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New precise determination of the high temperature unusual temperature dependent thermopower of liquid divalent cadmium and zinc*

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Abstract.   We do not know any precise measurement of the absolute thermopower (ATP) of liquid cadmium and zinc at high temperatures. For liquid cadmium, there are, in the literature, apparent contradictory results. Bath and Kliem and North and Wagner observed that the ATP increases with temperature between 350 °C and 650 °C, but Bradley observed the opposite behaviour between 600 °C and 750 °C. In this work we measured accurately the absolute thermopower of liquid cadmium from the melting point up to 900 °C. We find a maximum around 520 °C, and then the thermopower decreases down to a surprising negative value. To our knowledge, it is the first time that such an unusual behaviour is reported. Nevertheless, it is qualitatively consistent with all the authors mentioned and the apparent contradictory results should only be due to the different temperature ranges of measurements. Using the ATP expression from the Faber–Ziman formalism, we can fit very well the experimental absolute thermopower versus temperature curve with only one adjustable parameter. For this, we have considered that the temperature dependence of the ATP is dominated by the resistivity, and we have introduced the experimental resistivity temperature dependence in the ATP expression. The very good fitting quality demonstrates that our hypothesis is consistent. In contrast, the liquid zinc ATP only increases with temperature. Nevertheless, near 1100 °C, the highest temperature achieved, it shows saturation that may be an indication of a decrease at higher temperature. The same type of fitting gives also quite good results.

1. Introduction

The resistivity ($\rho(k_F, T)$) and the thermopower ($S(k_F, T)$) analytical expressions derived from the Ziman formalism [4–6] are given by:

$$\rho(k_F, T_K) = \left[\frac{3\pi^2 m_e^2}{4\hbar^3 e^2} \frac{\Omega_0}{k^6} \int_0^{2k} u(q, k)^2 a(q) q^3 \, \mathrm{d}q \right]_{k=k_F} \tag{1}$$

$$S(k_F, T_K) = -\left(\frac{\pi^2 k_B^2 T_K}{3|e| E} \chi \right)_{E=E_F} \tag{2}$$

with

$$\chi = -\left(\frac{\partial \ln \rho(E)}{\partial \ln E} \right)_{E=E_F} = -\left(\frac{k}{2\rho} \frac{\partial \rho(k)}{\partial k} \right)_{k=k_F} \tag{3}$$

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where m_e is the mass of the electron, k is the wavevector, q is the magnitude of the scattering vector, $u(q, k)$ is the screened ionic form factor or pseudopotential, $a(q)$ is the structure factor, E_F is the Fermi energy, k_F is the Fermi wavevector, T_K is the absolute temperature and Ω_0 is the atomic volume. By substituting equation (1) in (3), the dimensionless parameter χ can be written as:

$$\chi = 3 - 2p - \frac{r}{2} \tag{4}$$

with

$$
\begin{aligned}
p &= u(2k_F, k_F)^2 a(2k_F) \left(\frac{1}{(2k_F)^4} \int_0^{2k_F} u(q, k_F)^2 a(q) q^3 \, dq \right)^{-1} \\
&= \frac{12\pi^2 m_e^2 \Omega_0}{\hbar^3 e^2 k_F^2} \frac{u(2k_F, k_F)^2 a(2k_F)}{\rho(E_F)}
\end{aligned} \tag{5}
$$

and:

$$
\begin{aligned}
r &= \left(k_F \int_0^{2k_F} \left[\frac{\partial u(q, k)^2}{\partial k} \right]_{k=k_F} a(q) q^3 \, dq \right) \left(\int_0^{2k_F} u(q, k_F)^2 a(q) q^3 \, dq \right)^{-1} \\
&= \frac{3\pi^2 m_e^2 \Omega_0}{4\hbar^3 e^2 k_F^5} \frac{1}{\rho(E_F)} \int_0^{2k_F} \left[\frac{\partial u(q, k)^2}{\partial k} \right]_{k=k_F} a(q) q^3 \, dq.
\end{aligned} \tag{6}
$$

The parameter 3 is the free electron contribution, the term $2p$ comes from the derivation of the upper limit of the resistivity integral and the term $r/2$, the energy dependence contribution, comes from the derivation of the integrand.

