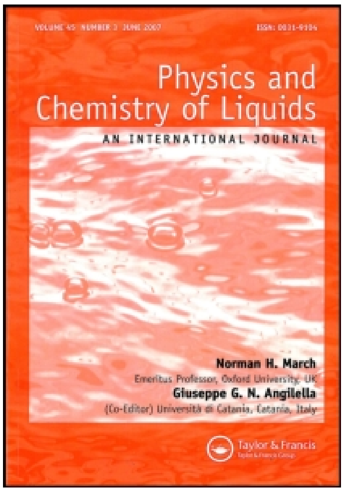

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Temperature Dependence of the Electrical Resistivity of Liquid Lead between Its Freezing Point and 800 °C

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Abstract—The electrical resistivity of liquid lead was measured between its freezing point, $t_F = 327.5$ and 800 °C with a relative accuracy better than 2.5×10^{-2} %. The resistivity was found to be a concave function of temperature of the form $\rho(X) = a_1 \cdot X + a_2 \cdot [1 - \exp(-a_3 \cdot X)] + \rho_0$, where $X = t - t_F$, in the whole range studied. The temperature coefficient of resistivity is a continuous and decreasing function of temperature. A possible explanation of the observed phenomenon is suggested.

For a large number of metals, the specific heat C_P and the thermal expansion coefficient α exhibit a remarkably similar behaviour on both sides of the solid–liquid transition temperature. The observed enhancement of these quantities below and above the freezing point† has been interpreted by Borelius⁽¹⁾ as being due to the " pre- and after-melting " effects caused by the extension of the melting process. A similar correlation exists between C_P and the temperature coefficient of resistivity (TCR) in the solid state.⁽²⁾ If this correlation holds also in the liquid state, the TCR should for a large number of metals be a decreasing and continuous function of temperature approximately in such a range where the aftermelting effect appears in C_P. In this range then, the resistivity must be a concave function of temperature (d^2R/dT^2 is negative). With the possible exception of lithium,⁽³⁾ the concave part of the resistivity temperature curve has not yet been observed.

To observe the aftermelting effect on the TCR, the difference between the freezing and the critical points of a given metal must be

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† Since the freezing point of lead is one of the secondary reference points of the International Practical Temperature Scale of 1968 (327.502 °C)⁽²²⁾ we will adhere to the notation " freezing " instead of " melting " point.

rather large. Only then will the aftermelting effect develop fully and not be cancelled by the much larger effect of the internal vaporization.† However, even in those metals where this condition is fulfilled, the internal vaporization prevails as the temperature is further increased. The curvature of the resistivity/temperature plot will then change and the curve will become convex (d^2R/dT^2 changes sign). For this reason, metals with relatively low critical points such as for instance most of the alkali metals and mercury will very probably show only the convex part of the resistivity curve. Lead, because of its low freezing point and a very high critical point, estimated to be about 5400 °K,⁽⁴⁾ shows a very pronounced aftermelting effect in C_P and α.⁽²⁾ Moreover it has a high specific resistivity at the freezing point: 95 $\mu\Omega$cm.

These properties make it a very suitable choice for the investigation of the aftermelting effect in the TCR. The purpose of this paper is to report some careful electrical resistivity measurements on liquid lead which show that the TCR is indeed a decreasing and continuous function of temperature in the whole range studied, viz. 327.5–800 °C.

In order to determine the electrical resistivity, the dc four-probe method with iron electrodes was used. The solubility of Fe in Pb has been reported to be 2.3×10^{-4} wt% at 600 °C⁽⁵⁾ which is so low that for our purposes Fe can be considered insoluble in Pb. We did not in fact observe any time-dependent drift which could be attributed to the alloying of Fe with Pb. The liquid metal containers are of a special helical type and had a total length of about 150–200 cm and an internal diameter of approximately 2 mm. In combination with a sensitive compensator (Tinsley's 4363D-Auto Vernier Potentiometer), it was possible to measure the voltages to 2 parts per million.

