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HAL Id: jpa-00244634
https://hal.science/jpa-00244634
Submitted on 1 Jan 1979

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Apparatus for thermoelectric power measurements on metals and alloys in the liquid state. Application to antimony and cadmium antimony alloys

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(Reçu le 3 mai 1978, révisé le 22 décembre 1978, accepté le 2 janvier 1979)

Résumé. — On décrit un dispositif expérimental de mesure du pouvoir thermoélectrique absolu de métaux liquides, sous faible différence de température. L'appareillage a été testé avec le zinc, le cadmium, l'étain et l'antimoine. Pour l'antimoine on constate un désaccord avec les travaux antérieurs. Des résultats nouveaux sont donnés pour des alliages de cadmium et d'antimoine. Un changement de signe du pouvoir thermoélectrique, en fonction de la concentration, est observé au voisinage de la composition Cd0.5Sb0.5. Ce résultat est discuté en termes d'ordre local subsistant dans le mélange liquide.

Abstract. — An experimental arrangement, using the small temperature difference method, for the determination of absolute thermoelectric power of liquid metals is described. The apparatus has been tested with zinc, cadmium, tin and antimony. For antimony there exists some discrepancies with previous work. New results for cadmium antimony alloys are reported. A change of sign of the thermoelectric power, versus concentration, is observed around the composition Cd0.5Sb0.5. This result is discussed in terms of some local ordering existing still in the liquid mixture.

1. Introduction. — In recent years the thermoelectric properties of liquid metals and alloys have become of considerable interest. If the nearly free electron model of Ziman [1] and Faber and Ziman [2] is adequate for the systems under investigation, the theoretical predictions are in fairly good agreement with experimental results.

In this paper we describe an experimental arrangement which allows us to measure the absolute thermoelectric power (A.T.P.) S of liquid metals and alloys up to 1 000 °C. In choosing our method and the underlying experimental techniques, we look carefully at the following points: i) homogeneity of the alloys; ii) large possibility of choice and stability of the reference material, requiring no direct contact between the reference wire and the liquid metal to prevent corrosion; iii) elimination of parasitic voltages.

With a standard thermocouple arrangement (reference wire/metal or alloy under investigation/reference wire) two basic methods may be used for measuring S, according to the size of the temperature difference applied over the sample.

i) One junction is maintained at a constant temperature $T_0$, and the temperature $T$ of the other is varied over a large range. The thermoelectric power $S$ is then given by the slope of the curve of the thermal e.m.f. versus temperature $T$.

ii) Only a small temperature difference ($< 5$ K) is applied over the sample, but a special experimental procedure is needed to obtain reliable results.

If the liquid attacks conventional ceramics, metallic container may be used as has been done by Ioannides et al. [3].

Large temperature gradients may affect the homogeneity of the sample [4] and for this reason we have adopted the method involving a small temperature difference.

The principle of this method is described in some detail in the next paragraph, and in paragraph 3 we describe our experimental device and discuss carefully the accuracy of the measurements. Some investigations on zinc, cadmium, tin, antimony and cadmium antimony alloys, carried out with our apparatus, are presented and discussed in paragraph 4.

2. Principle of the method. — The principle of the method for thermoelectric measurements we used, is that described e.g. by Bradley [5], Ivory [6] or more...
recently by Valiant and Faber [7] and its essential advantage is to allow the suppression of constant parasitic voltages. The sample configuration is shown in figure 1. The liquid metal M is at each end in electrical contact with a thermocouple A/B. The wire A (in occurrence copper) has a well established A.T.P., and therefore serves as a reference material. In addition, the temperatures may be measured by means of these couples. But in practice it is difficult to measure accurately the small temperature difference over the sample if the two couples are not well calibrated, and to overcome this difficulty, the following procedure is used.

The left junction is maintained at a constant temperature $T_0$, and the right one may be stabilized at different temperatures $T_i$ around $T_0$. In practice $|T_0 - T_i|$ never exceeds 5 K. If the A.T.P.’s of the materials in presence are nearly linear functions of temperature around $T_0$, the plot of $V_{24}(T_i) = V_2 - V_4$ versus $V_{13}(T_i) = V_1 - V_3$ results in a straight line which slope is, as we shall see, independent of constant parasitic voltages and directly related to $S_M$, the A.T.P. of the alloy under investigation.

To examine more carefully this point, let $S_A$ and $S_B$ be the A.T.P. of the wires on the right side, $S_A'$ and $S_B'$, the corresponding values on the left side, the primes standing for some slight mismatch between the couples.

