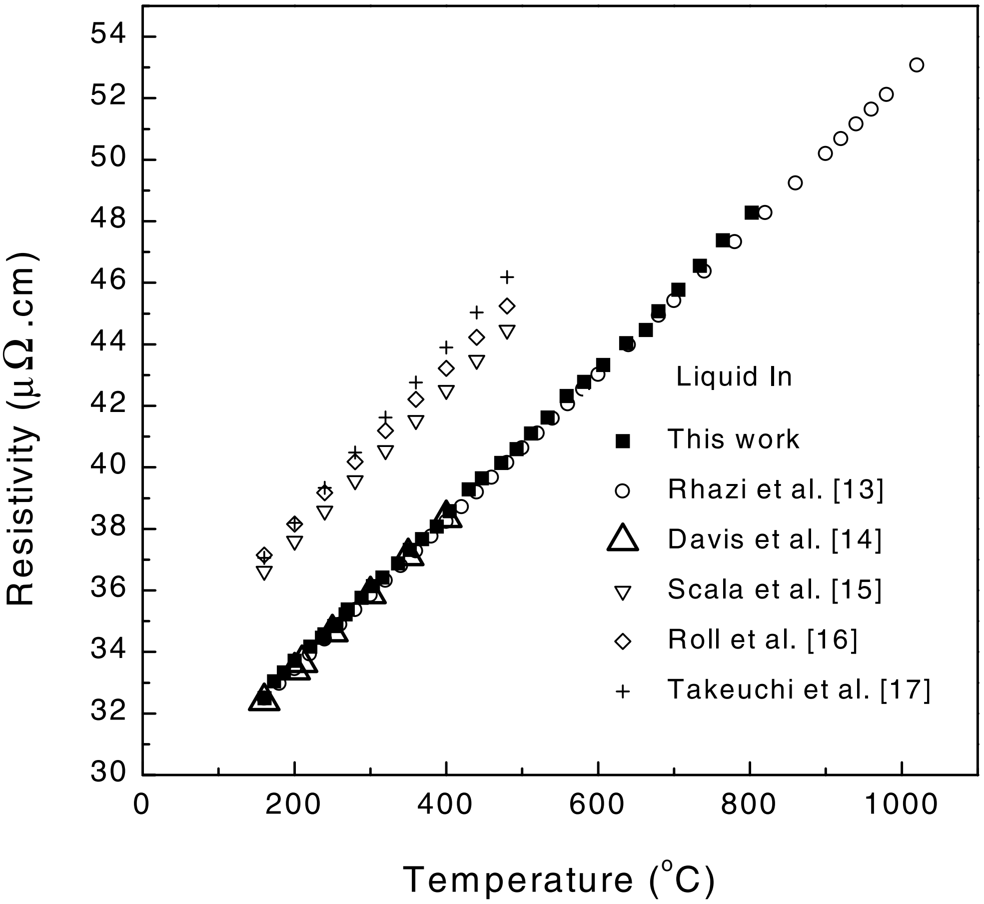

Figure 2. Electrical resistivity versus temperature for pure liquid indium.

The electrical resistivity versus temperature results for liquid GaSb and InSb are given in figure 3 and figure 4, respectively. All of the results obtained in this work in several experiments using different cells for liquid GaSb and InSb agree well with each other. They are different from those obtained by Glazov *et al* [2] and Regel [9]. It can be seen that our data are more accurate than theirs. The resistivities of liquid InSb and GaSb are 106.49 $\mu\Omega$ cm and 93.16 $\mu\Omega$ cm at the melting points, respectively.

