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Electrical resistivities of liquid Na–Bi and Rb–Bi alloys*

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Abstract. The electrical resistivities ρ of liquid Na–Bi and Rb–Bi alloys have been measured as functions of composition and temperature. Plotted as a function of composition the resistivity of Na–Bi exhibits a maximum at the composition corresponding to Na_3Bi while for Rb–Bi two maxima, at 25 and 40 at. % Bi, can be discerned. In both alloys, the maximum value of ρ is far beyond the metallic range. In the composition ranges around the maxima the temperature dependence $d\rho/dT$ of the resistivity is negative and $-d\rho/dT$ attains extraordinarily large values. The results can be explained by assuming that for Na–Bi a strong octet compound is formed whereas for Rb–Bi both an octet and a clustered compound are formed. Comparison with the other alkali–Bi alloys shows that in the sequence from Li–Bi to Cs–Bi a transition from a simple octet configuration to a clustered configuration occurs.

1. Introduction

The physical properties of liquid alkali–group V systems have attracted attention for many years. They form typically ionic alloys, in which metal–non-metal transitions (more specifically metal–salt transitions) occur as a function of composition.

NMR measurements [1] as well as resistivity measurements [2] of liquid Cs–Sb alloys have shown that a metal–non-metal transition occurs close to the composition Cs_3Sb . The same conclusion can be drawn from the thermopower of Cs–Sb in which there is a node at 25 at. % Sb [2]. Furthermore from neutron diffraction measurements, Lamparter *et al* [3] conjectured the existence of covalently bonded Sb-chain units in Cs–Sb alloys. This is more or less confirmed by the resistivity measurements which exhibit a broad maximum around the equiatomic composition. For Na–Sb, Redslob *et al* [2] found a steep conductivity minimum near the octet composition Na_3Sb .

For the Li–Bi system, a high resistivity maximum at Li_3Bi was observed by Steinleitner *et al* [4]. Petric *et al* have found two peaks in the excess stability of liquid K–Bi [5] and Rb–Bi [6] alloys near 50 at. % Bi and 25 at. % Bi, respectively, which can be interpreted as an indication of maximum structural ordering at these compositions.

More recently, an investigation of the resistivity of K–Bi alloys, performed at our laboratory, shows a distinct maximum at the octet composition, K_3Bi , accompanied by a weak hump near 40 at. % Bi [7]. For liquid Cs–Bi alloys the octet compound is no longer discernible and only a peak at 40 at. % Bi survives [7]. The shift from octet composition for K–Bi to 40 at. % Bi for Cs–Bi was associated with the formation of

* Dedicated to Professor H-G von Schnering on the occasion of his 60th birthday.

fragments of Zintl ions. The extremely high resistivity maximum in Cs–Bi ($4589 \mu\Omega \text{ cm}$, well in the range of localized electrons) is primarily a consequence of the large size of the Cs atoms and secondly of the large electronegativity difference between the components [8]. Previous studies of liquid Na–Bi alloys have been restricted to the vicinity of the stoichiometric composition [9]. The shape of the conductivity versus composition curve can be fairly well predicted from thermodynamic data. Hesson *et al* [10] have determined the densities of a number of liquid Na–Bi alloys. They observed a considerable volume contraction which has a maximum at approximately 25 at.% [11]. This is a characteristic property of liquid-ionic-compound-forming alloys [12–14].

To our knowledge, the resistivity of liquid Rb–Bi alloys has never been measured before. To extend the previously reported results and to obtain a more complete understanding of the transport and chemical properties of the liquid alkali–bismuth systems, we have undertaken resistivity measurements on liquid Na–Bi and Rb–Bi alloys in the whole composition range and as a function of temperature.

2. Experiment

The pure metals used in preparing the alloys for the resistivity measurements were obtained from different sources: sodium with a nominal purity of 99.93 wt% was obtained from Merck AG, and rubidium with a nominal purity of 99.99 wt% was obtained from Kawecki Berylco Industries Inc. Bismuth ingots, purchased from Ventron GmbH, Karlsruhe, were nominally 99.999% pure. The preparation of our samples and the resistivity measurements were carried out inside a He-filled glove box with an oxygen content lower than 1 ppm. We used the same experimental set-up as described by Meijer [15]. The liquid alloy was contained in an AISI 321 stainless steel tube. A current of about 2.5 A was passed through the tube and the liquid. Thermal voltages were eliminated by measuring the potential difference for each section without current. The temperatures were measured using chromel–alumel thermocouples. The accuracy of the temperature measurements is within $\pm 0.5 \text{ K}$. The actual resistivity measurements were controlled using a DOS personal computer provided with a IEEE bus. A PID Multitemp controller was used to stabilize the temperature at a number of pre-set values in steps of 10 K. At each step the homogeneity and time stability of the temperature were checked by the computer before a new set of measurements was initiated. Pb was used as a reference material for calibration. Because of the poor electrical contact between the stainless steel tube and pure liquid Pb, we added 0.44 at.% Na into the pure Pb and calculated the resistivity from known data on $d\rho/dc$ for $c_{\text{Na}} \rightarrow 0$ [16]. The resistivity data for the pure metals and alkali–bismuth alloys were determined by averaging the resistivity values from three different sections of the tube using stainless steel electrodes spot welded to it. We have checked all procedures by measuring pure Bi several times before starting the investigation of the alkali–Bi systems. We found that the measurements were reproducible. The absolute values of the resistivity for pure Bi agreed within 1% with the data obtained by Ginter *et al* [17] using a quartz cell fitted with tungsten electrodes. For each alkali–bismuth system, more than 20 samples of various compositions covering the whole concentration range were investigated. Because of the evaporation of the alkali metals at high temperatures, we limited our measurements to