With a given external reference temperature $T_R$, and with $S_{MA} = S_A - S_M$ and $S_{MB} = S_B - S_M$, we have

$$V_{13}(T_i) = \int_{T_R}^{T_i} S_A \, dT + \int_{T_i}^{T_0} S_M \, dT + \int_{T_0}^{T_R} S_A' \, dT + V_A$$

where $V_A$ stands for some parasitic e.m.f.’s in the measuring circuit. A similar expression is obtained for $V_{24}(T_i)$, by replacing the subscript A by B. For two temperatures $T_i$ ($i = 1, 2$ for example) we may calculate:

$$p = \frac{\Delta V_{24}}{\Delta V_{13}} = \frac{\int_{T_1}^{T_2} S_{MB} \, dT}{\int_{T_1}^{T_2} S_{MA} \, dT}$$

(2)

In writing (2), we suppose that $V_A$ and $V_B$ do not vary appreciably with $T_i$, an consequently they do not appear in the slope $p$.

If $V_{13}$ (or $V_{24}$) does not vary between $T_1$ and $T_2$, we have directly from (1) $S_M = S_A$ (or $S_M = S_B$). In the other case, with use of a Taylor expansion around the mean temperature $T_m = (T_1 + T_2)/2$, we obtain

$$\int_{T_1}^{T_2} S_{MA}(T) \, dT = \left[ S_{MA}(T_m) + \frac{1}{24} \frac{\partial^2 S_{MA}}{\partial T^2} (T_m) (\Delta T)^2 \right] \Delta T$$

where $\Delta T = T_2 - T_1$. Since $S_{MA}$ is nearly linear between $T_1$ and $T_2$, and $\Delta T < 10$ K, the second term is very small and may be neglected, and we have:

$$p = \frac{S_{MB}(T_m)}{S_{MA}(T_m)}.$$  

The A.T.P. of the metal is then given by

$$S_m(T_m) = \frac{1}{p - 1} S_{BA}(T_m) + S_A(T_m).$$

(3)

In practice, $p$ is deduced from a least square adjustment of the $V_{24}(T_i)$ versus $V_{13}(T_i)$ curve.

3. Experimental arrangement and accuracy. — The liquid metal or alloy is contained in a quartz cell disposed in a horizontal arrangement. Figure 2 shows a part of the cell, the left side being symmetrical. A copper wire is used as a counter electrode, and the second wire is alumel. The two copper/alumel thermocouples are embedded into two dense graphite, or tungsten plugs, so as to insure electrical contact with the liquid sample and to prevent corrosion. A cement, Protoceram 12 (1), is fitted behind the plugs to keep the liquid from leaking out. The experiments are performed in an atmosphere of argon, and a pressure up to 4 bars can be applied.

Fig. 1. — Schematic sample configuration. The regions within the dashed lines are isothermal.

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Fig. 2. — Cell for thermopower measurements.

(1) Supplied by Microphysic, France.
It is possible to vary the composition of the liquid alloy, by adding one of the components, by means of the vertical tube in the central part of the cell. To obtain good homogeneity, we used two procedures. Firstly, the alloy may be stirred by moving the whole arrangement around a horizontal axis. Secondly, we use the fact that the cement is not perfectly tight for a gas under pressure. If a lateral overpressure is applied through the cement, the liquid accumulates in the central vessel of the cell, and by releasing the lateral pressure, the electrical contacts with the plugs are again restored.

The e.m.f.'s $V_{12}$, $V_{34}$, $V_{13}$ and $V_{24}$ are measured with a K-5 Leeds and Northrup potentiometer associated with a null detector Keithley model 155. The external reference temperature is kept at 0 °C. The furnace temperature is accurately controlled, and an auxiliary heating coil allows to vary the temperature $T_i$ at the right side. For a given $T_0$, the Seebeck voltages are measured for several $T_i$, and the A.T.P. is deduced from formula (3). The A.T.P. of copper was taken from Cusack [8].

$$S_{Cu} = 0.05 + (5.45 \times 10^{-3}) \, T \, \mu V \cdot K^{-1} \tag{4}$$

where $T$ is the absolute temperature. The e.m.f. versus temperature curve of the copper/alumel thermocouples, and their thermopowers are obtained by careful comparison with a calibrated Pt Rh 10 %/Pt thermocouple.