We can write

$$S = -\frac{\pi^2 k_B^2 T_K}{3|e| E_F(T_K)} \left[3 + \frac{\beta}{\rho(E_F)} \right] \tag{7}$$

with

$$\beta = -2 \frac{12\pi^2 m_e^2 \Omega_0}{\hbar^3 e^2 k_F^2} u(2k_F, k_F)^2 a(2k_F) - \frac{1}{2} \frac{3\pi^2 m_e^2 \Omega_0}{4\hbar^3 e^2 k_F^5} \int_0^{2k_F} \left[\frac{\partial u(q, k)^2}{\partial k} \right]_{k=k_F} a(q) q^3 \, dq$$

and

$$E_F(T_K) = \frac{\hbar^2 k_F^2(T_K)}{2m_e} \qquad k_F^3(T_K) = 3\pi^2 \frac{Z}{\Omega_0(T_K)} \qquad \Omega_0(T_K) = \frac{M}{N_a d(T_K)} \tag{8}$$

where Z is the number of conduction electrons, M is the molecular weight, N_a is the Avogadro number, and $d(T_K)$ is the density.

2. Experimental details

The resistivity and the thermopower are measured simultaneously using a home-made apparatus, which is described in detail in the works of Vinckel *et al* [7, 8]. In this way, the resistivity measurement is performed by the direct contact four-probe technique and the thermopower is measured by employing a small temperature gradient method that suppresses the errors due to inhomogeneities of the electrodes. The liquid metal is contained in a U silica cell [9]. From time to time we tested if bubbles were present in the capillary. A pressure variation of about 0.3 bars allows us to do this very easily. The resistivity increases if bubbles are present, but the thermopower is not influenced by the presence of bubbles. In our measurements we are sure that no bubbles were present. The measurements are realized with tungsten and tungsten–rhenium (26%) electrodes. These wires are calibrated with 'platinum

67' [10–12], the temperature being measured with a calibrated Pt/Pt–10% Rh thermocouple. The cadmium and zinc were supplied by the Aesar-Johnson Matthey Co. and were 99.999% purity. Because of the high vapour pressure and low boiling point of these two metals, it is necessary to apply pressure to avoid formation of bubbles inside the liquid metal due to boiling. The 8 bar pressure that we applied allowed us to measure liquid cadmium up to 900 °C and liquid zinc up to 1100 °C; i.e. quasi 200 °C above the boiling point of each metal.

3. Results

3.1. Cadmium

In figure 1 we present our new liquid cadmium temperature dependence resistivity measurement together with our previous one (Gasser [13]) and compared to the experimental work of Takeuchi and Endo [14], and Roll and Motz [15]. The accuracy on the resistivity is estimated to be about 0.5%, the scattering being much smaller (about 0.1%). At low temperature, all the curves have nearly zero slopes, but our measurements are slightly smaller than those made in all the previous studies. By increasing the temperature, the slope of our measurement curves, as well as those of Roll and Motz [15] become more important. Surprisingly, the measurements of Takeuchi and Endo [14] remain temperature independent. Our result can be fitted by the polynomial expression:

$$\rho_{\exp}^{Cd}(T_C) = 37.08 - 0.019\,23T_C + 3.197 \times 10^{-5}T_C^2 - 1.024 \times 10^{-8}T_C^3$$

between 321 °C and 900 °C. T_C is the temperature in Celsius.

Figure 2 shows our experimental temperature dependence of thermopower together with the measurements of North and Wagner [2], Bath and Kleim [1], and Bradley [3]. The accuracy on the thermopower (systematic error) is estimated to be less than 0.3 μV K^{-1}, which can be considered as very good. It is clear in figure 2 that the reproducibility of the measurements (accidental error) is much better and is near $\pm$0.05 μV K^{-1}. Thus, the temperature dependence must be considered as known.