All samples were melted under vacuum (0.1–0.01 torr) in a hf furnace and kept at temperatures between 800 and 900 °C for at least 24 hours. Afterwards they were machined and cut to the desired dimensions. The containers were thoroughly washed in chromium-sulphuric acid and then rinsed in distilled water and methanol. After drying, they were put into the furnace and evacuated at a temperature of about 400 °C for a few days to remove

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† Internal vaporization causes, according to Borelius,⁽¹⁾ the large enhancement in the specific heat C_P observed below the critical point.

the gases adsorbed on the walls. Only after this procedure had been completed were the containers filled with the liquid metal. All measurements were performed at an overpressure of 30–50 torr. The change in resistivity of the sample caused by lowering the pressure from about 800 torr to 0.1 torr was negligibly small and well within the stated limits of relative error.

Three series of measurements were made under the following experimental conditions:

1*st series:* Pb sample of 4N purity (" ANALAR " p.a. grade, typical content of impurities in ppm: 300 Cu, 100 Ni, 100 Fe, 100 Bi, max 500 Sb and Sn, 100 As). The container was made of pyrex glass and the sample was protected by argon gas during the measurements. Temperature range: 327.8–501.4 °C.

2*nd series:* Pb sample of the same quality, container made of fused silica and the sample protected by a mixture of nitrogen and hydrogen (2%). Temperature range: 327.8–807.1 °C.

3*rd series:* 6N sample from Koch-Light Ltd (typical analysis in ppm: 0.3 Ag, 0.2 Cu, 0.1 Mg, 0.1 Si), container made of pyrex glass and the sample protected as in the 2nd series. Temperature range: 326.2 (undercooled state) – 433.1 °C.

The temperature was measured in the 1st and 2nd series with two Pt-Pt/10% Rh thermocouples. Since the sensitivity of the thermocouples to small changes in temperature was lower than that of the specimen, we used two Pt-resistance thermometers in the 3rd series. This alteration and a better stabilization of the temperature enabled us to increase the relative accuracy from $\pm 1.5 \times 10^{-1}\%$ to $\pm 2 \times 10^{-2}\%$ in the temperature determination and from $\pm 2.2 \times 10^{-2}\%$ to $\pm 2.6 \times 10^{-3}\%$in the resistivity determination. The temperature variation along the container did not exceed ±0.2 °C and was typically ±0.1 °C.

The resistivity values measured were first corrected for the thermal expansion of the container and afterwards scaled so as to obtain 95 $\mu\Omega$cm for the specific resistivity at the freezing point. This value was chosen as a convenient mean of the published values of 94.85,(6) 94.73,(7) 95.0,(8) 95.4,(9) 96.0,(10) and our own determination of 95.07 $\mu\Omega$cm made with the sample and container of the 3rd series.