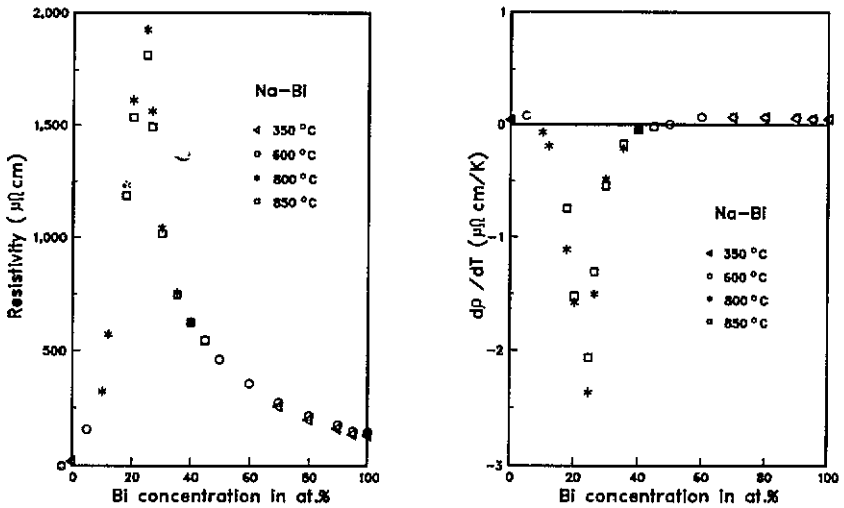


Figure 1. (a) The resistivity ρ of liquid Na-Bi alloys at the temperatures indicated in the figure. (b) The temperature dependence $d\rho/dT$ of the resistivity of liquid Na-Bi alloys at the temperatures indicated in the figure.

temperatures lower than 860 °C and 680 °C for Na-Bi and Rb-Bi, respectively. The relative error in the resistivity measurements is estimated to be within 2%.

3. Results

Figure 1 shows the resistivity ρ and its temperature derivative $d\rho/dT$ of liquid Na-Bi alloys. Analogous results for Rb-Bi are shown in figure 2. Most of our results were fitted to second-degree polynomials in T . From figure 1, it is seen that the resistivity of the Na-Bi system exhibits a sharply peaked maximum, where it attains a value of $1925 \mu\Omega\text{cm}$ at 800 °C. The composition corresponding to this maximum is approximately the stoichiometric composition for an octet compound, Na_3Bi . The temperature derivative $d\rho/dT$ is negative in a certain composition range and has an extremely deep minimum. The maximum value of $(-d\rho/dT)$ is $2.36 \mu\Omega\text{cm K}^{-1}$ at $c_{\text{Bi}} = 24.8 \text{ at.}\%$, very high indeed compared with, for example, Na-Pb, where it is only $0.78 \mu\Omega\text{cm K}^{-1}$.

In the Rb-Bi system, two resistivity maxima can be observed: one corresponding to an octet compound and the other at 40.1 at.% Bi, with resistivity values of $\rho = 1836 \mu\Omega\text{cm}$ for $T = 650 \text{ }^\circ\text{C}$ and $\rho = 2152 \mu\Omega\text{cm}$ for $T = 550 \text{ }^\circ\text{C}$, respectively. As shown in figure 2, the temperature derivative $d\rho/dT$ of the electrical resistivity changes sign and becomes negative in the composition range between 10 and 50 at.% Bi. It has minimum values of $-2.55 \mu\Omega\text{cm K}^{-1}$ at $c_{\text{Bi}} = 25.0 \text{ at.}\%$ and $-2.89 \mu\Omega\text{cm K}^{-1}$ at $c_{\text{Bi}} = 40.1 \text{ at.}\%$, respectively. The minima occur at the same compositions as the maxima in ρ .