In the case of our measurements, the thermopower curve increases from +0.5 μV K^{-1} near the melting temperature, up to +1.0 μV K^{-1} around 520 °C, and then decreases down to the surprising negative value of -0.3 μV K^{-1} at approximately 900 °C. To our knowledge, it is the first time that such an unusual behaviour is reported. North and Wagner [2] and Bath and Kleim [1] found that the thermopower increases with the temperature, but Bradley [3] found the opposite behaviour. These apparent contradictory results could be due to the different temperature measurement ranges, and are qualitatively consistent with our measurements. Nevertheless, these results are smaller than our data because they are based on the Cusack's [16, 17] absolute thermopower reference. For a coherent comparison, we corrected these data to take into account the difference between the reference of Cusack [16, 17] and that of Roberts [10–12]. After correction, the measurements of the authors mentioned above become higher than ours; this difference can be due to the cumulative errors coming from the different calibrations. However, the difference is small (between 0.25 and 0.5 μV K^{-1}) and not significant for the discussion.

Our experimental thermopower temperature dependence can be expressed by the polynomial:

$$S_{\exp}^{Cd}(T_C) = -1.57 + 0.009\,47T_C - 8.74 \times 10^{-6}T_C^2$$

between 321 °C and 900 °C.
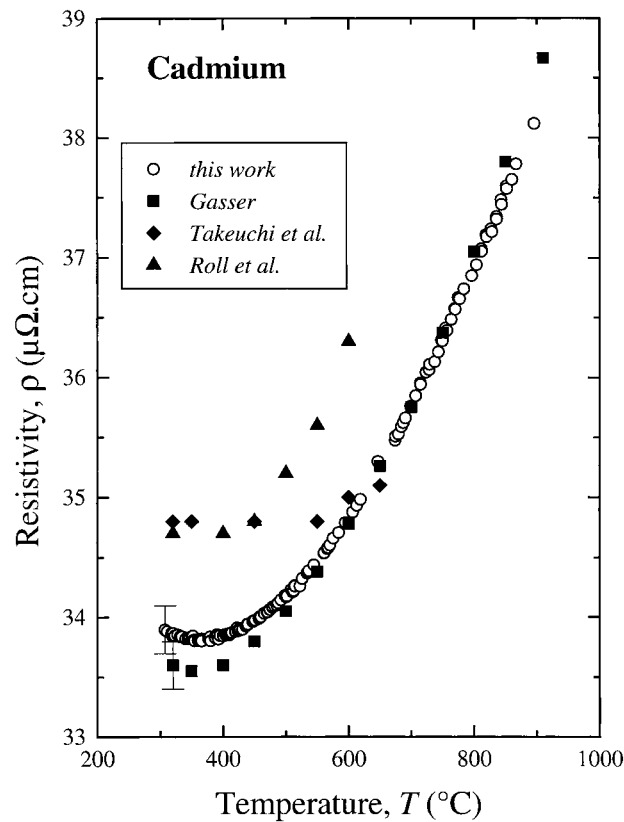
Figure 1. Our experimental electrical resistivity of liquid cadmium as well as data from Gasser [13], Takeuchi and Endo [14] and Roll and Motz [15]. The values of Gasser are very similar to our data. Those of Takeuchi and Endo as well as of Roll and Motz are greater but have been determined with an electrodeless method.

3.2. Zinc

Figure 3 shows our new measurements of liquid zinc temperature dependence resistivity together with our previous one (Makradi [9]) as well as the measurements of Gasser [13], Itami and Shimoji [18], Roll and Motz [15], and Scala and Robertson [19]. At low temperature, all the measurements are found in an error band of 0.2 $\mu\Omega$ cm. Above 600 °C, by increasing the temperature the dispersion becomes important. Our new experimental determination of the temperature dependence of the zinc resistivity can by summarized by the polynomial expression:

$$\rho_{\exp}^{\text{Zn}}(T_C) = 49.78 - 0.056\,80 T_C + 8.587 \times 10^{-5} T_C^2 - 6.171 \times 10^{-8} T_C^3 + 1.899 \times 10^{-11} T_C^4$$

between 420 °C and 1100 °C.