The TDR for liquid GaSb and InSb (figures 3 and 4) increases with increasing temperature near the melting point and then is independent of temperature above the melting point temperature (about 74 °C and 92 °C, respectively). The TDR at higher temperature is 2.36 and 2.59×10^{-2} $\mu\Omega$ cm °C^{-1} for liquid GaSb and InSb. This character of the resistivity for liquid

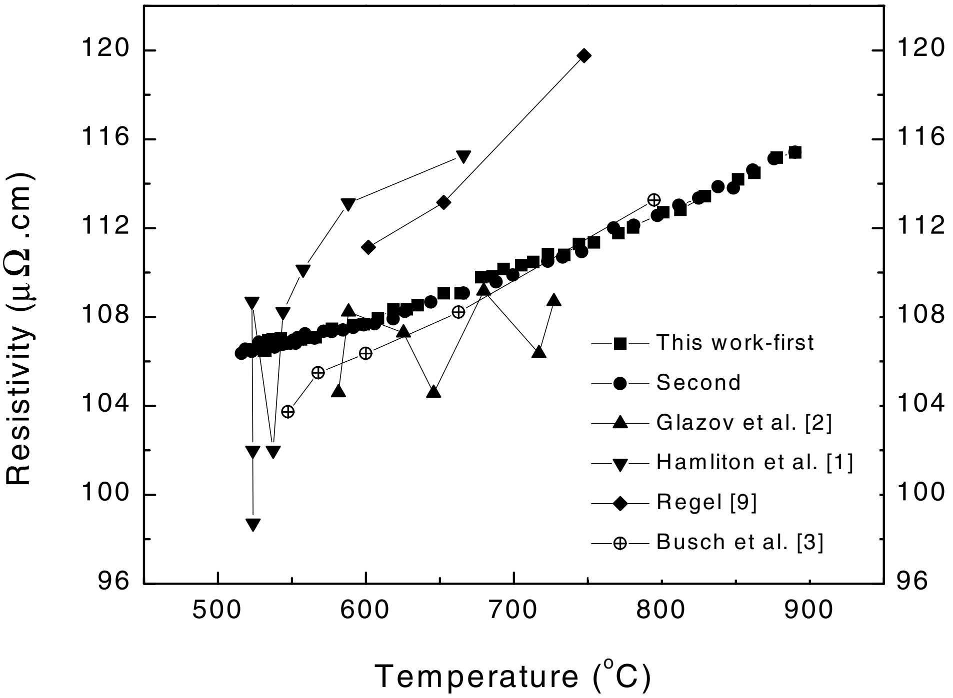

Figure 3. Resistivity versus temperature for liquid InSb.

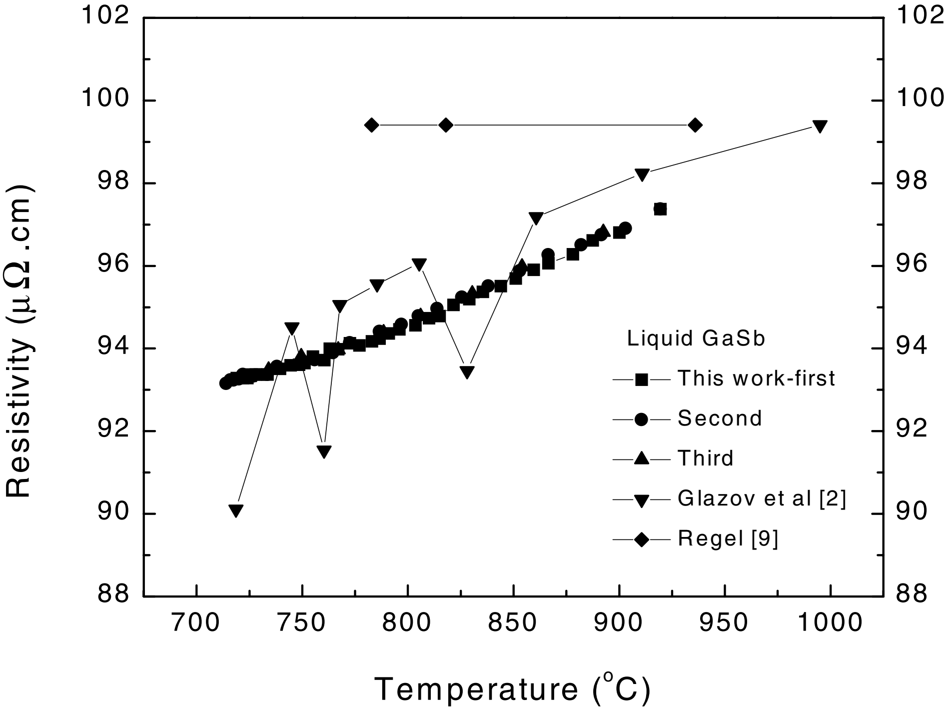

Figure 4. Resistivity versus temperature for liquid GaSb.

