Resistivity of liquid K-Bi and Cs-Bi alloys

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Abstract. We have measured the electrical resistivity of liquid K–Bi and Cs–Bi alloys as a function of composition and temperature. In both alloy systems strong indications for chemical compound formation were found: in a large composition range the resistivity attains values that are characteristic for Mott's 'regime of diffusive motion'. In K–Bi the octet compound K_3Bi dominates. In Cs–Bi at 550 °C the resistivity reaches a maximum of more than 4000 $\mu\Omega$ cm at a composition of 40 at. % Bi ($T = 550$ °C). This is explained by assuming that the Bi ions form poly-anions (Zintl ions), quite possibly chain fragments $Bi_n^{(n+2)-}$ of variable length. The equi-atomic liquid alloy CsBi displays the unusual feature of a high resistivity (2000 $\mu\Omega$ cm) combined with an almost negligible temperature dependence.

1. Introduction

The experimental work described in this paper forms part of a search for the effects of compound formation and, more particularly, of poly-anion formation on the electrical properties of liquid alloys [1, 2]. Such effects show up most clearly in the alkali–Pb alloys [3, 4]. In all alkali–Pb alloy systems the resistivity reaches non-metallic values: the electron mean free path is equal to the inter-atomic distance, and the conductivity is roughly proportional to $n^2(E_F)$ [5]. Thus, the resistivity maximum occurs when $n(E_F)$ is minimum. In the alkali–Pb alloys two mechanisms of compound formation can be distinguished that cause a minimum of $n(E_F)$ at a certain composition. In Li–Pb and Na–Pb the resistivity maximum occurs at or very near the octet composition A_4Pb. Bonding is intermediate between ionic and metallic and the minimum in $n(E_F)$ lies in between a band that is predominantly Pb 6p, and a band (above the Fermi level) that is predominantly made up of Li 2s states.

In K–Pb, Rb–Pb and Cs–Pb, compound formation is at the equi-atomic composition. In all probability, this shift of stoichiometry is caused by the formation of poly-anions (Zintl ions), in this case $(Pb_4)^{4-}$ tetrahedra [6, 7]. The rules that govern the competition between these two mechanisms of compound formation are laid out in [8]: it turns out that the alkali ion size is the most important factor.

These ideas have found application to other alloy systems. In Na–Sn and Li–Ge, as well as Li–Si [9–12], formation of poly-anions, although not necessarily tetrahedra, is the probable cause of the observed behaviour of the resistivity and alkali Knight shift. Furthermore, the characteristic shift of stoichiometry from alkali-rich to equi-atomic compounds was also seen in alkali–group-IIIb alloy systems [3, 13–16]. The question

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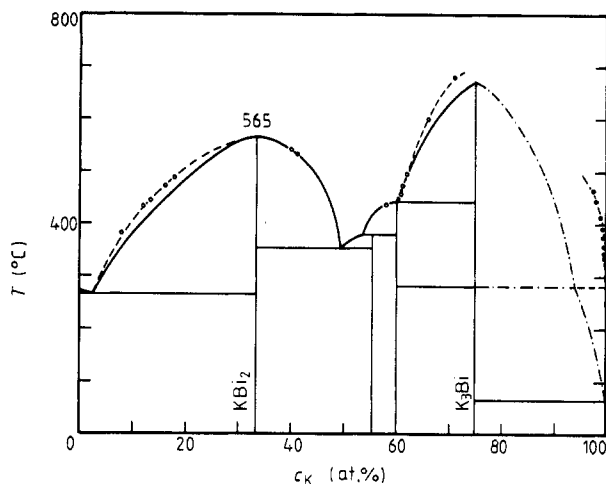
Figure 1. The phase diagram of the K–Bi system according to [27].

thus naturally arises of whether the alkali–group-V alloy systems conform to the same pattern.

Of the liquid-alkali–pnictide systems the antimony systems have been studied most intensively. The solid octet compound Na_3Sb persists in the liquid state, but the findings for liquid Cs_3Sb are a little ambiguous [17, 18].

At the equi-atomic composition, the phase diagrams suggest increasing stability from NaSb to CsSb. In the solid equi-atomic compounds, the Sb ions occur in tellurium-like spirals [19], in accordance with the Zintl principle [6, 7]. There is no equi-atomic compound LiSb in agreement with the general rules for Zintl ion formation as formulated by Geertsma [8]. The conductivities of liquid Cs–Sb alloys display a deep local minimum near the equi-atomic composition. They suggest a persistance of chalcogenide-like chain fragments in the liquid. The same conclusion was drawn by Lamparter and co-workers [20] from their neutron diffraction results.

