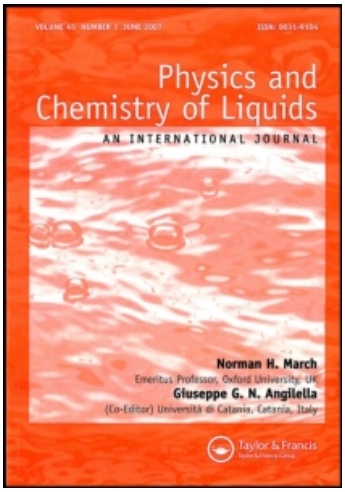


**Physics and Chemistry of Liquids**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

# Hump phenomenon on resistivity-temperature curve in liquid Bi, Sb and their alloys

Xian-Fen Li[a]; Fang-Qiu Zu[a]; Lan-Jun Liu[a]; Jin Yu[a]; Bing Zhou[a]
[a] School of Materials Science and Engineering, Hefei University of Technology, Hefei, People's Republic of China

**To cite this Article** Li, Xian-Fen , Zu, Fang-Qiu , Liu, Lan-Jun , Yu, Jin and Zhou, Bing(2007) 'Hump phenomenon on resistivity-temperature curve in liquid Bi, Sb and their alloys', Physics and Chemistry of Liquids, 45: 5, 531 — 539
**To link to this Article: DOI:** 10.1080/00319100701344594
**URL:** http://dx.doi.org/10.1080/00319100701344594

*Physics and Chemistry of Liquids*
Vol. 45, No. 5, October 2007, 531–539

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# Hump phenomenon on resistivity–temperature curve in liquid Bi, Sb and their alloys

XIAN-FEN LI, FANG-QIU ZU*, LAN-JUN LIU, JIN YU and BING ZHOU

School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, People's Republic of China

(*Received 3 November 2006; in final form 17 March 2007*)



The electrical resistivities of liquid Bi, Sb, and some of their alloys Pb–Bi, Pb–Sb have been investigated as a function of temperature, and the effect of heating-rate on the turning points of liquid Bi has also been investigated. Obvious and interesting hump phenomena are observed on resistivity–temperature curves of liquid Bi, Sb, and Pb–Bi, Pb–Sb alloys on heating at the temperature far above their liquidus. Moreover, the transition temperature of liquid Bi increases with heating-rate increasing, which shows that this kind of transition is in accordance with kinetic characteristics. However, comparing the heating curve with the cooling one, we found that the anomalous hump phenomenon is irreversible in liquid Bi, Sb, and Pb–Bi, Pb–Sb alloys.

*Keywords*: Liquid Bi, Sb; Liquid Pb–Bi, Pb–Sb alloys; Electrical resistivity; Hump phenomenon

*PACS:* 72.15. Cz; 61.20.-p; 61.25.Mv

## 1. Introduction

It has been proposed that systems with solid polymorphism may exhibit several liquid phases with local structures similar to the local structures of various crystals. Experimental evidence of sharp structural transitions between liquid polymorphs of Se, S, Bi, P, $I_2$, Sn, Sb, $As_2Se_3$, $As_2S_3$, and $Mg_3Bi_2$ are consistent with pressure–temperature phase diagrams with first-order liquid–liquid phase transitions [1,2]. However, the afore-mentioned phase transition is mainly about the pressure-driven phase transition, and it should be further investigated whether there exists temperature-induced phase transition in one-component systems and their alloys, and what the rules are. If so, clarification may undoubtedly shed light on further recognition of the nature of liquid state as a whole.