To calculate $S_M$ after formula (3), we do not take the actual values $S_A$ and $S_{BA}$ of the wires under use, but their standard values which we denote respectively by $S_0^A$ and $S_{0BA}$. The absolute uncertainty on $S_M$ is given by

$$\Delta S_M = \left( \frac{S_{BA}}{p - 1} \right)^2 \Delta p + \frac{1}{p - 1} \Delta S_{BA} + \Delta S_A.$$  \tag{5}$$

To evaluate the dispersion of the thermoelectric properties of the wires, we have compared the copper and alumel wires of the different cells with the corresponding wires which served for calibration purposes. All these wires were cut off the same reels, to ensure the best reproducibility of their thermoelectric properties, and for example at 650 °C, the dispersion range was found to be smaller than 0.01 μV·K⁻¹ for copper and smaller than 0.08 μV·K⁻¹ for the copper/alumel thermocouple. After Cusack [8] the absolute uncertainty on the A.T.P. of the reference wire $S_0^A$ is estimated to be less than 0.15 μV·K⁻¹. Nevertheless, a recent work due to Roberts [9] shows that the absolute scale generally admitted has to be shifted by an amount of nearly 0.3 μV·K⁻¹, and we shall come back to this point later.

The main uncertainty on the slope determination arises from the error on the voltage measurements, which is of the order of 0.3 μV. To reach the best precision on the electrical measurements, we have to ensure that $T_0$ equals the mean temperature $T_m$ that is, $T_i$ is varied symmetrically around $T_0$. With pure antimony at 650 °C as a representative example, the uncertainty of the slope due to electrical measurements is 1.4 %.

A supplementary error on the slope is introduced by the nature of our experimental arrangement and arises from two effects:

i) the regions around the junctions are not really isothermal, giving rise to a slight temperature difference between the thermocouples and the liquid metal against the plugs;

ii) the temperature at the left junction remains not perfectly constant during a slope determination and may vary slightly from $T_0$ to $T_0'$. Figure 3 shows the actual thermal configuration and the notations used. If the thermocouple A/B is at temperature $T_i$ ($i=1,2$) the junction tungsten/liquid metal is at a temperature $T_i + \delta T_i$, where $\delta T_i$ is small. Similar notations are used for the left side. If we keep only the most important contributions, the error $\alpha$ corresponding to this two effects, may be written, in the general case where $S_{MA}$ and $S_{MB}$ are not too small:

$$\alpha = \left( \frac{S_{MA}(T_0)}{S_{MA}(T_m)} \right) + \left( \frac{S_{MB}(T_0)}{S_{MB}(T_m)} \right) \frac{\Delta T_0}{\Delta T} \tag{6}$$

where $\Delta T = T_2 - T_1$ and $\Delta T_0 = T_0' - T_0$. The second term is a systematic error. To determine numerically the above expression we have measured the thermal profile of the furnace at different temperatures, and for the A.T.P. of tungsten we have used the values published by Cusack and Kendall [10]. Around 650 °C we obtained $\delta T_i \approx 0.3$ K. $\Delta T_0$ does not exceed 0.3 K. With $S_{MA} = 5 \mu V \cdot K^{-1}$, $S_{MB} = -24.4 \mu V \cdot K^{-1}$ which are typical values for antimony as an example, and with $\Delta T = 10$ K, the value of $\alpha$ is less than 0.5 %.

Finally the absolute uncertainty of the A.T.P. of the metal, after formula (5) is $\Delta S_M = \pm 0.24 \mu V \cdot K^{-1}$. A further error may arise for an alloy from the uncertainty in composition, which is estimated to be less than 1 %.

![Fig. 3. — Actual thermal configuration. W : tungsten (or graphite).]
The precision on the temperature $T$ is better than 2 K over the whole temperature range.

It is however useful to emphasize here that our uncertainty determination is based on the A.T.P. of copper and its absolute uncertainty as given by Cusack [8]. A new determination of the A.T.P. of lead up to 350 K, by direct Thomson heat measurements, has been made by Roberts [9], and it was found less negative than the widely used scale of Christian et al. [11]; this discrepancy is not too surprising, bearing in mind that the absolute scale was established from too few sets of Thomson heat data, as discussed e.g. by Barnard [12]. The resultant effect on the A.T.P. of copper at higher temperatures may probably be an increase by an amount of the order of 0.2 to 0.3 $\mu$V. K$^{-1}$. Because a possible correction for the high temperature scale above 350 K is not established, we use formula (4) for the A.T.P. of copper.

