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The thermopower of liquid Na–Sn alloys

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Abstract. The thermopower, Q , of liquid Na–Sn alloys has been measured as a function of temperature and composition. This alloys system shows a non-NFE behaviour in large parts of the composition range. For dilute Na–Sn alloys, it is shown that the measurements are consistent with a very simple phase-shift calculation. For concentrated alloys, a theoretical interpretation is complicated by the existence of two competing mechanisms for compound formation of approximately equal strength. Near the octet composition Q changes sign, and its behaviour may be qualitatively interpreted by a rigid band model. The clustering compound, responsible for the highest maximum in the resistivity, is hardly visible in Q , except for an anomaly in the temperature dependence.

1. Introduction

According to measurements by van der Marel *et al* [1] the resistivity of liquid Na–Sn alloys, when plotted as a function of composition, exhibits two maxima (figure 1). One maximum ($580 \mu\Omega\text{cm}$, temperature 10 K above the liquidus) is found at 23 at. % Sn and is associated with the formation of an essentially ionic octet compound. The other maximum ($890 \mu\Omega\text{cm}$, temperature 10 K above the liquidus) occurs at 43 at. % Sn and is now interpreted as being due to the formation of a liquid Zintl compound with the Fermi level in a covalent gap in the density of states. The mechanism of Zintl compound formation in liquid alloys has been described in a number of papers to which the reader is referred [2, 3]. In most alkali–lead or alkali–tin alloys only one compound is formed: either the ionic octet compound (Li–Pb, Li–Sn) or the clustered Zintl compound, the latter almost exactly at the equiatomic composition (K–Pb, Rb–Pb, Cs–Pb, see [4, 5]). The Zintl ion is then a $(\text{Pb}_4)^{4-}$ tetrahedron. The behaviour of Na–Sn is ambiguous. The existence of two liquid compounds in Na–Sn has been confirmed by measurements of the Knight shift [6], magnetic susceptibility [7] and the stability function [8].

Measurements of the Seebeck coefficient are useful to probe the density of states at the Fermi surface. In the domain of strong scattering [9], which applies to the electrons in Na–Sn in the vicinity of the resistivity maxima, the conductivity is proportional to $n^2(E_F)$, $n(E_F)$ being the density of states at the Fermi level, E_F .

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Combining this with the well-known Mott formula for the thermopower Q , valid when the current is carried by Fermi electrons,

$$Q = -(\pi^2 k^2 T/3|e|) [d \ln(\sigma(E))/dE]_{E=E_F} \quad (1)$$

the thermopower Q should be zero at a minimum of the density of states. Indeed Nguyen and Enderby [10] found a node in the thermopower of the Li–Pb system close to the octet composition Li_4Pb . Obviously, measurements of the thermopower are likely to contribute to our understanding of the electronic nature of the two compounds in the Na–Sn system.

2. The experimental setup

For the thermopower measurements, an experimental setup as sketched in figure 2 was constructed. The essential part of this apparatus is formed by an alumina crucible (1) containing the liquid metal sample, into which two 'fingers' are dipped (2) to measure temperature and thermal voltage. These sensors consist of a two-bore alumina tube (2a), closed off by a small metal cap, made of a Titanium–Zirconium–Molybdenum (TZM) alloy (2b). This alloy, containing 0.5 wt% Ti and 0.1 wt% Zr, is known to resist attack by liquid Sn up to 800 °C [11]. The metal to ceramics connection was made by use of a special glass frit, consisting of a mixture of CaO, SiO_2 and Al_2O_3 . Through each of the alumina tubes, a thermocouple (3) is brought into thermal contact, and a copper wire (4) into electrical contact with the liquid. Pt–Pt(10% Rh) thermocouples (type S) were used. The thermocouple cold junctions are in a massive Cu block, the temperature of which is measured by a Pt resistance thermometer. Copper was chosen as the electrode material for measuring the thermal voltage, as the absolute thermopower of Cu is accurately known [12], and small in absolute value.