In our previous study, the distinct anomaly of a hump shape was observed on resistivity–temperature curves for liquid Bi–Sb alloys on heating at relatively high

*Corresponding author. Tel.: +86-551-2905057. Email: fangqiuzu@hotmail.com

*Physics and Chemistry of Liquids*
ISSN 0031-9104 print/ISSN 1029-0451 online © 2007 Taylor & Francis
DOI: 10.1080/00319100701344594

temperatures [3]. In this article, liquid bismuth (Bi), antimony (Sb), and some of their alloys Pb–Bi, Pb–Sb are chosen as the investigation objects to further probe the character of the hump phenomenon. Bi and Sb (group v) are semimetals which both exhibit a similar rhombohedral crystal structure. Element Bi is a semimetal with unusual properties [4], $Bi_{1-x}Sb_x$ alloys are very attractive materials for electric refrigeration, and properly oriented bismuth–antimony crystals are reported as being the best n-type thermoelectric materials around 80 K [5,6]. In view of their fundamental as well as applied questions, Bi, Sb and their alloys have attracted great attention so far.

Although the transport properties of Bi and Bi–Sb alloys had been reported by some authors in 0–300 K temperature range [7,8], and the electrical resistivity of liquid Sb has been measured several times up to 900–950°C [9–14]. However, references [9–13] show that the resistivity was measured at different constant temperatures and was repeated several times to get the average value, and that of reference [14] only during cooling process. Moreover, the measured temperature region [9–14] is not so wide, and the interval point of temperature measured is larger. Considering the influence of the kinetic factors and structural relaxation, we think that different measuring process may result in the difference of experimental phenomenon. In this article, the electrical resistivities of liquid Bi, Sb, and Pb–Bi, Pb–Sb alloys have been investigated with temperature elevated continuously in wider temperature range in order to probe the hump phenomenon and the possible liquid–liquid transition. The results show that obvious and interesting hump-shape changes occur on the resistivity–temperature ($\rho$–$T$) curves of liquid Bi, Sb and Pb–Bi, Pb–Sb alloys at the temperature far above their liquidus. Moreover, different heating-rates are adopted to investigate the effect of heating rate on the turning point of liquid Bi. The result shows that the transition temperature increases with heating-rate increasing, and this kind of transition is in accordance with kinetic characteristic. However, comparing the heating curve with the cooling one, we presume that the anomalous change on first cycle heating is irreversible.



## 2. Experimental procedure

In this experiment, Bi, Sb samples and some of their alloys are prepared with pure Bi (4N), Sb (4N), and Pb (4N) granules. After being melted and held at the temperature about 250–350°C above the liquidus for 30 min covered with flux $B_2O_3$, the melts are poured into quartz cells for the corresponding $\rho$–$T$ experiments.

The electrical resistivities are measured by the DC four-probe method, and the DC current-reversal technique is used to cancel the thermal EMFs (electromotive force) which may be brought with the connection points and temperature fluctuations in the test leads [15]. A PC is used to control the power supply, set the rate of heating and cooling, record the experimental data at constant time intervals during continuously heating or cooling process. The rate of heating is set as 2, 5, 7.5, and 10°C $min^{-1}$ in liquid state. The potential drop is measured by KEITHLEY-2182 nanovoltmeter with the PF66M current source providing the constant current. Tungsten wires with diameter 1 mm are employed as current and potential electrodes. The whole measuring process is under the protection of pure argon (5 N) to prevent oxidation.

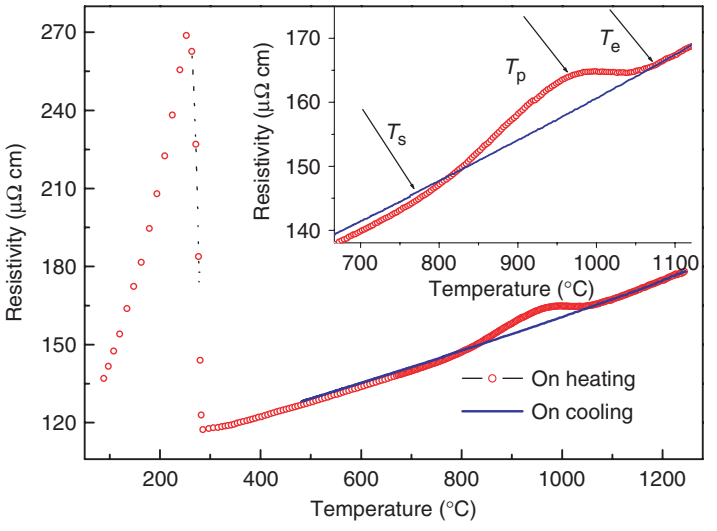


Figure 1. The $\rho$–$T$ curve of pure Bi during heating and cooling ($2^{\circ}C\,min^{-1}$).



