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2001 J. Phys.: Condens. Matter 13 8445

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Concentration and temperature dependence of the electrical resistivity of liquid gallium–antimony alloys

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Received 28 November 2000, in final form 9 July 2001

Published 30 August 2001

Online at stacks.iop.org/JPhysCM/13/8445

Abstract

In this paper, the electrical resistivity of liquid $\text{Ga}_{1-x}\text{Sb}_x$ has been carefully measured as a function of temperature and concentration. For liquid $\text{Ga}_{1-x}\text{Sb}_x$, the electrical resistivity versus temperature is linear for all concentrations for which measurements were made except $x = 1$ and 0.5 , where the temperature coefficient of the resistivity increases with the increase of temperature near each melting point, but is independent of temperature above certain temperatures. It is very interesting that the electronic transport properties of liquid Ga–Sb are very different from those of liquid In–Sb, although they both belong to the liquid III–V system. The results obtained in this work have also been discussed on the basis of a ‘two-structure’ model.

1. Introduction

For most III–V compound semiconductors such as GaSb, the solid–liquid transition is accompanied by a transition from a semiconducting to a metallic state and an increase of the coordination number. However, the coordination number of this kind of melt is far less than that of a simple liquid metal, whose coordination number is about 11. In addition, many anomalous physical properties also distinguish liquid GaSb from simple liquid metals. For example, it is concluded that there are heterogeneous atomic coordinations and some tetrahedral units (about 15%) in liquid GaSb near the melting temperature [1], and also that some features of the density of states for crystalline GaSb are observable in that for liquid GaSb [2].

Electrical resistivity is a very useful tool in studying liquid materials because it is sensitive to structural change, so the resistivity of liquid GaSb has been measured by many authors [3–5], but the results do not agree well with each other. In this work, we have carefully measured the resistivities of liquid $\text{Ga}_{1-x}\text{Sb}_x$ and found that there are some anomalous phenomena in the resistivities versus temperature and concentration.

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2. Experimental procedure

The direct-current four-probe method was used in this work, and U-shaped quartz cells (about 11 cm long and 0.3 cm in diameter) fitted with Mo electrodes (figure 1) were used as sample cells. The whole arrangement was heated slowly under vacuum (about 10^{-6} Torr) until the quartz cell was filled with liquid sample, then the measurements were performed at atmospheric pressure under high-purity argon gas (99.9995 wt%). This process can effectively eliminate the gas bubbles existing in liquid samples and prevent oxidation and reduce vaporization of the liquid sample. When measuring the resistivity at pressures of about 500 Torr and 0.1 Torr, no pressure dependence of the resistivity indicates that no gas bubbles exist in the samples.

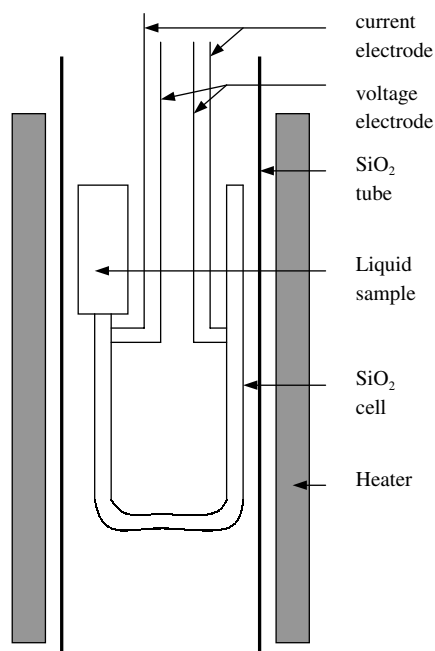


Figure 1. A schematic diagram of the sample cell.