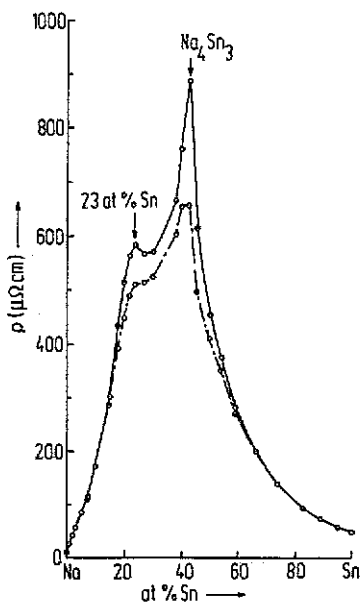


Figure 1. The electrical resistivity of Na–Sn alloys as a function of composition at temperatures of 10 K (full curve) and 70 K (chain curve) above the liquidus temperatures [1].

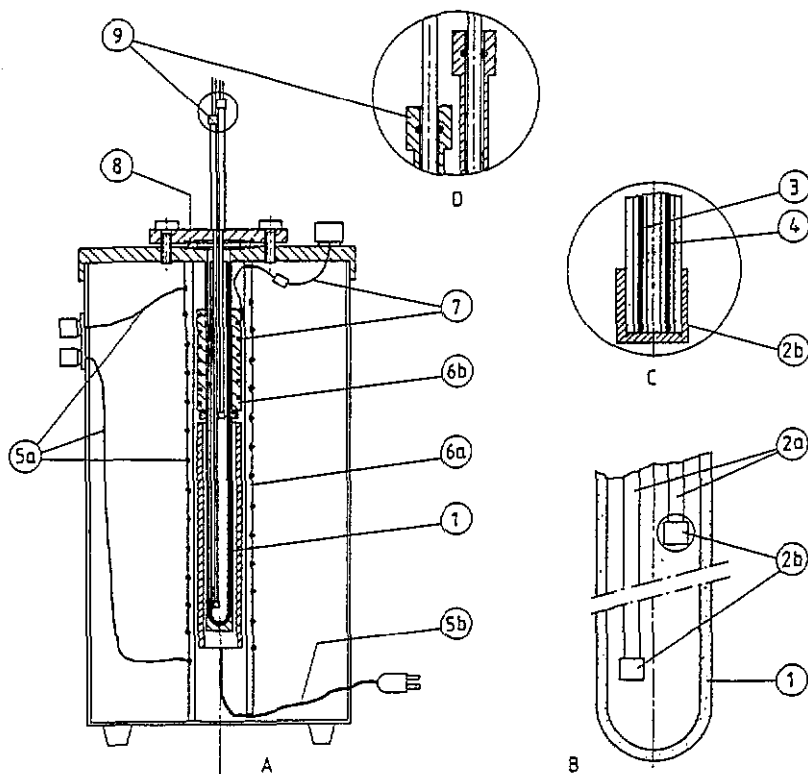


Figure 2. The thermopower equipment. A: overview; B: alumina crucible with two 'fingers'; C: detail of 'finger'; D: O-ring closure. 1: alumina crucible; 2a: two-bore alumina tubes, closed off by 2b: TzM caps; 3: Pt-(Pt-10 at.% Rh) thermocouples; 4: Cu wires; 5a: heater coil; 5b: Chromel-Alumel thermocouple; 6a, b: Cu cylinders; 7: auxiliary furnace; 8: copper ring seal; 9: O-ring closure.

This measuring cell is enclosed in a specially constructed furnace. A heater coil (5a), wound around the entire length of the furnace, is used to set the overall temperature. This coil dissipates a maximum power of approximately 400 W. Two massive copper cylinders (6a, b) have been put in to ensure an optimal homogeneity of temperature. A smaller coil (7) (maximum power 60 W), wound around the upper cylinder, is used to control the temperature difference between the upper and the lower sensor.

The measuring compartment is closed off vacuum-tight by a copper-ring seal (8), supplemented by an O-ring closure (9) at some distance from the top of the furnace.

This experimental setup performed well in practice; but experimental problems may sometimes arise through two main causes. The first of these is the technical difficulty of making an absolutely leak-free seal between the two-bore alumina tube and the small metal caps (2a and 2b in figure 2). If small leaks develop during an experiment, the Cu wires and the thermocouple sheaths may be attacked by the liquid metal; also, more seriously, quite large parasitic voltages (probably of electrochemical origin) will invalidate the thermopower measurements. A second difficulty was experienced in pure Na at high temperatures (above 500 °C): the attempt to reach a stable temperature difference was hindered by convection currents in the liquid.

A Hewlett-Packard HP87 microcomputer was used to control the conditions of the measurements and to collect the data necessary for obtaining thermopower values at various temperatures. Diagrams and other details can be found in the PhD thesis of the first author. This thesis is available on request.