GaSb and InSb is different from that of a simple liquid metal, whose TDR is usually linear over the whole temperature range investigated (like that of pure liquid indium; see figure 2).

The electronic resistivity is a structure-sensitive quantity, so the changes in electrical resistivity and TDR reflect changes in the structure, the nature of the chemical binding, and the electronic structure near the Fermi level.

Although changes occur in the coordination number when solid GaSb and InSb are melted, the observed coordination numbers of these liquids are still lower than those of normal liquid metals ($\sim$12). The results of a structure study using the EXAFS method by Wang *et al* [8] show that although the coordination number is $\sim$6 for liquid GaSb and InSb, there are about 15% fourfold-coordinated species in these liquid alloys. In another words, there is evidence of weak covalency in these liquid alloys, and the metallic bonding in liquid GaSb and InSb is not complete. This suggestion is supported by the measured K-edge XANES spectra of Ga and Sb in liquid GaSb [5]. These observations support the 'two-component' model for the structure of liquid InSb and GaSb. According to this simple model, solid-like or ordered clusters exist in this kind of liquid near the melting point. With increasing temperature, the ordered clusters retained break gradually and the localized electrons become free.

The observed behaviour of the resistivity as a function of temperature for liquid InSb can be qualitatively explained on the basis of the model mentioned above, if one considers the fact that the resistivity of clusters is higher than that of liquid InSb near the melting point. Assuming the magnitudes of the resistivities of the clusters to be approximately the same as that of the bulk solid, it can be concluded that the clusters gradually disappear near the melting point and almost vanish above about 617 °C, which leads to the behaviour observed in this work. In the solid state, semiconductors exhibit a negative TDR. This coefficient would also apply for the covalent clusters retained in molten InSb, which could explain why the TDR at lower temperature is less than that at higher temperature. This analysis can also be applied to liquid GaSb.

The thermoelectric powers of liquid GaSb and InSb are shown in figures 5 and 6. The data for liquid InSb from the present work are close to those reported by Enderby and Walsh [18], and very different from those obtained by Glazov *et al* [2]. For liquid GaSb, the data are very different from those reported by other authors. It can also be seen from figures 5 and 6 that the thermoelectric power is almost independent of temperature at higher temperature but dependent on temperature below 786 °C and 617 °C for liquid GaSb and InSb, respectively.

The thermoelectric power is related to the electronic resistivity; both are sensitive to the structure, so the changes in thermoelectric power with temperature are, in our opinion, a consequence of the structural modification of liquid GaSb and InSb.

4. Conclusions

The electrical resistivity and thermoelectric power of liquid GaSb and liquid InSb alloys have been carefully measured as functions of temperature. It can be seen that the data obtained from our experiments are more accurate than those from earlier investigations. Non-continuous changes of the temperature coefficient of resistivity and thermopower at 786 °C in liquid GaSb and 617 °C in liquid InSb have been observed. Together with other physical properties, the results obtained in this work suggest that the structure changes with temperature for liquid InSb and GaSb. It seems possible that more extensive and more accurate results on the structure factors of liquid InSb and GaSb alloys might well provide useful quantitative evidence as regards the mechanism of the change in the temperature dependence of the resistivity and the thermopower.