4. Discussion

Table 1 shows the extremal values of ρ and $d\rho/dT$ as well as the corresponding compositions for the complete series of alkali-Bi systems. In Li-Bi and Na-Bi the resistivity

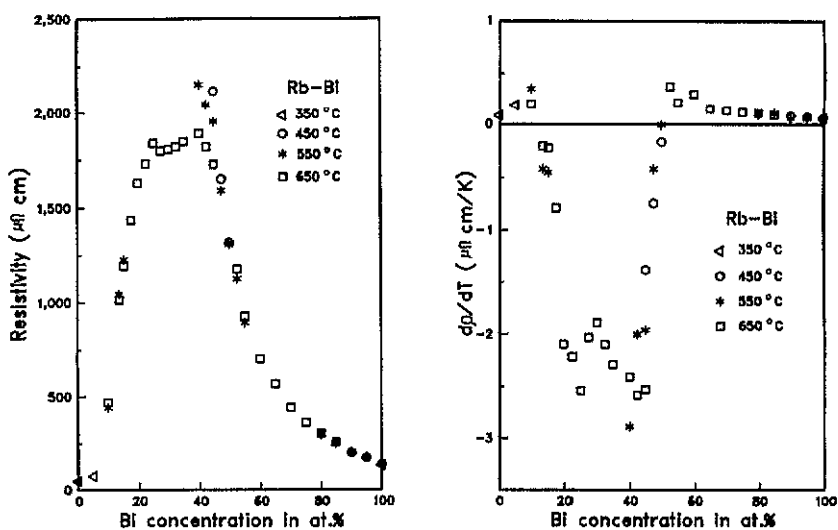


Figure 2. (a) The resistivity ρ of liquid Rb-Bi alloys at the temperatures indicated in the figure. (b) The temperature dependence $d\rho/dT$ of the resistivity of liquid Rb-Bi alloys at the temperatures indicated in the figure.

Table 1. Compound-forming compositions for the alkali-Bi alloys systems, and values of ρ and $d\rho/dT$ at these compositions. $\Delta\varphi = \varphi_{\text{Bi}} - \varphi_{\text{alkali}}$ is the electronegativity difference. The classification is according to Mott and Davis [22].

System	Reference	c (at.% Bi)	T (°C)	ρ ($\mu\Omega$ cm)	$d\rho/dT$ ($\mu\Omega$ cm K ⁻¹)	$\Delta\varphi$	Classification
Li-Bi	[4]	24.3	1080	2000	-2.25	1.30	Regime II
Na-Bi	Present work	24.8	800	1925	-2.36	1.45	Regime II
Na-Bi	[9]	24.8	850	1894	-3.88		Regime II
K-Bi	[7]	25.7	700	2113	-3.01	1.90	Regime II
		40.0	450	2008	-3.01		Regime II
Rb-Bi	Present work	25.0	650	1836	-2.55	2.05	Regime II
		40.1	550	2152	-2.89		Regime II
Cs-Bi	[7]	41.0	550	4589	-9.59	2.20	Regime III

maximum corresponds almost exactly to the octet composition, with 25 at.% Bi. The peak at around 40 at.% first shows up as a shoulder in K-Bi. It develops into a separate maximum for Rb-Bi. For Cs-Bi we observe only a broad maximum at 40 at.% Bi. In a previous publication [7] this shift of stoichiometry was explained in terms of the formation of variable-size polyanions. The experimental results mentioned in section 3 corroborate this explanation.

There exists a strong similarity between the alkali-bismuth and the alkali-lead alloys. In the latter the octet compound found in Li-Pb gives way to an equiatomic compound as the size of the alkali atom increases [18]. Most of the experimental results can be explained in terms of a simple, although perhaps idealized model: the formation of well

Table 2. Compound formation in alkali-bismuth compared with alkali-lead systems.

Peak positions	Alkali-lead	Alkali-bismuth
Only octet compound	Li-Pb	Li-Bi, Na-Bi
Octet + shoulder for clustered compound	Na-Pb	K-Bi
Both octet and clustered compound	—	Rb-Bi
Only clustered compound	K-Pb, Rb-Pb, Cs-Pb	Cs-Bi

defined 'Zintl ions', i.e. tetrahedral units $(Pb_4)^{4-}$ [19]. It was shown by Geertsma *et al* [20] that Zintl ion formation is favoured by a large size of the alkali atom.

In the pnictides the Zintl ion would correspond to an infinite Te-like chain, which cannot persist in the liquid. Therefore, it was assumed that only fragments of such chains are present in the liquid alloys. This assumption also explains the shift in stoichiometry from 50 at. % in the case of the ideal Zintl ion to 40 at. % actually found in liquid alkali-Bi alloys. It should be noted that crystallographically the existence of Te-like chains has been confirmed for antimony alloys only [21] and not yet for alkali-bismuth alloys.