4. Results and discussion. — 4.1 Metals. — We have measured the temperature dependence of the A.T.P. of zinc, cadmium, tin and antimony. The A.T.P. are well represented by linear functions $S = aT + b$ for all these metals, $T$ being the absolute temperature (table I).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a \cdot 10^4$ ($\mu$V. K$^{-1}$)</th>
<th>$b$ ($\mu$V. K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>44.9</td>
<td>-3.06</td>
</tr>
<tr>
<td>Cd</td>
<td>10.2</td>
<td>-0.20</td>
</tr>
<tr>
<td>Sn</td>
<td>-12.4</td>
<td>0.03</td>
</tr>
<tr>
<td>Sb</td>
<td>3.6</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

Zinc, cadmium and tin are quoted as 99.999 % pure and antimony is quoted as 99.99 % pure.

For zinc and cadmium, the values for $a$ and $b$ are identical, within the limits of accuracy, with those obtained previously by Bath and Kleim [13]. For tin, our results performed up to 800 °C are in accordance with the values now well established in the literature, see e.g. Marwaha and Cusack [14], Tougas [15], Yatsenko and Golovin [16], or Mikhailowski and Khar'kov [17] where the reader should find some numerical comparisons for these three metals.

Our results for antimony were obtained with four different cells, having either tungsten or graphite plugs, and show that a possible dissolution of graphite in liquid antimony [18] has no significant effect on its thermoelectric power. Our measurements (Fig. 4) are in agreement with the value given by Enderby et al. [19] near the melting point, and, near the same temperature, with the results of Matsuura and Suzuki [20], but the slope of the temperature dependence is different. Stronger discrepancies appear with

the results of Blakeway [21], Dutchak and Stets’kiv [22] and Asanovich et al. [23] (see table II).

Considering these discrepancies, we have also measured the A.T.P. of antimony with calibrated chromel/platinum thermocouples. Platinum was used as the reference wire and for its A.T.P. we took the formula given by Laubitz [24].

\[ S_{pl} = -18.63 \times 10^{-3} T(1 - 0.057 \times 10^{-6} T^2) \]  

where $T$ is in K and $S$ in $\mu$V. K$^{-1}$. This equation was obtained by averaging three determinations, the maximum spread being 1.5 %. Our new values are reported on figure 4, and agree with our former results, within the uncertainty on formula (6). We made a further check by calibrating platinum against copper, with use of equation (4). A calculation of the A.T.P. of antimony was then performed, based on the new A.T.P. of platinum. The results are only slightly modified (Fig. 4 : curve B) and good accordance with the copper based results is achieved. There is an overall consistency for our results whether copper or platinum is used as a reference material, therefore we may be reasonably confident that our values are close to the true ones.
4.2 CADMIUM ANTIMONY ALLOYS. — We have measured the A.T.P. of Cd₅Sb₁₋ₓ alloys up to 650 °C for the compositions \( x = 0.93, 0.90, 0.80, 0.75, 0.70, 0.57, 0.50, 0.43, \) and 0.35. The temperature dependence is linear for all these systems. The concentration dependence of \( S \) at 500 °C and 600 °C is given in figure 5. For the equiatomic composition \( \text{Cd}_{0.5}\text{Sb}_{0.5} \), our result is in good accordance with that given by Enderby and Walsh [25]. At our knowledge, no previous results exist for the other compositions.

![Graph of thermoelectric power vs. Sb concentration](image)

The values of \( S \) are small (\( |S| \leq 2 \mu \text{V.K}^{-1} \)), typically in metallic range, but it is interesting to notice here the change of sign near the composition \( x = 0.5 \), corresponding to a maximum (\( \approx 200 \mu \text{Ω.cm} \)) and negative temperature coefficients for the resistivity [26, 27]. Such electrical properties were also found for systems like Ag-Sb [20, 28]. Some other systems such as Cu-Sn exhibit the same trends but with a monotonic concentration dependence of the A.T.P. [29, 30]. For the last system, the Faber-Ziman theory accounts for the concentration dependence of the resistivity. Furthermore, the negative temperature coefficient of the resistivity may be related to the condition \( 2k_F \approx k_p \), where \( k_F \) is the Fermi wave vector and \( k_p \) the wave number of a main peak of the partial interference functions. For Cd-Sb the three partial interference functions are not known, but \( 2k_F \) is certainly located beyond the main peak [27], and the foregoing argument cannot be used.

Some other experimental results show that there exists attractive interaction between the unlike components. The viscosity, measured by Fisher and Phillips [31], exhibits a relative maximum at the composition \( x = 0.5 \), which decreases with increasing temperature. The heat capacity isotherms of Schick and Komarek [32] show a positive deviation from the Neumann-Kopp rule, which disappears above nearly 530 °C. The centrifuge experiments of Kumar and Sivaramakrishnan [33] suggest that interactions between atoms in the alloy persist in the liquid state.