## 3. Results and discussions

The resistivity of pure bismuth *versus* temperature is shown in figure 1. Its resistivity decreases remarkably on melting. Since bismuth is semimetal in the solid state, this phenomenon can be attributed to an increase in the number of conduction electrons on melting while the covalent bonds are broken up [16]. After melting, it becomes metallic and its resistivity increases linearly with temperature except the temperature range $T_s$–$T_e$ ($T_s$ *is defined as the starting-temperature of the change*, $T_p$ *as the peak temperature and* $T_e$ *as the ending-temperature, shown in the inset of* figure 1). Interestingly, the $\rho$–$T$ curve presents hump shape in the temperature range from $T_s$ to $T_e$. During the subsequent cooling and the second cycle heating and cooling (as shown in figure 2), the $\rho$–$T$ curve remains linear all the time in liquid, which indicates the anomalous change is irreversible.

As seen from figure 3, the resistivity of pure antimony decrease evidently on melting which is close to that of pure bismuth. But the heating and cooling $\rho$–$T$ curves present arc shape in liquid state. Moreover, the heating curve from $T_s$ to $T_e$ presents a similar abnormal behavior as that of pure bismuth (shown in the inset of figure 3), only the magnitude of $T_s$, $T_p$, and $T_e$ (as shown in table 1) is different. Since the emphasis of this article is to probe the possible anomalous change of resistivity with temperature, comparison of the $\rho$ value with that of other references was not carried out.

Moreover, different heating rates were adopted to investigate the effect of heating rate on the anomalous change of liquid Bi, as well as its kinetic behavior. The results are shown in figure 4 and table 1. From figure 4 and table 1, it can be seen that the similar hump phenomenon appears on each $\rho$–$T$ curve in liquid state at different heating-rate on first heating cycle. And $T_s$, $T_p$, $T_e$ increase with the heating-rate increasing, which is in accordance with kinetic characteristic. In addition, similar hump phenomena are found on the $\rho$–$T$ curves of liquid Pb–Bi and Pb–Sb alloys, as shown in figures 5 and 6. These results indicate that the anomalous phenomena were further strengthened owing

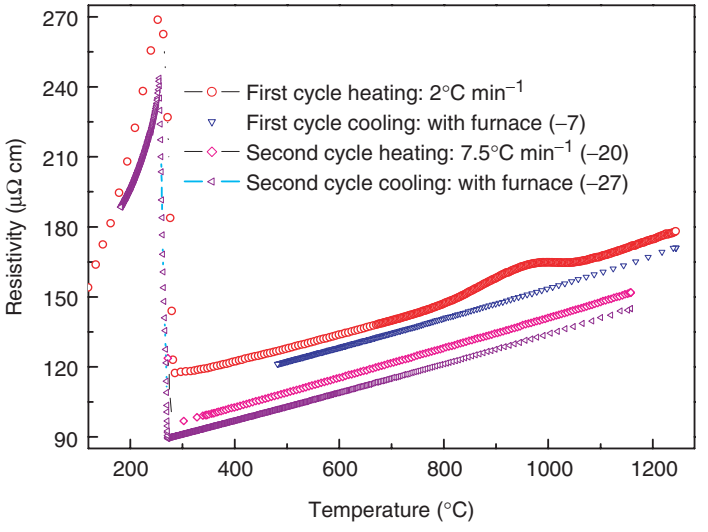


Figure 2. The $\rho$–$T$ curve of pure Bi during two cycle heating and cooling.