The geometrical constant was determined for each individual cell at room temperature by measuring the resistivity of high-purity mercury [6]. Before the measurement, the sample was heated to about $10\text{ }^{\circ}\text{C}$ above its melting point and held at this temperature for about two hours to guarantee that the sample was melted completely. During the measurement, 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. To eliminate the thermoelectric effect, the voltages for both directions of currents were measured using a Keithley 2182 nanovoltmeter with a $0.1\text{ }\mu\text{V}$ resolution. In this work, the heating and cooling rates were kept at $2\text{ }^{\circ}\text{C s}^{-1}$ and each measurement was performed after stabilizing the temperature for eight minutes. The resistivity values reported are averages of several values for both current directions at each temperature. During each measurement the temperature drift did not exceed $0.2\text{ }^{\circ}\text{C}$ and the temperature variation along the container was always smaller than $\pm 0.1\text{ }^{\circ}\text{C}$. Temperature was measured by a chromel–alumel thermocouple, which was checked against high-purity antimony and a level Pt/Pt–10%Rh thermocouple, and whose accuracy was determined as $\pm 1\text{ }^{\circ}\text{C}$.

The samples used in this work were prepared from 6N-purity Sb and 7N-purity Ga. A single crystal of GaSb was used for the 50 at.% composition. Other starting materials were mixed in an evacuated quartz tube at a temperature of about 80 °C above the respective melting points for about 24 h and then quenched into liquid water. The accuracy of the d.c. measurement in this work is estimated to be better than $\pm 1.7\%$ [7].

3. Experimental results

3.1. Liquid Ga

The resistivities of liquid Ga (99.9999 at.%) obtained in this work are shown in figure 2 along with some published data [8–12] for comparison. The value of 26.2 $\mu\Omega$ cm at 50 °C is in satisfactory agreement with the reported values of 26.13 $\mu\Omega$ cm [8], 26.23 [9], and 26.20 [13], and the temperature coefficient of resistivity (TCR) value ($20.15 \times 10^{-3} \mu\Omega \text{ cm } ^\circ\text{C}^{-1}$) lies within 3% of that from reference [13].

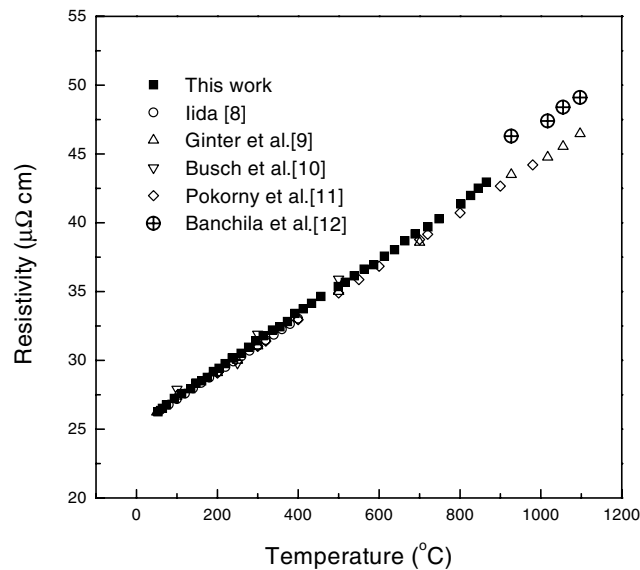


Figure 2. Resistivity versus temperature for liquid Ga.

3.2. Liquid Sb

As seen from figure 3, the resistivity values obtained in this work at 630 °C (112.1 $\mu\Omega$ cm) and 700 °C (113.4 $\mu\Omega$ cm) are close to those of Steeb *et al* [14] (112.3 $\mu\Omega$ cm) and Tomlinson and Lichter [15] (113.5 $\mu\Omega$ cm), respectively.

The experimental results indicate that the TCR for liquid Sb increases with increasing temperature near the melting point and then is independent of temperature above 722 °C (see figure 4), which is close to the value observed by Ohno *et al* [16] (750 °C). The resistivity at higher temperature can be fitted to a linear expression:

$$\rho = 92.7 + 29.2 \times 10^{-3} T \quad 722 \leq T \leq 860 \text{ } ^\circ\text{C} \quad (1)$$

where ρ is in $\mu\Omega$ cm and T in °C.