Remarkably, the Darken excess stability of liquid K–Sb as calculated from EMF data by Saboungi and co-workers [21] has a huge maximum around the equi-atomic compound only and exhibits no significant effects of compound formation near the octet composition.

From magnetic susceptibility data, Steinleitner [18, 22] concludes that the liquid does not consist of fully ionised Cs^+ and Sb^{3-} (Bi^{3-}) ions. This view is supported by band-structure calculations on solid Cs_3Sb as performed by Robertson [23, 24] and by Tanaka and Niizeki [25]. According to these calculations, Cs_3Sb is ionic, although the charge transfer is incomplete.

Returning to the alkali–bismuth alloys we notice that the phase diagrams, given in figures 1 and 2 [26, 27], differ strongly from those of the antimony alloys. More particularly the K–Bi, Rb–Bi and Cs–Bi phase diagrams exhibit a characteristic two-peak structure. There is a high-melting-point temperature octet compound at the alkali-rich side. The other peak is at the ABi_2 composition. At the equi-atomic composition, we have a deep eutectic, with peritectically formed compounds at the alkali-rich side. In liquid K–Bi alloys, the excess stability [27] has its main peak at the K_3Bi composition.

2. Experiment and results

The resistivity measurements were performed by the metal tube method described in [28], but modified to allow for the high temperatures. For tube material, we used AISI
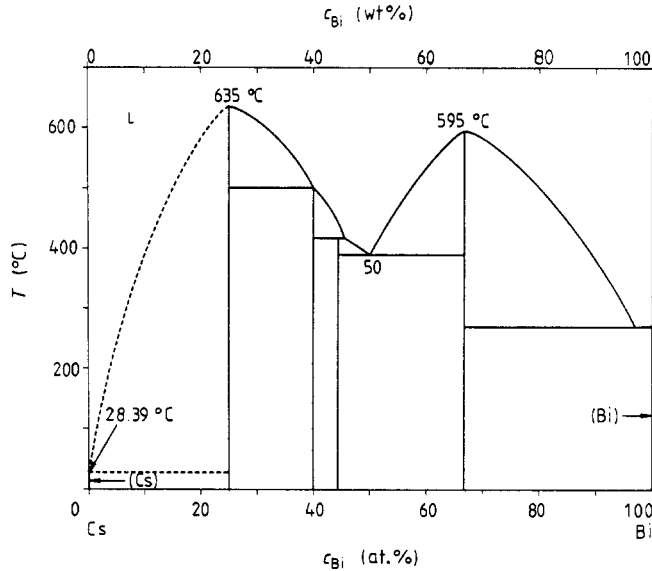
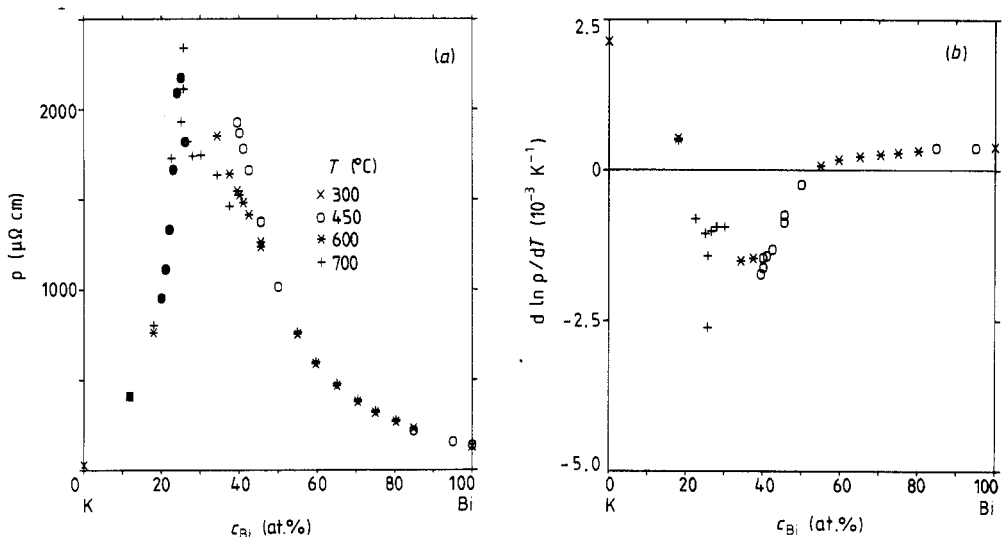**Figure 2.** The phase diagram of the Cs–Bi system (from [26]).