Figure 4 reports our new and previous [9] experimental thermopower data compared to data in the literature [1, 20]. Our measurements increase with the temperature up to approximately 2.2 μV K^{-1} around 950 °C, and then saturate. The discordance with the other authors' measurements may be due to the calibration reference. The expression below is a very good fit of our experimental thermopower:

$$S_{\exp}^{\text{Zn}}(T) = -2.62 + 0.008\,48 T_C - 3.85 T_C^2$$

between 420 °C and 1100 °C.
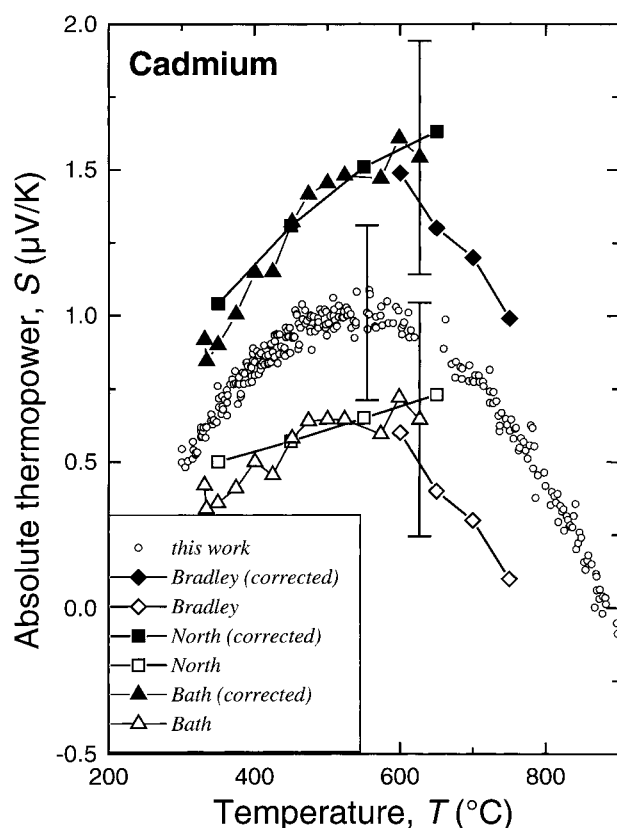
Figure 2. Our experimental absolute thermopower of liquid cadmium as well as data from North and Wagner [2], Bath and Kleim [1], and Bradley [3]. The *old* results are based on the Cusack's [16, 17] absolute thermopower reference. After correction of the difference between the references of Cusack [16, 17] and Roberts [12], a small difference persists, probably due to cumulative calibration errors. The lines are guides for the eyes.

4. Discussion

4.1. Cadmium

On one hand, the hard sphere structures are not very realistic for liquid cadmium, nor for liquid zinc, and on the other hand the numerical data of the experimental structures are available in Waseda's book [21] only for one or very few temperatures. For these reasons, one cannot expect to reproduce the thermopower temperature dependence using *ab initio* calculations. The first assumption is to consider that the bracket in equation (7) is temperature independent. With this assumption, the thermopower varies linearly with temperature. This is represented by the dotted line in figure 5, which evidently cannot explain the anomalous temperature dependence of liquid cadmium. We can choose an alternative way, which consists of the postulate that the absolute thermopower of liquid cadmium is dominated by the temperature dependence of the resistivity. So we include the experimental resistivity in the thermopower equation (7) at the place of a computed resistivity. This needs a correct choice of the term β in expression (7). The simplest assumption is to consider that β is a constant. Figure 5 shows the experimental thermopower curve as well as the fitting one that has been made using: $Z = 2$, the Crawley
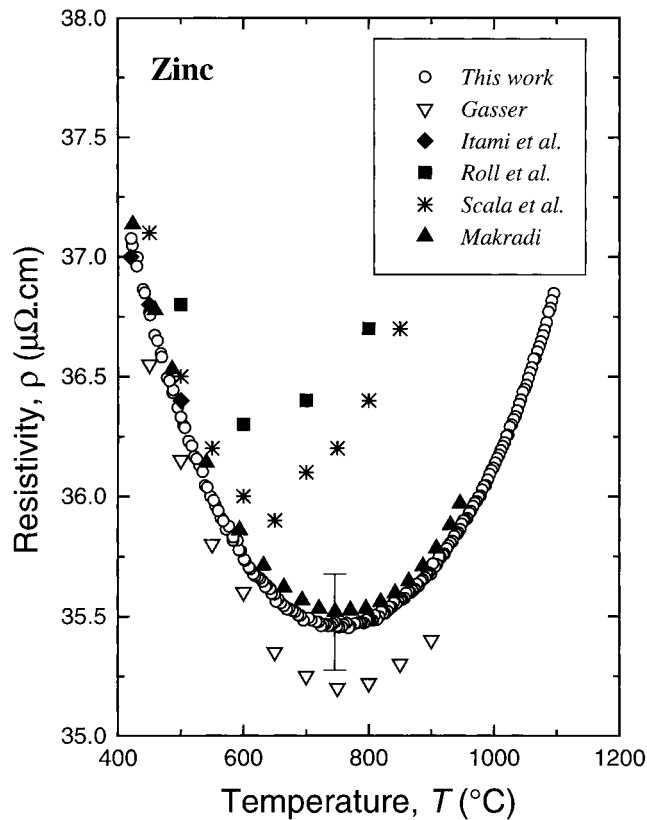
Figure 3. Our experimental resistivity of liquid zinc as well as data from Gasser [13], Itami and Shimoji [18], Roll and Motz [15], Scala and Robertson [19], and Makradi [9]. It is clear that our data are nearest to the recent results [9, 13] than to the older ones [15, 18, 19].