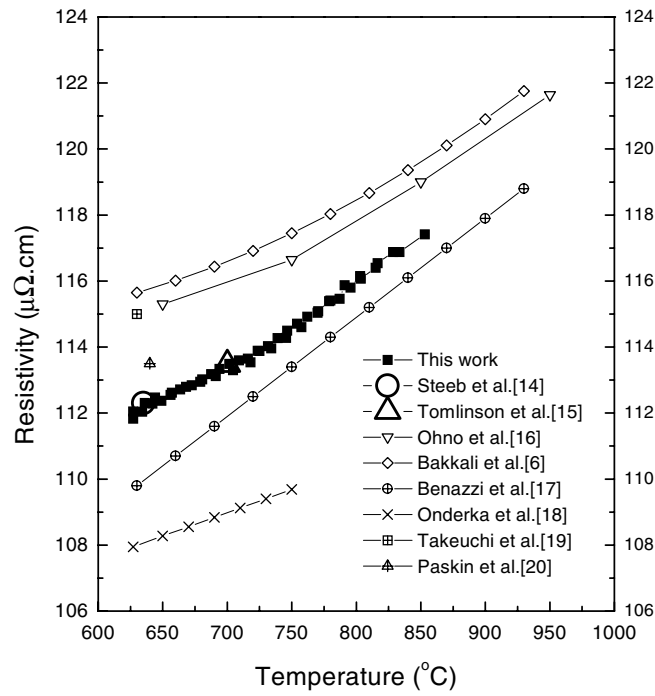


Figure 3. Resistivity versus temperature for liquid Sb.

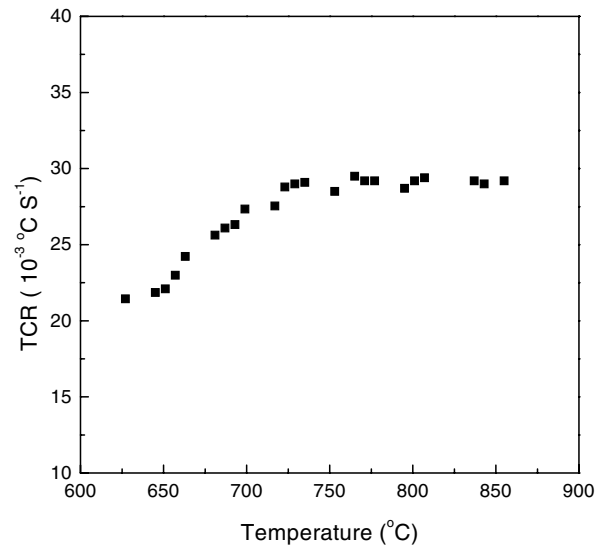


Figure 4. The temperature coefficient of resistivity (TCR) versus temperature for liquid Sb.

3.3. Other liquid $Ga_{1-x}Sb_x$ alloys

Figures 5 and 6 show that the curve of resistivity versus temperature is linear at almost all concentrations for liquid $Ga_{1-x}Sb_x$ except at $x = 0.5$ and 1.0 , where the TCR versus

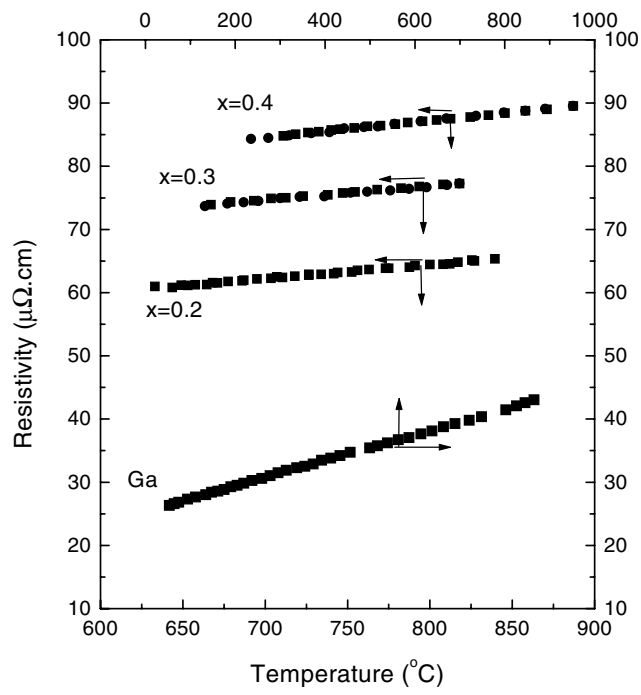


Figure 5. Resistivity as a function of temperature for liquid $\text{Ga}_{1-x}\text{Sb}_x$ with $0 < x < 0.5$. The lines are guides for the eyes.