The measurements were carried out according to the 'small ΔT ' method [12]. Typically, ΔT was raised from -1°C to $+3^\circ\text{C}$ in about 25 steps.

In order to reduce the measured $d(\Delta V)/d(\Delta T)$ slopes to the absolute thermopower, we have taken as the absolute thermopower of cold-rolled copper [13]:

$$Q_{\text{Cu}} = 1.54 + 5.45 \cdot 10^{-3} T(^{\circ}\text{C}) \pm 0.15 \mu\text{V K}^{-1}. \quad (2)$$

It is important to realize that all absolute thermopower data ultimately derive from Thomson-effect measurements, carried out (for, e.g., Pb) from superconducting temperature to the experimental temperature. Thus, a more precise determination of Q_{Cu} would affect all absolute thermopower data published to date. We adopt (2) as a standard. But it should be kept in mind that Q can be determined at best with a still appreciable error of $0.15 \mu\text{V K}^{-1}$. This error also puts limits to the accuracy to which the composition corresponding to the nodes in Q can be determined.

The investigated Na-Sn alloys are both chemically and mechanically aggressive. The latter needs some explanation: the dissociation of the high-temperature solid compound Na_4Sn_3 below 357°C is accompanied by severe cracking and volume expansion [1, 14]. Therefore, the alloys, originally prepared in a separate tungsten crucible, were first cast into a massive Cu mould. The resulting ingots were then introduced into the measuring cell. Immediately after a measurements series, the liquid was removed from the alumina crucible.

3. Results

3.1. Thermopower of pure Na and Sn

As our apparatus is designed for high-temperature measurements on corrosive materials we had to compromise in the choice of refractory materials and the geometry of the cell. This should be kept in mind when comparing our data with literature values obtained under more favourable conditions. For sodium, the agreement with earlier measurements by Feitsma *et al* [15] and van der Marel and van der Lugt [16] was always within $0.5 \mu\text{V K}^{-1}$. Feitsma *et al* [15] compare their data with those of Kendall [17], Davies [18] and Bonilla *et al* [19], finding close agreement in each case.

For tin the agreement with the results of Marwaha and Cusack [20] was within $0.1 \mu\text{V K}^{-1}$.

3.2. Thermopower of liquid Na-Sn alloys

Figure 3 is an overview of all thermopower data of Na-Sn alloys. For various reasons, the experimental spread in Q is not the same for all data points. For the pure metals, it is quite small ($\Delta Q < 0.1 \mu\text{V K}^{-1}$). The data for Na-rich samples are less reliable ($\Delta Q < 0.5 \mu\text{V K}^{-1}$ for $c_{\text{Sn}} < 25$ at. %); this was mainly caused by convection currents in the liquid, disrupting the temperature stability of the probes. For $c_{\text{Sn}} > 25$ at. %, finally, the accuracy in our measurements is estimated to be better than $0.3 \mu\text{V K}^{-1}$. In these estimated errors, the uncertainty in Q_{Cu} is not included. There exists satisfactory agree-

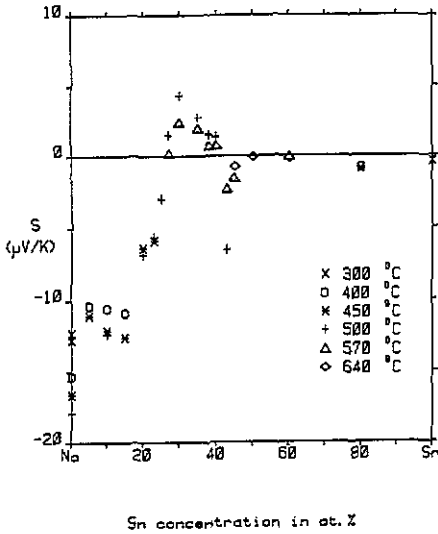


Figure 3. Thermopower of liquid Na-Sn alloys as a function of composition at temperatures indicated in the figure.