Figure 3. (*a*) The resistivity, ρ, of liquid K–Bi alloys at the temperatures indicated in the figure. The filled-in symbols are results from [29]. (*b*) The temperature dependence of the resistivity, d ln ρ/dT, of liquid K–Bi alloys at the temperatures indicated in the figure.

321 stainless steel, which is not attacked to any significant extent by the alkali–Bi alloys. Since high resistivities were expected, we were careful to select a tube that was as thin-walled (0.25 mm) as possible without losing mechanical stability. This allows determination of resistivities up to 5000 $\mu\Omega$ cm with a relative accuracy of better than 2.5%. In figure 3 we show the resistivity ρ, and the logarithmic temperature derivative, d ln ρ/dT, of liquid K–Bi alloys. Analogous results for Cs–Bi are shown in figure 4.

For K–Bi, we have completed the picture by including data around the octet composition K_3Bi obtained by Freyland, as quoted by Egan [29]. Our own measurements
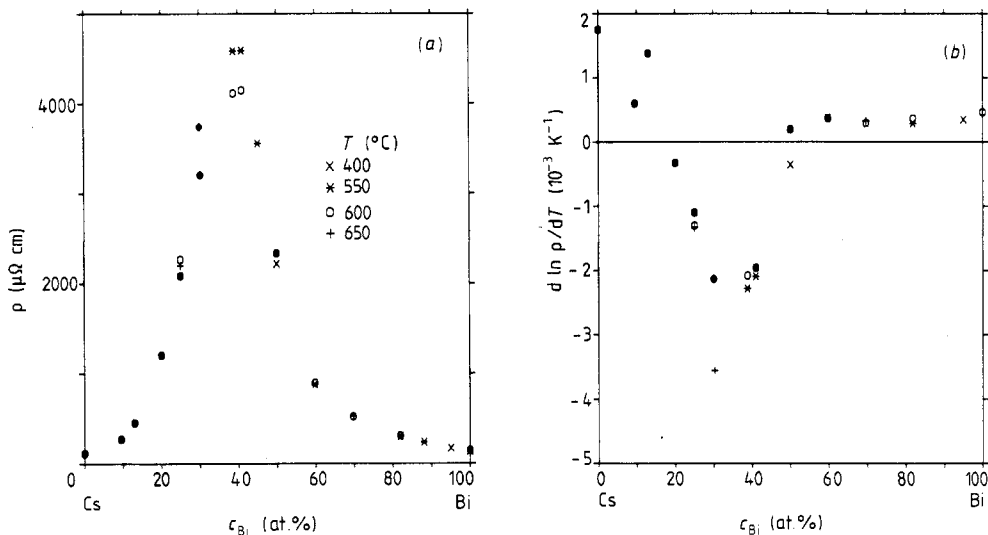
Figure 4. (*a*) The resistivity, ρ, of liquid Cs–Bi alloys at the temperatures indicated in the figure. The filled-in symbols are due to Steinleitner [18]. (*b*) The temperature dependence of the resistivity, d ln ρ/dT, of liquid Cs–Bi alloys at the temperatures indicated in the figure. The filled-in symbols represent results due to Steinleitner [18].

near the octet composition suffer from some uncertainty in the composition (≈ 1 at.%) due to the evaporation of potassium. Egan [29] does not state the temperature for the resistivity data of Freyland. However, it is apparent from the figure that this temperature must have been close to 700 °C.

As to the interpretation of the resistivity data, the shape of the curve for K–Bi may be compared to that for Na–Pb (see [9]). The $\rho(c)$ curve is dominated by the octet compound K_3Bi. A shoulder may be discerned between 40 and 50 at.% Bi. Note that we have a shoulder rather than a second resistivity maximum: the appearance in the figure of a second peak near 40 at.% Bi must be attributed to the much lower temperature of measurement (the open circles denote a measuring temperature of 450 °C, whereas the data around K_3Bi apply to a temperature of 700 °C). The true shape of the shoulder comes out most faithfully if one connects the asterisks (*) denoting the measurements at 600 °C.