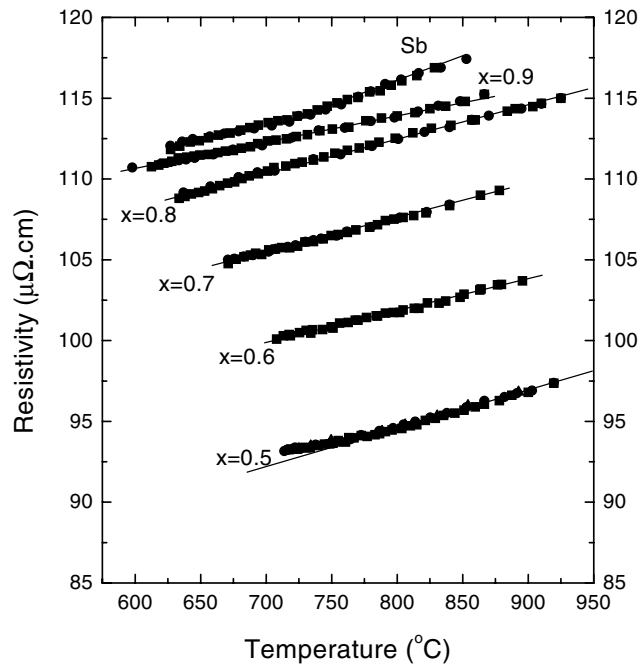


Figure 6. Resistivity as a function of temperature for liquid $\text{Ga}_{1-x}\text{Sb}_x$ with $0.5 \leq x \leq 1.0$. The lines are guides for the eyes.

temperature shows a similar behaviour to that of liquid Sb. In order to display clearly the non-linearity of the resistivity versus temperature, figure 7 shows an enlarged view for liquid $\text{Ga}_{1-x}\text{Sb}_x$ with $x = 0.5, 0.9$, and 1.0 .

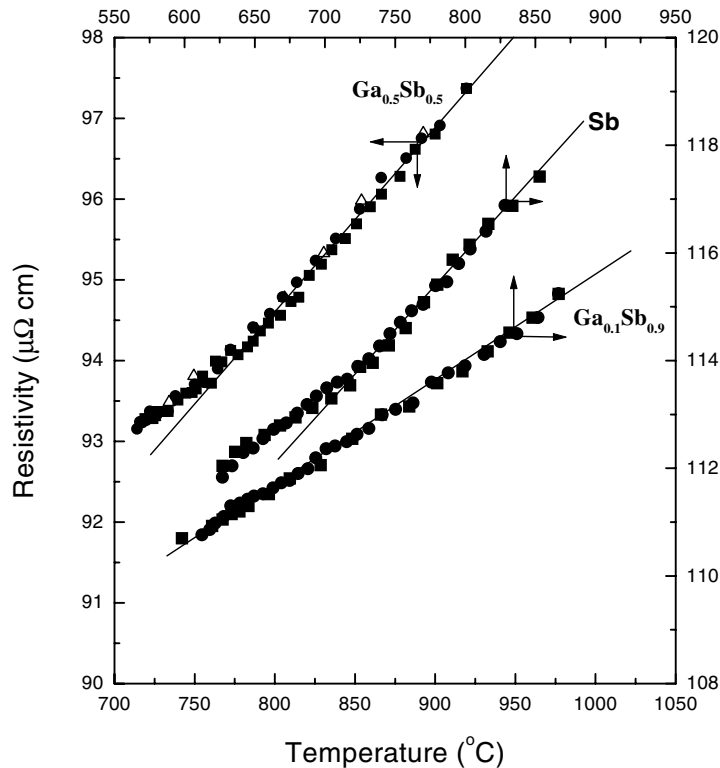


Figure 7. Resistivity as a function of temperature for liquid $\text{Ga}_{1-x}\text{Sb}_x$ with $x = 0.5, 0.9, 1.0$. The resistivities of some concentrations are plotted separately for clarity.

It is very interesting that these results are very dissimilar to those observed for liquid $\text{In}_{1-x}\text{Sb}_x$ [21], although both of these liquid alloys belong to the liquid III–V system. For liquid $\text{In}_{1-x}\text{Sb}_x$, the TCR versus temperature shows an obvious turning point over the concentration region $0.4 \leq x \leq 1.0$.