experimental density [22], $d_{exp}^{Cd}(T_K)$, and our experimental resistivity, $\rho_{exp}^{Cd}(T_C)$ data. The fitted curve (solid line) reproduces very well the thermopower experiment, i.e. it increases at low temperature with a maximum around 500 °C and then decreases down to negative values for temperatures higher than 850 °C. It is very clear that the temperature dependence of the thermopower is dominated by the thermal variation of the resistivity.

The term β includes a local ($2p$) and a non-local ($r/2$) contribution. We can deduce from the calculations of Evans [23–25] based on the Shaw potential, as well as from Bath [26], who has made calculations with different dielectric functions, that the local contribution is preponderant. All the calculations made in the references of the bibliography, for cadmium and zinc at different temperatures, show that $2p$ is between 3.5 and 9 times greater that $r/2$, thus probably the temperature dependence of $2p$ has the most important effect on the temperature dependence of the thermopower.

The temperature has a very complicated influence on $2p$:

(a) the amplitude of the main peak of the structure factor is reduced (North and Wagner [27] showed that the height of the first peak of cadmium is reduced from 2.55 to 2.21 between 350 and 650 °C),

(b) the Fermi energy is reduced due to a diminution of the mass density, thus the normalization factor ($-2/3E_F$) of the t matrix is reduced,
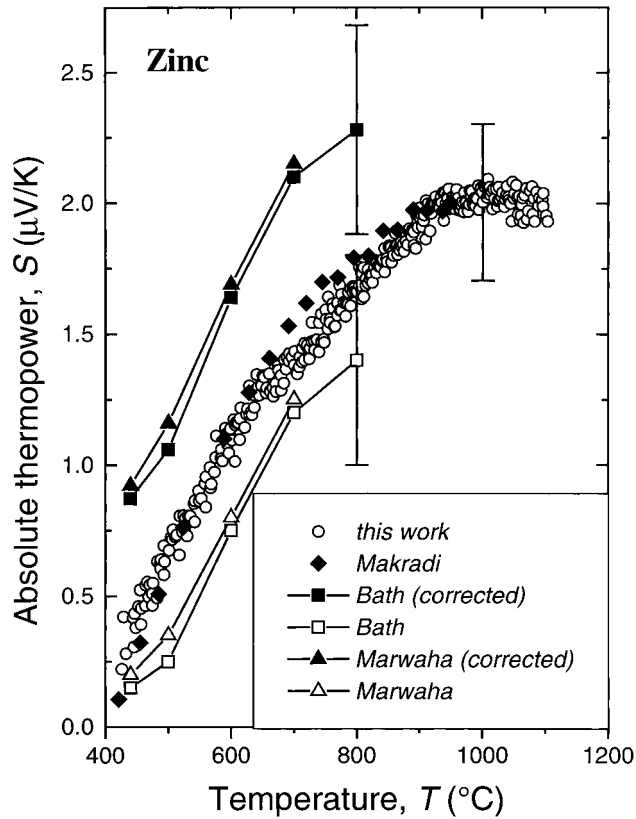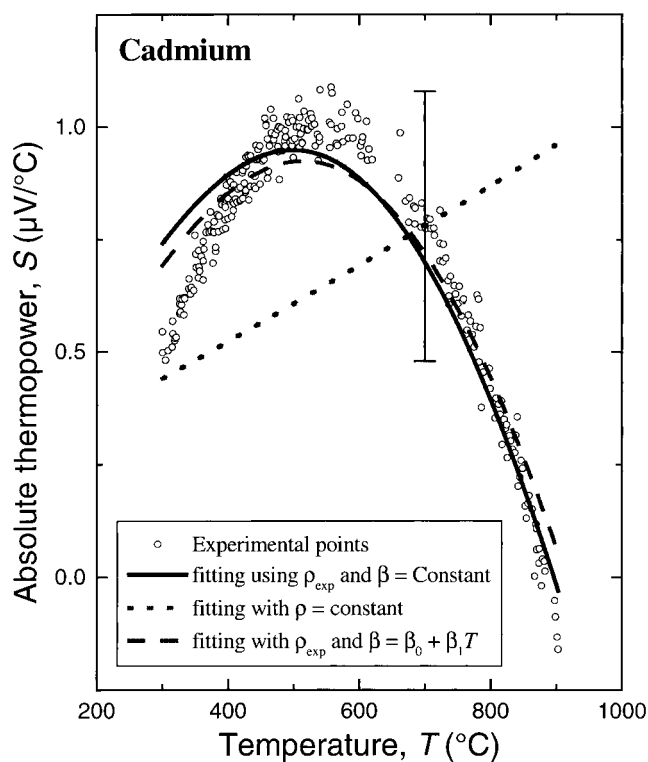
Figure 4. Our experimental absolute thermopower of liquid zinc as well as data from Marwaha and Cusack [20], Makradi [9], and Bath and Kleim [1]. There is a very good agreement between all the experimental data.

(c) the limit of integration $2\,k_F$ is reduced due to a diminution of the mass density; Gasser [13] showed that the integrand of cadmium at $2\,k_F$ is reduced,

(d) the prefactor of $2p$ contains in the numerator the atomic volume Ω_0 which increases with temperature,

(e) the prefactor of $2p$ contains in the denominator the term k_F^2 which decreases with temperature.