Within the limits of experimental accuracy all three series gave

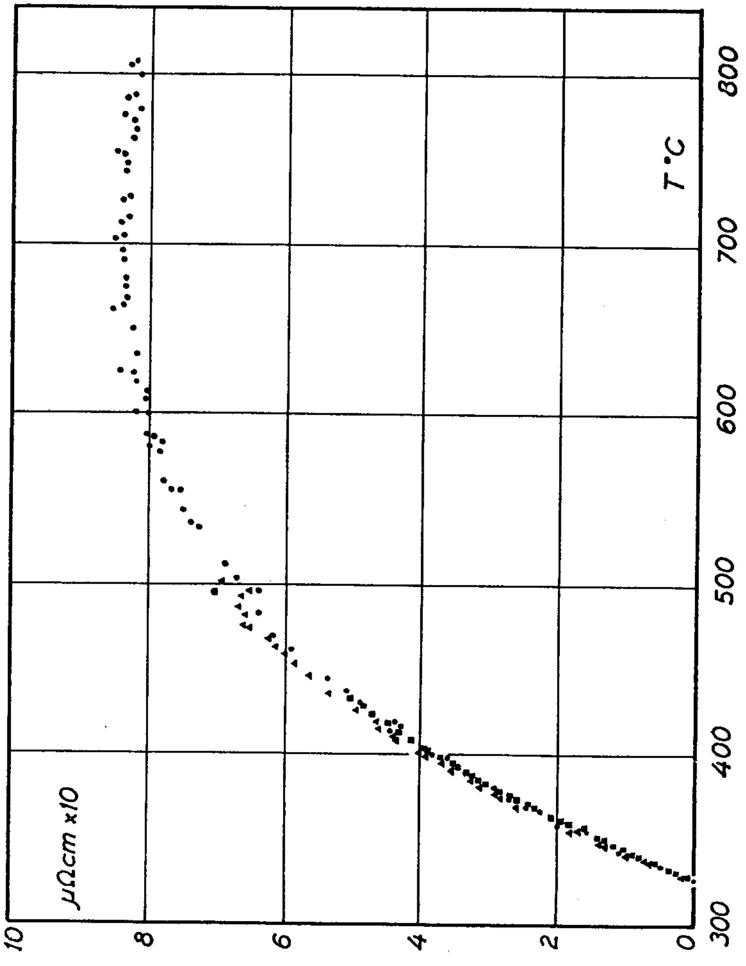

Figure 1. " Deviation from linearity " of the resistivity/temperature curve as a function of temperature. Triangles, dots and squares represent the data of the 1st, 2nd and 3rd series respectively.

unique and reproducible results. No effect of thermal cycling was observed. To see the deviation from linearity of the resistivity/temperature plot more clearly we have approximated the results between 750 and 800 °C by a straight line, shifted the line so that it passed through the 95 $\mu\Omega$cm value at the freezing point and subtracted the values of resistivity given by the linear relation from the measured ones. The plot of this " deviation from linearity " versus temperature is shown in Fig. 1.

The following expression gives the best fit for our data:

$$\rho(X) = a_1 X + a_2[1 - \exp(-a_3 X)] + \rho_0 \qquad (1)$$

where a_1, a_2 and a_3 are constants, X is the " reduced " temperature: $X = (t - 327.5)$ °C, and ρ_0 is the specific resistivity at the freezing point, 95 $\mu\Omega$cm. The least-squares method gave a set of values for a_1 and a_2 for a given a_3. Varying a_3 and taking as a criterion of the fit the magnitude of the sum of the squares of relative errors, S, we obtained the following values for the constants ($S = 1.98 \times 10^{-6}$, standard deviation less than 0.013 $\mu\Omega$cm):

$$a_1 = 4.4773 \times 10^{-2}\ \mu\Omega\text{cm} \cdot \text{deg}^{-1}$$

$$a_2 = 1.3754\ \mu\Omega\text{cm}$$

$$a_3 = 5.535 \times 10^{-3}\ \text{deg}^{-1}$$

The resistivity can be alternatively expressed as a function of $\epsilon = (T - T_F)/T_F$ (T in Kelvin). Then $\rho(\epsilon) = a\epsilon + b[1 - \exp(-c\epsilon)] + \rho_0$ where $a = 26.8930$ $\mu\Omega$cm, $b = a_2 = 1.3754$ $\mu\Omega$cm, and $c = 3.3246$. Differentiation of (1) gives the TCR:

$$\frac{1}{\rho_0} \cdot \frac{d\rho}{dT} = [a_1 + a_2 \cdot a_3 \cdot \exp(-a_3 X)] \cdot \frac{1}{\rho_0} \qquad (2)$$

TCR is plotted against temperature in Fig. 2 and the numerical results for both resistivity and TCR are given in Table 1.

Previous measurements of the resistivity of liquid lead by Northrup and Suydam,(7) Roll and Motz,(8) Takeuchi and Endo,(10) and Adams and Leach(9) gave a constant TCR in the whole studied range.

TABLE 1

T °C	$\rho(T)$ $\mu\Omega$cm	$\frac{1}{\rho_0}\left(\frac{d\rho}{dT}\right)_P \cdot 10^5$ deg^{-1}
327.5	95.000	55.14
350	96.168	54.20
400	98.701	52.49
450	101.162	51.20
520	103.569	50.21
550	105.936	49.47
600	108.272	48.90
650	110.584	48.47
700	112.878	48.15
750	115.159	47.90
800	117.430	47.72

Recently, Davies and Leach reported a discontinuous change in the TCR of liquid lead (and tin)(6) in a direction that is compatible with our results. They observed an abrupt decrease in the TCR at 393 °C of about 4.5% in magnitude. There are, however, no signs of similar discontinuities in other transport coefficients or in C_P and α. For a comparison with the present results, the values of TCR obtained by Roll and Motz,(8) Adams and Leach,(9) and Davies and Leach(6) are also shown in Fig. 2.