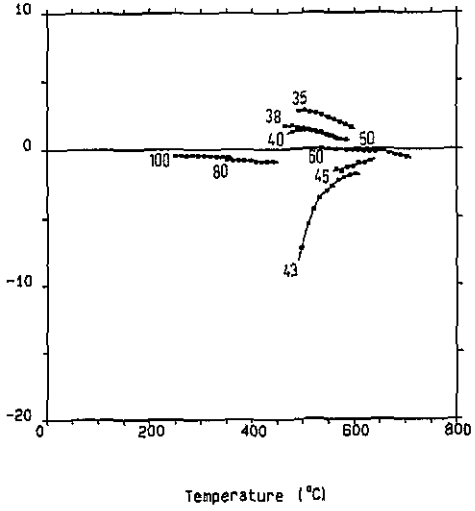
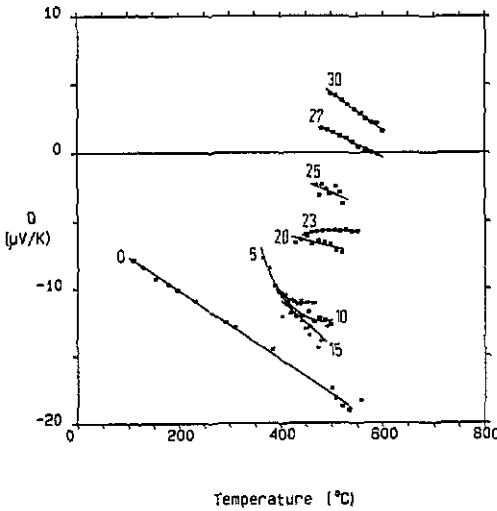


Figure 4. Thermopower of liquid Na-Sn alloys as a function of temperature. The numbers in the figure indicate the atomic percentage of tin.

ment with previous measurements by Davies [18] in the sodium-rich region.

In figure 4 the data are displayed as a function of temperature. Whereas, on the whole, the temperature dependence is not spectacular, we draw attention to the case of $c_{Sn} = 43$ at. %. At this composition, where the resistivity attains a maximum, the $Q(T)$ curve suggests an exponential behaviour.

4. Discussion

The experimental results presented in this chapter are not yet within reach of a quantitative theoretical interpretation. From the resistivity measurements it follows that

the diffraction model is not applicable. Quantitative theories for the regime of strong scattering are not available. Moreover any theoretical calculation will be seriously complicated by the formation of poly-anions. Therefore, the discussion in this section must be of a qualitative character.

First of all, the effects of compound formation, as manifested in the thermopower measurements, are, on the whole, much weaker than was expected. Comparing the thermopower and resistivity data (figures 3 and 1), the following division of the composition range seems natural.

4.1. The range of Na-rich metallic alloys extending up to 5 at. % Sn

In the limit of extreme dilution, the well-known expression for the residual resistivity in terms of impurity phase shifts η_l ,

$$\left. \frac{d\rho}{dc} \right|_{c=0} = \frac{4\pi\hbar}{Ze^2k_F} \sum_{l=0}^{\infty} (l+1) \sin^2(\eta_l - \eta_{l+1}) \quad (3)$$

where Z is the valency of the host, and all phase shifts are calculated at E_F , may be differentiated in order to obtain the residual thermopower:

$$\left. \frac{dQ}{dc} \right|_{c=0} = \frac{\pi^2 k^2 T}{3|e|} \frac{\hbar}{e^2 k_F} \frac{4\pi}{Z\rho_0} \sum_{l=0}^{\infty} (l+1) \left. \frac{d\alpha_1}{dE} \right|_{E=E_F} \sin \alpha_1 \cos \alpha_1 \quad (4)$$

where we wrote α_1 for $(\eta_l - \eta_{l+1})$, and where ρ_0 is the resistivity of the host material. With the simplifying assumption that only p wave scattering is important at E_F , we have from the Friedel sum rule

$$Z = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1)\eta_l \quad (5)$$

a value of $\pi/3$ for η_1 . With this one phase shift, we predict a residual resistivity of $d\rho/dc$ ($c=0$) = $12.8 \mu\Omega\text{cm/at.}\%$. The experimental value is $11.6 \mu\Omega\text{cm/at.}\%$; as the calculation is a crude one, the agreement is perhaps somewhat fortuitous. If we further assume a simple resonant behaviour for η_1 , $\eta_1(E) = \tan^{-1}[\Gamma/2(E_0 - E)]$, and pick $\Gamma = 5 \text{ eV}$ as a plausible value, we obtain for the residual thermopower a value of $2.6 (\mu\text{V K}^{-1} \text{ at.}\%)$ at $T = 600 \text{ K}$. This is also in reasonable agreement with experiment.