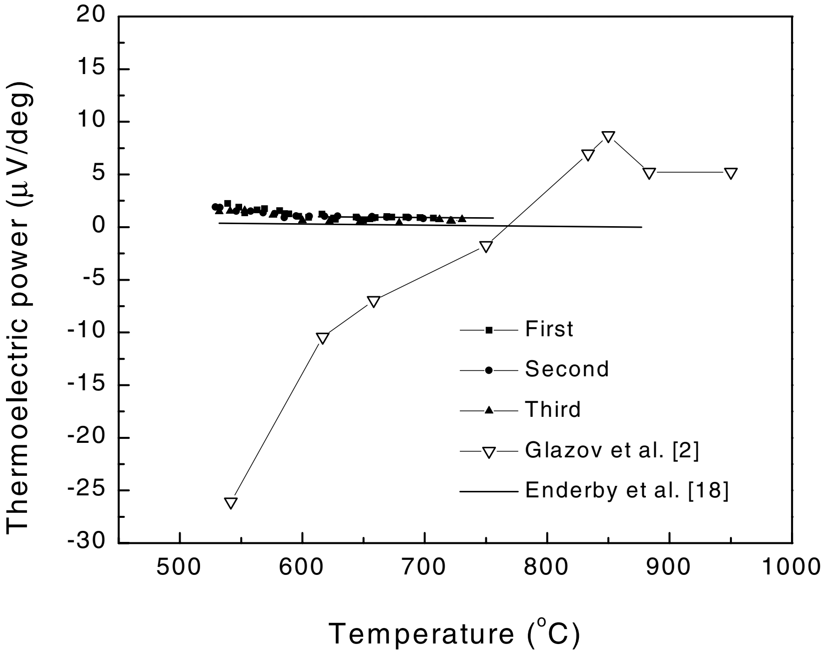

Figure 5. The thermoelectric power of liquid InSb versus temperature.

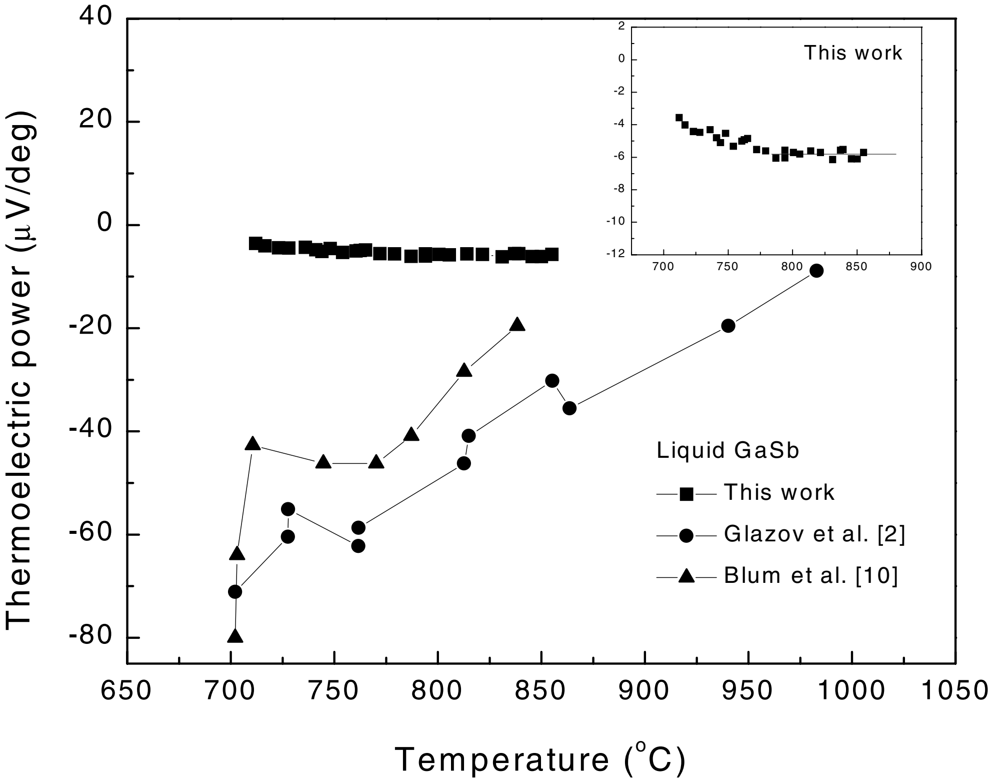

Figure 6. The thermoelectric power of liquid GaSb versus temperature.

Acknowledgments

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