Figure 8 shows the resistivity as a function of concentration for liquid $\text{Ga}_{1-x}\text{Sb}_x$ at certain temperatures together with the data for liquid $\text{In}_{1-x}\text{Sb}_x$. It is clear that the resistivity increases smoothly with increasing Sb content, whereas the curve of resistivity versus concentration passes through a maximum value at about $x = 0.8$ for liquid $\text{In}_{1-x}\text{Sb}_x$.

4. Discussion

4.1. Pure liquid Sb

Due to a Peierls distortion, caused by electronic instability, from the simple cubic structure, the crystalline Sb shows semi-metallic behaviour and all the electrons are in localized states. Upon melting, the Peierls distortion is drastically altered or destroyed, whereupon many electrons become free and the resistivity abruptly decreases. So the destruction of the Peierls distortion has a large influence on the resistivity of Sb, as can be seen in figure 9.

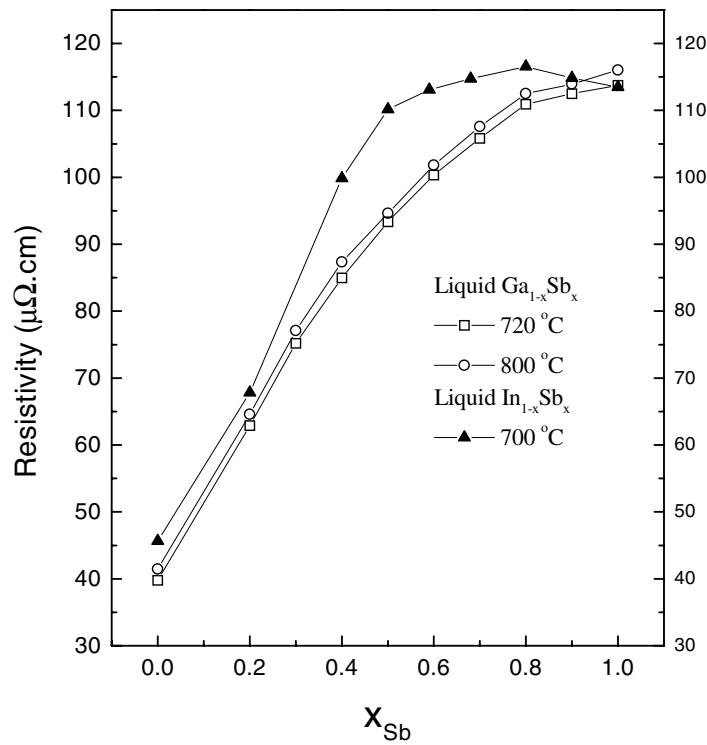


Figure 8. Electrical resistivities of $Ga_{1-x}Sb_x$ and $In_{1-x}Sb_x$ as functions of composition and temperature. The data for liquid $In_{1-x}Sb_x$ are derived from reference [21].

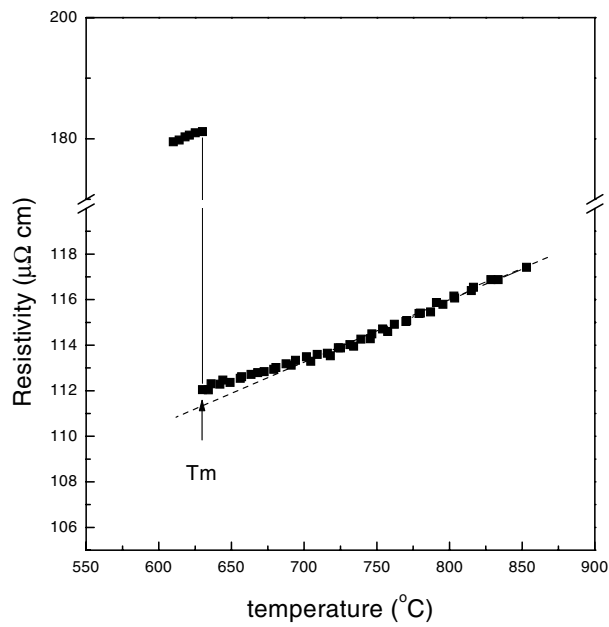


Figure 9. Electrical resistivity versus temperature for liquid Sb near the melting point. The dashed line is a guide for the eyes.