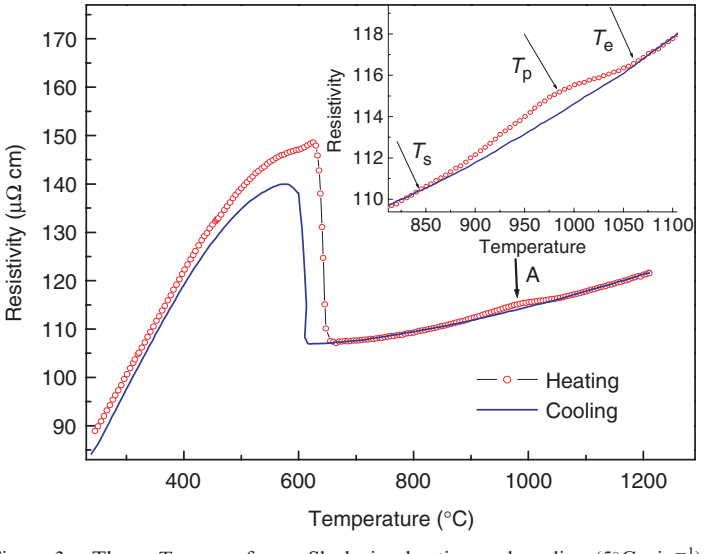


Figure 3. The $\rho$–$T$ curve of pure Sb during heating and cooling (5°C min$^{-1}$).

Table 1. Different turning-points of Bi and Sb at different heating-rate.

| | Heating rate (°C min$^{-1}$) | $T_s$ (°C) | $T_p$ (°C) | $T_e$ (°C) |
|---|---|---|---|---|
| Pure Bi | 2 | 766 | 967 | 1060 |
| | 5 | 826 | 1009 | 1115 |
| | 7.5 | 850 | 1098 | 1200 |
| | 10 | 871 | 1105 | 1242 |
| Pure Sb | 5 | 844 | 986 | 1064 |

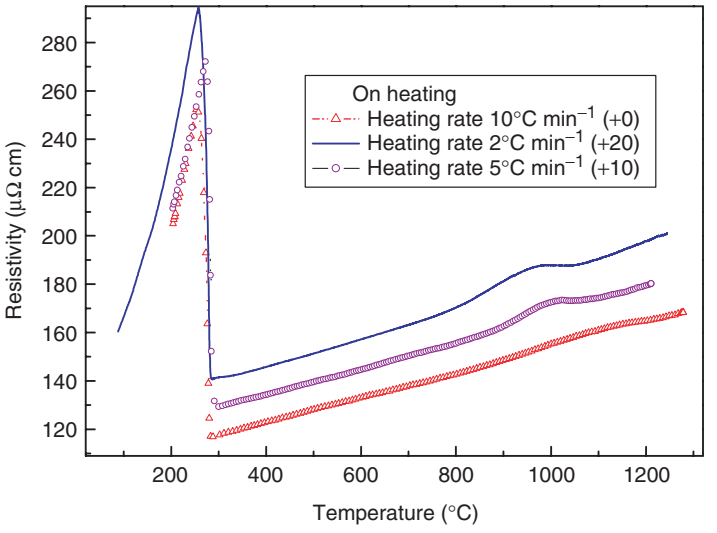


Figure 4. The $\rho$–$T$ curves of different Bi samples at different heating-rate on heating.



to the interaction among liquid Bi, Sb and Pb; at the same time, the existence of anomalous phenomena in liquid Bi–Sb [3], Pb–Bi, and Pb–Sb alloys further proves the existence of the anomalous change in liquid Bi, Sb. Since the experiment is under protection of pure Ar gas (5N), the samples after experiments showed no evidence of oxidation.