The reason why the curvature has not been observed in the earlier measurements(6,7,8,9,10) is, most probably, the substantially lower relative accuracy of these measurements. In the case of Roll and Motz,(8) the accuracy in the resistivity determination was estimated to be ± 1%. The small curvature of the resistivity/temperature curve falls within this uncertainty range. The discrepancy between our measurements and those of Davies and Leach(6) cannot be explained by a lower relative accuracy of their results since these authors claim approximately the same figure as we do (± 0.03– ± 0.05%). A possible reason may be the fact that the measurements of Davies and Leach are extended over too short a temperature interval. Also, if we may judge from Fig. 3 of their article, the intervals between the points measured were too large. (Both these features apply equally well to the earlier measurements.(7,8,9,10)) These circumstances effectively mask the observation of the curvature.

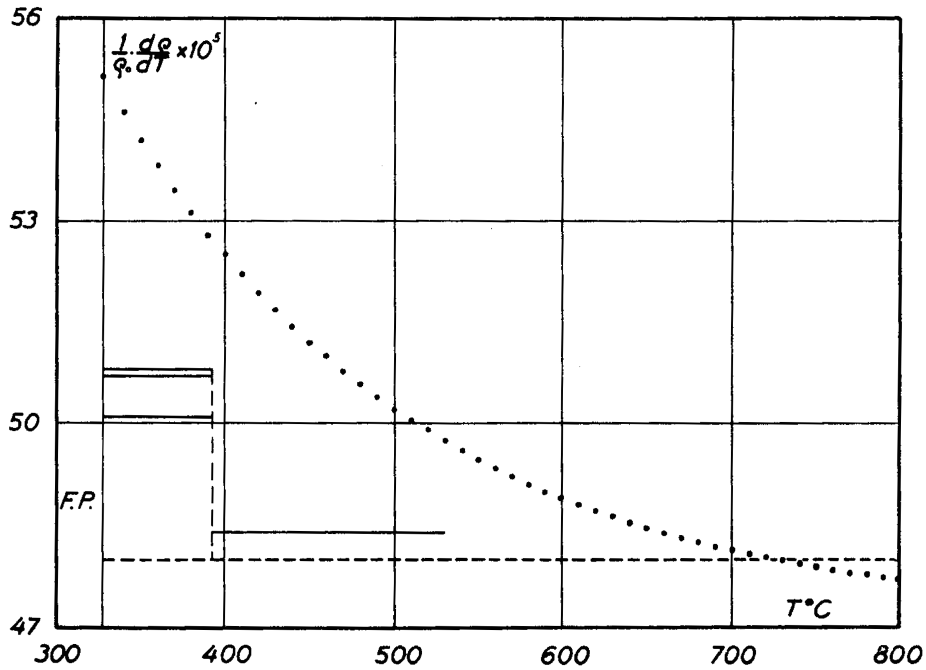

Figure 2. Temperature coefficient of resistivity of liquid lead as a function of temperature. The TCR values calculated from Eq. (2 are represented by the dotted curve. Solid lines show the results of Davies and Leach(6) for three independent runs. Above 393 °C (dashed vertical line) two runs of Davies and Leach gave the TCR values identical with the results of both Roll and Motz(8) and Adams and Leach(9) [48×10^{-5} deg^{-1}], represented by the dashed line.