Geffken et al. [34] used the electromotive force method, and the calculated thermodynamic functions of mixing indicate an attractive interaction between unlike atoms with a maximum effect around \( x = 0.57 \). If we use their experimental results to evaluate the long wavelength limit of the concentration-concentration correlation function \( S_{\text{cc}}(0) \) introduced by Bhatia and Thornton [35] we observe a negative departure from ideal behaviour centered roughly around \( x \approx 0.6 \). The shallowness of the dip indicates that rather weak binding effects occur at this composition. The Hall coefficient of \( \text{Cd}_{0.5}\text{Sb}_{0.5} \) measured by Enderby and Walsh [25] shows a deviation from the free electron value of about 30 % in accordance with the fact that some bonding subsists in the liquid state, but as temperature is raised the deviation becomes greater, not consistent with the scheme of electrons becoming free when bondings are broken.

Faber [36] discussed the resistivity of the compound forming liquid alloys. Some authors, for example Kumar and co-workers explain their results by supposing that clusters are present in the melt, and the deduced cluster radii are rather large (150 Å). The electrical properties (maximum in resistivities, change in sign of the thermopowers) may effectively be interpreted on the basis of a cluster hypothesis [37], but their existence is still the field of some controversy. Ratti and Bhatia [38] applied the idea of chemical complexes formation to systems like Mg-Bi where the high value of the resistivity maximum falls into non metallic range, but corresponds to a change in sign of the A.T.P. [39], like Cd-Sb. They found good agreement for the resistivity, and the change of sign of the thermopower at the compound concentration may be explained. However their study is only valid if the tendency to form chemical complexes is strong. For systems with weaker bondings Takeuchi and Matsuura [28] used a pseudomolecule model to explain the properties of binary systems, particularly Ag-Sb, and such a viewpoint should be more adequate for Cd-Sb alloys. Thompson [40] used the concentration dependence of \( S_{\text{cc}}(0) \) to infer some general trends for the electronic transport properties: the resistivity integral can be written in terms of the three number-concentration structure factors \( S_{\text{NN}}(q) \), \( S_{\text{NC}}(q) \) and \( S_{\text{cc}}(q) \) [35] which obey sum rules. For \( S_{\text{cc}}(q) \) we have

\[
\int_0^\infty [S_{\text{cc}}(q) - x(1 - x)] q^2 dq = 0
\]

and to satisfy this relation \( S_{\text{cc}}(q) \) has to oscillate about the value \( x(1 - x) \) corresponding to an ideal mixture. In alloys, such as Cd-Sb where for some composition range \( S_{\text{cc}}(0) \) exhibits a dip below \( x(1 - x) \) as \( q \) increases \( S_{\text{cc}}(q) \) has to go above \( x(1 - x) \). If \( 2k_F \) lies in this region, a high contribution may occur to the resistivity \( \rho \) from the \( S_{\text{cc}} \) term. Further, if \( T \) increases, \( S_{\text{cc}}(q) \)
tends toward the ideal value, and a decreasing contribution to \( \rho \), versus temperature, is expected. If the contributions to \( \rho \) arising from the other structure factors (essentially SNN) do not mask the effect of Scc, a maximum of resistivity, and a negative temperature coefficient is expected at the composition centered \((x \approx 0.6 \text{ for Cd-Sb})\) on the dip of \( S_{\text{cd}}(0) \).

According to different authors, the compositions where there is a marked tendency for the atoms to group may correspond to CdSb, Cd\(_4\)Sb\(_3\) \((x = 0.57)\) or Cd\(_3\)Sb\(_2\) \((x = 0.60)\). The proximity of these compositions makes it difficult to give a definite answer but our thermoelectric power results are in favour for the equiatomic composition. We must also emphasize that the possible existence of more than one compound is not incompatible with the specific heat and resistivity data.

5. Conclusion. — An experimental device has been described which allows accurate and reliable measurements of absolute thermoelectric power to be made on liquid binary systems up to 1 000 °C. The experimental procedure used ensures good homogeneity. The measurements are rather lengthy and the possibility of changing the composition is interesting in this respect. Further, if the A.T.P. is a slowly varying function with composition, the use of the same cell makes it easier to follow the variation. The apparatus was tested with pure metals and some discrepancies with earlier works are observed for liquid antimony. New results on cadmium antimony alloys are reported. The change of sign, near \( x = 0.5 \), for the A.T.P. versus concentration has been related, in parallel with the resistivity data, to the tendency for unlike atoms to group in the liquid phase.

References