In the Cs–Bi system, the octet compound is no longer discernible. The resistivity peak is rather broad, and a maximum value of 4600 $\mu\Omega$ cm (500 °C) is reached for $c_{Bi} = 40$ at.%. Together with our own results, we have plotted measurements from Steinleitner's thesis [18]; the agreement is seen to be very good. Apart from the resistivity maximum, which is accompanied in the usual way by a minimum in d ln ρ/dT, we draw attention to the peculiar behaviour of the equi-atomic alloy. Although its resistivity is 2000 $\mu\Omega$ cm, d ln ρ/dT is very nearly zero.

3. Discussion

3.1. The octet compound

Hackstein [30] presents an overview of resistivity data for the A_3B octet compounds, where A is an alkali metal and B either Bi or Sb. Even in Cs–Bi, which has a resistivity

maximum at $C_B \simeq 40$ at.%, the resistivity of the compound at 75% Cs (2000 $\mu\Omega$ cm) is clearly far beyond the nearly free-electron (NFE) regime. The resistivity peak in Cs–Bi is so broad that an explanation in terms of compound-forming at one composition only is probably not appropriate. Rather, the atomic structure appears to readjust itself with composition, enabling the electrons to form saturated bonds and keeping the density of states at the Fermi level low. The same remark applies to K–Bi: although in this system the octet compound is more clearly developed, the region of non-NFE behaviour extends to $c_{Bi} \simeq 50$ at.%. In both cases the width of the resistivity peak demonstrates a change in chemical bonding with increasing Bi content.

In Li–Bi Steinleitner and co-workers [31] found a resistivity maximum at Li$_3$Bi, in agreement with predictions from Geertsma's model [8].

3.2. Poly-anions in K–Bi and Cs–Bi alloys

From our experience with the alkali–group-IVb alloys, we are inclined to attribute the resistivity maximum in Cs–Bi at $c_{Bi} \simeq 40$ at.%, as well as the shoulder in K–Bi, to poly-anion formation. This explanation was already put forward by Steinleitner [18]. From the Zintl picture, we expect Bi$^-$ ions to form linear chains, as the chalcogenides do. This would be in agreement with Lamparter's conclusions on the structure of Cs–Sb [20], mentioned in the introduction. For entropy-related reasons, fragments of Bi chains, rather than infinite Bi chains, will occur in the liquid. In order to saturate the dangling bonds of a finite chain segment, extra electrons are needed. This explains why the resistivity maximum in Cs–Bi occurs at $c_{Bi} \simeq 40$ at.%. This composition corresponds to an average chain length of four—that is, a Bi$_4^{6-}$ Zintl ion. The average chain length, however, will be strongly dependent on composition, decreasing to 1 (single Bi ions) for the octet composition Cs$_3$Bi. We mention that poly-anion chain segments of various length are present in the crystal structures of several alkaline-earth pnictides, such as Sr$_3$As$_4$ (As$_4^{6-}$). Such chain segments quite possibly occur in the structurally unresolved solid compounds Cs$_3$Bi$_2$ and Cs$_5$Bi$_4$. A crystal structure determination of these compounds would be highly desirable.

3.3. The sign of the temperature dependence of the resistivity

According to the classification given by Mott and Davis [5] the resistivities of the Cs–Bi alloys with bismuth fraction approximately between 20 and 70 at.% belong to the categories of regime II, sometimes called the regime of diffusive motion of electrons, and, near the very top, regime III. According to Mott and Davis [5], the temperature dependence of the resistivity, $d\rho/dT$ is definitely negative in regime III and, according to their equation (5.17), is almost zero in regime II.

For alloys belonging to regime I (nearly free-electron model) a high resistivity due to compound formation is commonly accompanied by a negative $d\rho/dT$. This is predicted by the Faber–Ziman model because in the vicinity of the composition of the compound $2k_F$ is likely to pass the first diffraction maximum. In the case of ionic liquid alloys like Li–Pb, which according to the rule of thumb 300 $\mu\Omega$ cm $< \rho < 3000$ $\mu\Omega$ cm belong to regime II, $d\rho/dT$ proves to be always strongly negative in practice. The reason for this is that at higher temperatures the short-range order is destroyed and consequently the salt-like electronic structure is destabilised, an effect not considered in the more general theory given by Mott and Davis [5].

A negative $d\rho/dT$ is also expected from 'Mooij's rule' [32], which, indeed, is formulated for transition-metal alloys. For the time being the small $d\rho/dT$ at the equiatomic composition remains a puzzling phenomenon.

Acknowledgments

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