The observation of irreversible changes in Bi- and Sb-based melts (different behavior at first cycle heating and the subsequent cooling and heating) may mean that initial liquid during first cycle of heating was in the metastable state and may mean the existence of large activation barriers between this state and a true equilibrium one. This metastable state of melt may exist for a long time, so one can suppose that there are some long-lived metastable clusters in the above liquids. However, after experiencing the high temperature transition from $T_s$ to $T_e$, the melt become true homogeneous stable solution. According to reference [17,18], the transformation of a single-component liquid from one liquid state to another is called the ''liquid–liquid transition'' (LLT). Since resistivity is one of physical properties sensitive to structure, its anomalous change with temperature indicates the liquid state change, but the anomalous change is irreversible, we can classify the irreversible transition in Bi- and Sb-based melts as metastable to stable transition.

Furthermore, differential scanning calorimetric (DSC) analysis was carried out on liquid Bi, as shown in figure 7. From figure 7, we can observe an endothermic peak on DSC curve in the temperature range 876–1047°C, which shows that the peak position corresponds roughly to that of the relevant resistivity peak but with a hysteresis due to a higher scanning rate. The calorific effect in the DSC curve means that the melts need to absorb enough energy to overcome the energy barrier, i.e., the activation energy, then the previous long-lived covalent clusters or short-range orders of Bi–Bi, Sb–Sb or Pb–Bi, Pb–Sb may start to disintegrate into smaller ones to make the high-temperature melt more disorder, and the system entropy of Bi melts undergoes a discontinuous change during the transition.

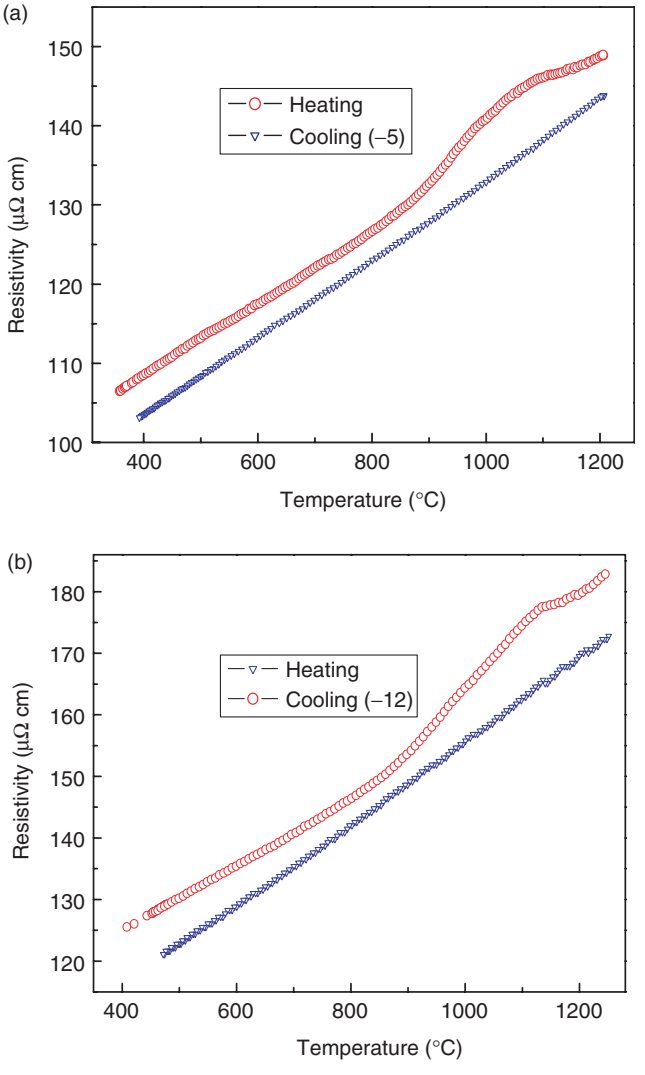




Figure 5. The $\rho$–$T$ curves of Pb–Bi alloys during heating and cooling ($7.5^{\circ}C\,min^{-1}$). (a) Pb–Bi32wt%, (b) Pb–Bi70wt%.