The first three contributions tend to decrease the term $p/2$; the last two tend to increase this term. Thus, a nearly constant β term is possible. It can however seem surprising that an 11% resistivity variation (from 34.3 $\mu\Omega$ cm at 520 °C up to 38.1 $\mu\Omega$ cm at 900 °C) induces such an important variation of the absolute thermopower, i.e. from +1.0 $\mu\Omega$ cm around 520 °C down to −0.3 $\mu\Omega$ cm at 900 °C. This comes from the fact that the cadmium (as well as the zinc) has a dimensionless parameter χ near to zero with the consequence that a small absolute variation of the resistivity induces a small absolute, *but* an important relative variation of χ, which can eventually change in sign. To confirm that effectively β has smaller temperature dependence than the resistivity, we make a third fitting, substituting for β with $\beta_0 + \beta_1 T$, which takes into account the first-order term. The fitting, showed by the dashed line in figure 5 is not notably better than the first one (with β temperature independent), and the temperature dependent term in β, i.e. $\beta_1 T$, is much smaller than the temperature independent term (β_0) (37 times smaller at

Figure 5. Experimental data (circles) as well as a fitting of the absolute thermopower S. The dotted line corresponds to a constant value of the bracket of equation (7). The full line corresponds to the inclusion of the experimental resistivity in the bracket with a constant value of β. A third fitting (dashed curve) is based on the hypothesis that β is a linear function of the temperature, i.e. $\beta = \beta_0 + \beta_1 T$. It gives very similar results to the second fitting, the non-linear term $\beta_1 T$ being much smaller than the temperature independent one (β_0).

900 °C). This demonstrates that our fitting using only one constant parameter β was justified. It is clear that the quality of the fitting demonstrates that the same physical phenomena are responsible from the temperature dependence of the resistivity and of the thermopower.