Whether the Peierls distortion survives or not in the liquid state is controlled by the ratio of the distortion energy ΔE to the thermal energy kT . For a light group-V element such as As, at the melting temperature the entropic term is not large enough to destroy the Peierls distortion. So liquid As still shows a Peierls distortion [22, 23]. This fact also suggests that the lattice periodicity is not a necessary condition for the occurrence of a Peierls distortion. For the heavy element Sb, although the Peierls distortion is almost destroyed upon melting, the results for structure and electronic properties confirm that a Peierls distortion still exists in liquid Sb [24, 25]. The self-diffusivity indicates that liquid Sb still shows semi-metallic behaviour [26]. All these results suggest that there are covalent bonds surviving in this melt near the melting point. With temperature increasing, the atomic vibrations become larger and the electron mean free path decreases; this results in a resistivity increase for liquid Sb. But in a region of temperature above the melting point, there is a factor causing decrease of the resistivity: covalent bonds gradually disappearing. This may be why the TCR of liquid Sb increases with temperature near the melting point. Our analysis is supported by the fact that there is a reduction in the amount of p character and a corresponding increase in s character at the Fermi surface for liquid Sb with the increase of temperature [27]. When the temperature is above 722 °C, the TCR being constant suggests that the structure of liquid Sb becomes homogeneous. So this indicates that the value of the distortion energy ΔE of Sb is less than 0.086 eV (the thermal energy of liquid Sb at 722 °C).

4.2. Liquid Ga–Sb alloys

The structure [1] and thermodynamic properties measurements [28] both support a ‘two-structure’ model of liquid GaSb near the melting point. On the basis of this structure model, we discussed the anomalous behaviour observed in the electrical resistivity and thermopower versus temperature for liquid GaSb in reference [29], and proposed that its structure changes with temperature. However, for liquid $\text{Ga}_{0.4}\text{Sb}_{0.6}$ and $\text{Ga}_{0.6}\text{Sb}_{0.4}$, the resistivity versus temperature is linear over the whole temperature range investigated. According to the discussion for liquid GaSb, it can be suggested that the chemical complexes only persist over a small concentration range near $x = 0.5$. This is very different from the case for liquid $\text{In}_x\text{Sb}_{1-x}$, where the resistivity changes abnormally with temperature for all alloys with $x < 0.4$. In our opinion, this phenomenon may be due to the weaker tendency of forming chemical complexes for liquid GaSb compared to that for liquid InSb. This suggestion can be supported by the value of the enthalpy of mixing (ΔH_M), which is directly influenced by the change in the interactions of the components. The value of ΔH_M is about -1.0 kJ mol^{-1} for liquid GaSb at 995 K [28], which is much less than that for liquid InSb ($\sim -3.04 \text{ kJ mol}^{-1}$ at 986 K) [30]. The curve of TCR versus temperature showing a turning point has already been observed for many liquid-Sb-based alloys on the Sb-rich side [6, 16, 31, 32], and this anomalous behaviour does not vanish until the solute concentration reaches a certain value. It should be stressed that this critical value is very different for different solutes. To date, no discussion of this feature has been published, and it is not clear why the resistivity change with temperature is different for different Sb-based alloys, especially on the Sb-rich side. From the experimental results, one thing that is clear is that this feature does not relate to the electronic structure of the solutes, because In and Sb are both group-III elements.

5. Conclusions

To summarize, the electrical resistivity of liquid $\text{Ga}_{1-x}\text{Sb}_x$ has been investigated over a wide concentration range. For liquid $\text{Ga}_{1-x}\text{Sb}_x$, the TCR is constant over the whole temperature

range investigated for most concentrations except $x = 1$ and 0.5, where the curve of resistivity versus temperature deviates from linearity near the melting points but is linear above certain temperatures.

The anomalies observed in the resistivity versus temperature curve for liquid Sb can be interpreted as indicating the disappearance of the Peierls distortion surviving in liquid Sb. The resistivity and other reported physical properties suggest that the tendency of forming chemical complexes is weaker for liquid Ga–Sb than for liquid In–Sb.

Acknowledgments

This work was supported by the Chinese National Science Foundation and a Key Research Project Grant of the Climbing Programme from the State Science and Technology Commission of China.

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