Based on the above-mentioned results, we suggest that there exists temperature dependence transition in liquid Bi, Sb, and Pb–Bi, Pb–Sb alloys. The transition starts from $T_s$, ends at $T_e$. We take it for granted that there exists Bi–Bi, Sb–Sb, Bi–Pb, Sb–Pb short-range orders (SROs) or covalent clusters in liquid Bi, Sb, and Pb–Bi, Pb–Sb alloys, respectively at the temperature above their melting point. In light of references [19–21], a remarkable shoulder could be observed on the right-hand side of the first maximum of the structure factors in liquid Bi or liquid Sb, which indicated the presence of covalent bonds in liquid Bi, Sb, respectively. According to the electron localization viewpoint [22], an interesting feature of liquid metals and alloys is the relative freedom which some of the electrons have. Some of the valence electrons are localized and

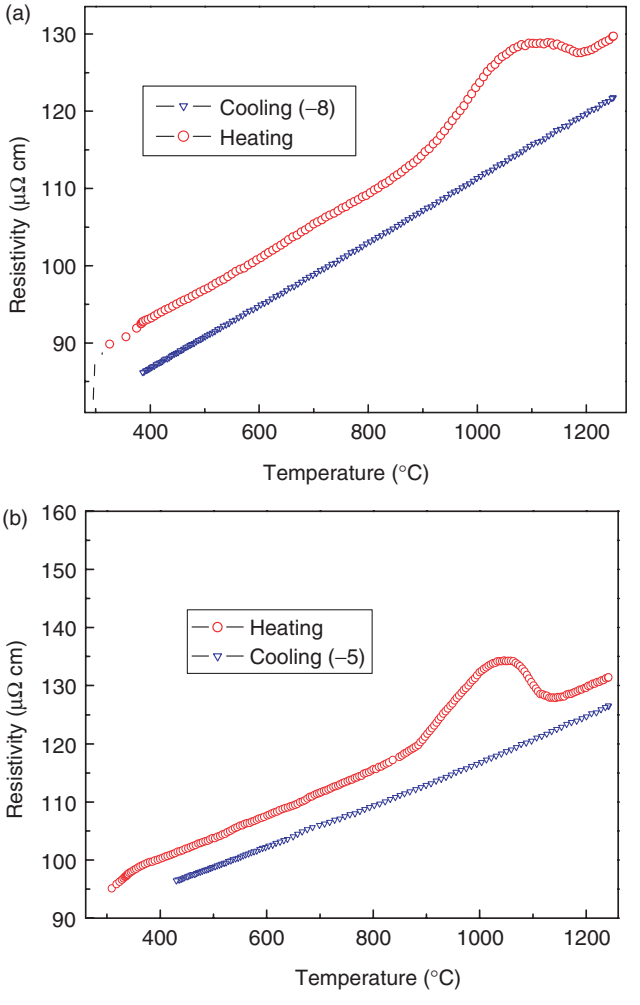


Figure 6. The $\rho$–$T$ curves of Pb–Bi alloys during heating and cooling ($7.5^{\circ}C\,min^{-1}$). (a) Pb–Sb11.2, (b) Pb–Sb30.

participate in the bonding, while others are free to occupy the whole volume of the metallic system, on a time-average basis. The electrons may be considered to move among potential-wells that may trap them, if they are deep enough. The trapping is more or less permanent if the potential-well arises from a covalent, directional homopolar bond. According to this viewpoint, it is deduced that, when the Bi or Sb or Pb–Bi, Pb–Sb melts are heated continuously to the turning point $T_s$, the kinetic energy of the atoms becomes high enough to overcome the energy barrier, i.e., the activation energy, then the previous long-lived metastable bigger covalent clusters or short-range orders of Bi–Bi, Sb–Sb or Pb–Bi, Pb–Sb start to disintegrate into smaller ones to make the high-temperature melt more disorderly. From the viewpoint of potential-wells, the amount of potential-wells may increase with the increasing of disorder degree, so the electrons that are trapped by potential-wells may increase to make the electrons