4.2. Zinc

The same mathematical treatment has been made for liquid zinc's thermopower, using $Z = 2$, a fourth-order polynomial fitting of our experimental resistivity, $\rho_{exp}^{Zn}(T_C)$ data, as well as the Crawley experimental density [22], $d_{exp}^{Zn}(T_K)$. The result is shown in figure 6. It is clear that this fitting (solid curve) is very much better than the resistivity temperature independent fitting (dots). As in the case for cadmium, Etherington and Wagner [28] have showed that the height of the main peak of the structure factor decreases very strongly with temperature (from 2.8 at 450 °C to 2.4 at 750 °C).

The fitted ATP increases up to 1000 °C and then begins to decrease slightly. This result suggests that the real thermopower may decrease at temperatures higher than the maximum achieved. Nevertheless, we cannot claim than it really decreases at high temperature. Only measurements at higher temperatures will demonstrate this.
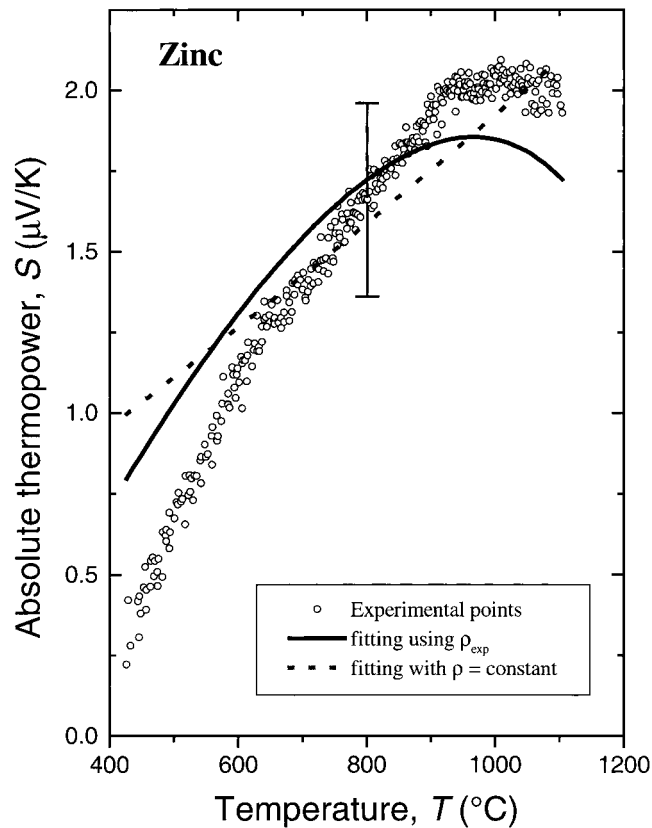
Figure 6. Same mathematical treatments as figure 5 but for liquid zinc. The fitting based on the experimental resistivity (solid curve) is qualitatively correct and clearly better than the fitting that uses a temperature independent resistivity (dots).

5. Conclusion

We have measured the resistivity and the thermopower of the liquid cadmium and zinc in a large temperature range. The measurements are carried out under pressure to avoid bubbles and distillation. The liquid cadmium thermopower shows an increase from approximately $0.5 \ \mu V \ K^{-1}$ near the melting point up to $1.0 \ \mu V \ K^{-1}$ around $520 \,°C$ and then decreases down to negative value $(-0.3 \ \mu V \ K^{-1})$ at high temperature. We have achieved a good fit of the experimental thermopower results with the Ziman's thermopower formula by introducing the experimental evolution of the resistivity with the temperature, using only one adjustable parameter. It is clear that this means that the temperature dependence of the thermopower can be explained by the same physical phenomena that the temperature dependence of the resistivity, i.e. the decrease of the main peak of the structure factor and occurrence of $2k_F$ near the maximum of the main peak.

The liquid zinc is qualitatively similar to the cadmium but the thermopower maximum is near to the maximum temperature achieved and we are not able to claim that the thermopower of this metal decreases also at high temperature. The fitting effectively suggests that it can be the case, but only measurements at higher temperatures will demonstrate this hypothetical decrease.

Acknowledgments

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