The above use of the Friedel sum rule does not contradict our view that an Sn impurity in Na is negatively charged by electron transfer from the surrounding Na atoms: this notion of charge transfer refers to the Sn Wigner-Seitz cell, whereas the phase shifts are determined at some asymptotically large R . Charge transfer, however, quickly causes deviations from a linear behaviour of ρ and Q versus c_{Sn} when the Sn concentration is increased, and we enter the second composition range to be discussed.

4.2. The range around the octet compound: $5 < c_{\text{Sn}} < 30 \text{ at.}\%$

The thermopower passes through zero for $c_{\text{Sn}} \approx 26 \text{ at.}\%$. There is a local minimum at $c_{\text{Sn}} \approx 18 \text{ at.}\%$, and a maximum at $c_{\text{Sn}} \approx 30 \text{ at.}\%$. This behaviour may be qualitatively explained by (1). The valence band is assumed to be 'rigid' in this sense, that the local densities of states at Na or Sn atoms, $n_{\text{Na}}(E)$ and $n_{\text{Sn}}(E)$, are independent of composition. This means that, with increasing Sn content, E_F passes through the minimum in the DOS

from above. At the compound-forming composition, E_F is at a minimum in the DOS. For Na-rich compositions, $d(n(E))/dE$ is positive at E_F , and for Sn-rich compositions it is negative. The situation is not unlike that in Li-Pb [10]. In Na-Sn, however, things are complicated by the presence of the second, clustering, compound: a competition between the octet and clustering mechanisms of compound formation occurs when $c_{\text{Sn}} > 20$ at. %.

4.3. The range around the resistivity maximum: $30 < c_{\text{Sn}} < 60$ at. %

Surprisingly, the strong resistivity maximum at 43 at. % is hardly reflected in the thermopower data; in fact, the resemblance to the thermopower of Li-Pb (where no clustering compound exists) applies to this composition range as well. From this, we must conclude that a rigid band approach utterly fails to explain the behaviour of Q near the resistivity maximum. The model of Egan [21], which describes both thermodynamic and transport properties near the compound-forming composition by an electron-hole equilibrium, also predicts a transition from pronouncedly negative Q at the Na-rich side, to positive values at the Sn-rich side. This means that, for Na-Sn, this model is ruled out by our findings.

The small values of Q that are actually observed indicate that $d(n(E))/dE|_{E=E_F}$ is small for any composition in this range. Thus, though the height of the minimum in $n(E)$ varies with composition, (as witnessed by the composition dependence of ρ), E_F is always near this minimum. As the location of the minimum depends on the number of covalent bonds between Sn^- ions, we conclude that the amount of covalent bonding is composition-dependent. This is a delicate process: when E_F is slightly shifted from the minimum in $n(E)$, Q may assume rather large values. We believe that the anomaly at $c_{\text{Sn}} = 43$ at. % is caused by such a slight shift in E_F . One may speculate that, at the compound-forming composition, the pseudo-gap in $n(E)$ is not only deeper, but also more steep than at neighbouring compositions. This explains why the effect is virtually restricted to $c_{\text{Sn}} = 43$ at. %. With rising temperature, the $n(E)$ profile is smoothed, and Q becomes small again.

Some evidence for the existence of 'variable size polyanions', the actual size being determined by the condition that the Fermi energy be in the gap of the polyanion states, has been found in other systems, particularly in liquid Cs-Bi [22, 23]. In this system fragments of the infinite 'Zintl ion', a tellurium-like chain of Bi ions, are supposed to occur. Also, the resistivities of liquid Li-Si alloys can be explained by assuming that a variety of negatively charged Si-clusters exists, though the underlying mechanism is probably quite different [24].

4.4. The metallic range at the Sn-rich side: 60 at. % $< c_{\text{Sn}} < 100$ at. %

In this region, the measured thermopowers are very small, between 0 and $-1 \mu\text{V K}^{-1}$. The Born approximation for scattering of the conduction electrons should hold, and the transport properties may be calculable by the diffraction model. However, electron spectroscopy (UPS) shows that the conduction band is not free-electron like even in pure Sn, though the Fermi states still may be [25]. In particular, the Sn 5s and 6p bands are separated by a gap. This means that, even in pure Sn, the transport properties can not be calculated straightforwardly in the NFE model. Before the scattering of conduction electrons may be calculated, a study of the valence band structure must be performed.

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