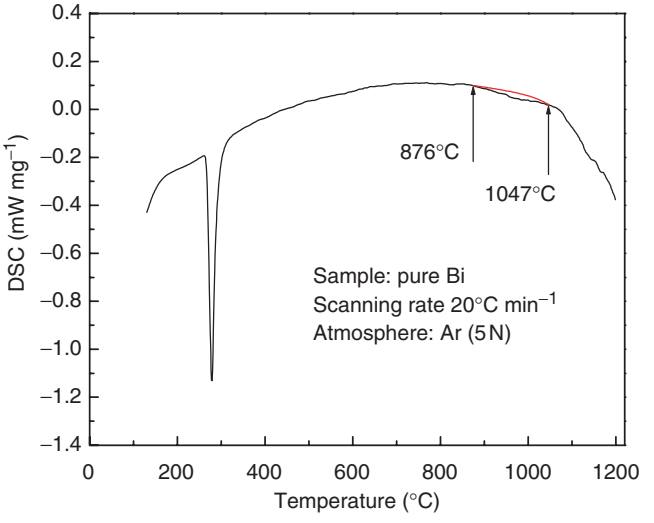


Figure 7. The DSC curve of liquid Bi on heating.



mobility lower and the electrical resistivity higher. However, when the temperature gets high enough to $T_p$, the resistivity increases slowly or decreases to some extent with temperature rising, we assume that the $T_s$ to $T_p$ phase and the $T_p$ to $T_e$ phase may belong to different transitions, and this needs to be probed further in future. Then the melts reach the state of true solution at $T_e$ [23]. After $T_e$, the resistivity increases linearly again with temperature. During the progress of transition, the density of electron state changed unevenly and the hump phenomenon was observed on $\rho$–$T$. In addition, compared the first cycle heating curve with the subsequent cooling and heating ones, the anomalous hump phenomenon of first cycle heating is irreversible.

The anomalous behaviors of resistivity in liquid Bi, Sb, and Pb–Bi, Pb–Sb alloys have been investigated with temperature changing. The results show that the investigated single-component system and their alloys presents obvious hump-shape change on $\rho$–$T$ curve. However, the hump phenomenon on first cycle heating is irreversible. Although the transition temperature and the magnitude of the hump may be affected by the heating rate, the hump phenomenon is reproducible with different samples. However, this kind of hump phenomenon was not observed in other single-component systems such as In, Pb [24], etc. In order to probe the inherent nature of this kind of phenomenon, it needs further exploration by other techniques; but this finding of the transition in one-component system may shed light on further recognition of the nature of liquid state.

## 4. Conclusions

In summary, the electrical resistivities of Bi, Sb and Pb–Bi, Pb–Sb alloys have been investigated as a function of temperature in wide temperature range, and obvious hump-shape transitions are observed on $\rho$–$T$ curves of liquid Bi and Sb and some of their alloys on first cycle heating.

The hump-shape transitions on $\rho$–$T$ curves indicate the temperature dependence of transition in liquid Bi, Sb at the temperature far above their liquidus, and it is in accordance with the kinetic characteristic. The long-lived metastable short-range orders or covalent clusters remaining in the liquid, start to disintegrate into smaller ones or break up during the transition, leading to the temperature dependence change of potential-wells and electron freedom, which causes the abnormal behavior of the resistivity in liquid Bi, Sb, and Pb–Bi, Pb–Sb alloys. Comparing the $\rho$–$T$ curve on first cycle heating with the subsequent cooling and heating ones, we presume that the hump-shape transition of first cycle heating is irreversible.

## Acknowledgements

This work has been supported by the National Natural Science Foundation of China Grant No. 50371024 and No. 50571033, by the key project of Chinese Ministry of Education No. 104106.



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