The correspondence between the alkali-bismuth and alkali-lead systems is given schematically in table 2. Note that the composition of the compounds is defined by the maxima of the resistivities.

For Cs-Bi the maximum is broader than for the lead compound, which is in agreement with the assumption of variable-size polyanions corresponding to a less well defined stoichiometry. It should be noted that the behaviour of Rb-Bi is very similar to that of Na-Sn for which also two peaks of approximately equal size are observed at 23 at. % Sn and 43 at. % Sn, respectively [16].

The octet compound is apparently more stable for the bismuth than for the lead alloys. Possible origins of this effect are the smaller on-site electron repulsion on the bismuth ions, a more favourable Madelung energy for the 1:3 than for the 1:4 compounds and destabilization of the clusters due to the fragmentation. It should be noted that the energy balance is rather delicate and that it is not easy to make predictions regarding the stability of any configuration, but in general the comparison between the alkali-lead and the alkali-bismuth systems supports the assumption of polyanion formation in the latter. Apparently, for both groups of systems, the size of the alkali atom is the determining factor for the octet-clustered transition.

According to their resistivity values the compounds belong to regime II (diffusive motion of electrons) of the classification by Mott and Davis [22]. The huge negative values of $d\rho/dT$ can be understood from the decomposition of the ordered structure at higher temperatures, which restores metallic behaviour.

So far, the picture is reasonably consistent. However, confusion arises when physical properties other than the resistivity are considered. Thermodynamic measurements have been carried out for Na-Bi [23, 24], K-Bi [2] and Rb-Bi [3]. In all these systems, strong evidence for the existence of a liquid octet compound (25 at. % Bi) has been obtained. For Na-Bi this is the only compound, in agreement with the resistivity results. For K-Bi and Rb-Bi a second compound is found, but at 50 at. % Bi (the concentration corresponding to the ideal Zintl compound) and not at 40 at. % Bi as indicated by the resistivity measurements. Here, Kurnakow's [25] rule, freely translated as 'look for the

extremal values of physical properties to find the stoichiometric composition' obviously leads to diverging results.

For Li-Bi and Na-Bi [26] a minimum in the susceptibility is found at 25 at. % Bi, where from the present results we would expect it. However, for Cs-Bi a distinct minimum is found at the same concentration [27], whereas none of the other physical properties gives the slightest indication for a compound at this composition. Unfortunately the measurements are restricted to alkali-rich alloys, so that the existence of a second compound, if any, could not be ascertained.

The volume contraction of liquid Na-Bi shows a maximum at 25 at. % Bi [10, 11], in agreement with the resistivity and thermodynamics results.

A glance at the phase diagrams [2, 3, 28] adds further to the confusion. Congruently melting octet compounds, all with melting points at the highest temperature of the liquidus, exist for all systems Li-Bi to Cs-Bi. For Li-Bi and Na-Bi this is the only compound of this kind, in accordance with the resistivity results. The phase diagrams of K-Bi, Rb-Bi and Cs-Bi are very similar. They all exhibit a second congruently melting compound at 66.6 at. % Bi with a melting point which is only slightly lower than that of the octet compound. Obviously there is no correspondence between the solid compound at 66.6 at. % Bi and the second compound in the liquid indicated by either the resistivity or the thermodynamic results. Indeed in the K-Bi, Rb-Bi and Cs-Bi phase diagrams a 40 at. % Bi solid alloy occurs which is either congruently or peritectically melting and which could possibly be associated with the second peak in the resistivity. Its crystal structure is unknown and the melting point is low compared with that of the octet compound. At 50 at. % (corresponding to the relative maximum of the stability function) there is a eutectic in these alloys. Nearby compounds with 44.4 at. % Bi are not stable at the melting point. So the origin of the second compound for alloys of bismuth with the heavier alkali metals remains unclear. The simple picture of structures persisting through the melting point, which was successful for the alkali-lead alloys, seems to be not applicable here.

At 50 at. % Bi the resistivity of liquid Rb-Bi is approximately $1310 \mu\Omega \text{ cm}$. The corresponding value of the temperature coefficient is zero within the limits of accuracy and becomes positive for 53 at. % Bi, where the resistivity is still $1125 \mu\Omega \text{ cm}$. A similar observation was made for Cs-Bi [7]. Resistivity values of this order usually are accompanied by a negative $d\rho/dT$. Enderby [29, 30] has suggested that a more detailed consideration of the Kubo-Greenwood formula taking into account the width of df/dE (f being the Fermi function) possibly could explain such anomalies. The discrepancies in the stoichiometric composition derived from various physical properties, mentioned above, may be understood in a similar way, but more knowledge of the chemistry is needed before one can give any speculations on the shape of $n(E)$. In particular a determination of the crystal structures of the solid compounds would be instructive.

Acknowledgments

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