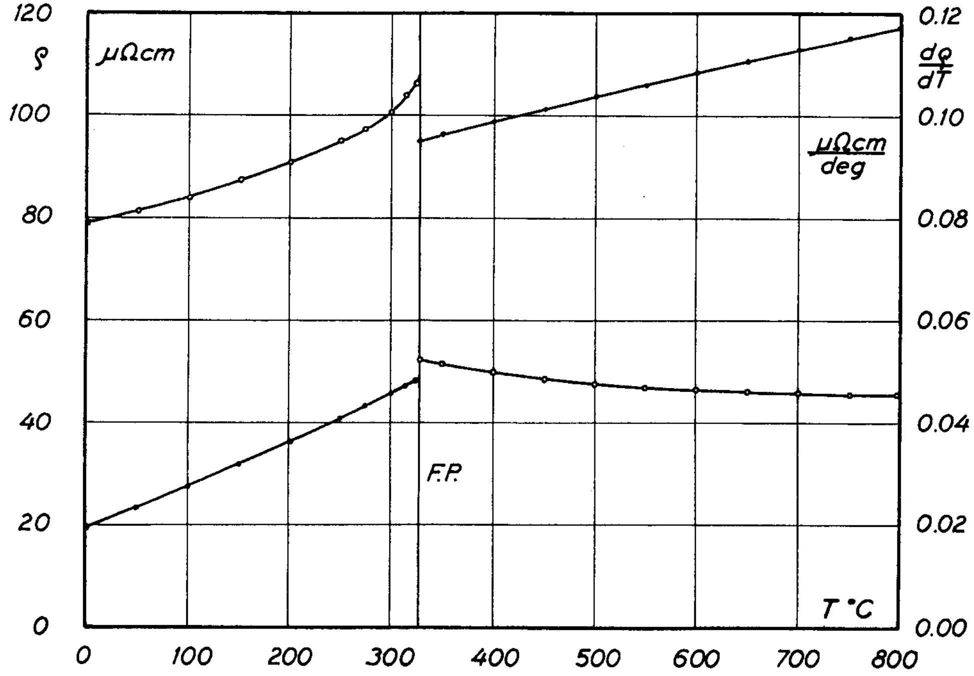

Figure 3. Resistivity (solid circles) and its derivative (open circles) with respect to temperature of solid and liquid lead plotted against temperature. Data for the solid lead were taken from the work of Pochapsky(23) with $\rho(0\,°\mathrm{C}) = 19.3\ \mu\Omega\mathrm{cm}$.

The observed behaviour of the resistivity and its temperature coefficient is in qualitative agreement with the theory of the extended melting process. For liquid lead, the theory implies that there should be a temperature-dependent contribution to TCR, having its maximum at the freezing point and decreasing with increasing temperature. This behaviour should be observable in approximately the same temperature range as the aftermelting contribution to C_p. Even though the available results for C_p of liquid lead are considerably less accurate than our resistivity measurements and thus only allow a qualitative comparison, C_p is still observed to be a monotonously decreasing and continuous function of temperature up to about 1200 °C.(11) Between the freezing point and 800 °C—the highest temperature at which the resistivity was measured—TCR was found to behave in the same way.

Extension of the melting process is, according to Borelius,(1) the cause of the aftermelting effect. The nature of this phenomenon is still an unsolved problem and the present measurements do not give any definite clue to its solution. We can however account for the decreasing TCR if we assume a " two-component model " of liquid lead where one component is formed by ordered microregions having a structure similar to that of the solid lead just below its freezing point and the other forms the disordered rest. As Fig. 3 shows, the resistivity and TCR of the solid lead are, respectively, lower and higher than those of the liquid lead. The decreasing TCR will therefore be a consequence of the decrease in amount and dimensions of the ordered microregions with increasing temperature.

The existence of ordered microregions above the freezing point is however not certain. The calculation by Burton(12) show that the spherical clusters of atoms may really be stable at temperatures above the melting point of the bulk solid. The calculations were made with the 6–12 Lennard–Jones potential for argon and it is not clear whether a similar result would be obtained for a metallic potential. However, even if the results were affirmative, we would still be in a rather uncertain position due to the known results of the structure factor measurements. The " melting " of the ordered microregions with increasing temperature causes the structure of the liquid metal to change gradually and this change should be detectable by X-ray or neutron diffraction measurements. Evidence from these experiments is, unfortunately, still inconclusive. In the case of liquid lead, there is, in this sense, both indirect and direct evidence in favour of the " two-component model ". The indirect evidence is given by the results of the Fourier analysis of the structure factors of liquid gold, silver and lead, described by Richter and Breitling.(13) Microregions with ordered structure seem to be present in all metals investigated. The direct evidence is rather slight but nevertheless exists. A splitting of the main peak of the structure factor of liquid lead was first observed by Khruschev *et al.*(14) in a neutron diffraction experiment 2.5 degrees above the freezing temperature and disappeared 20 degrees above this temperature. More convincing results were recently reported by Romanova and Mel'nik.(15) The splitting of the main peak was observable up to 110 degrees above the freezing temperature of lead. Similar effects were reported by the same authors for liquid gallium and tin.(16,17) The authors estimate the accuracy of the intensity determination to be ± 1% at the highest measurable diffraction angle.

On the other hand, the neutron diffraction determinations of the structure factor of liquid lead by North *et al.*(18) do not reveal any subsidiary " humps " or peaks which would indicate the suspected microregions. The accuracy was in this case, however, estimated to be between ± 3 and ± 5%. The X-ray diffraction measurements by Kaplow *et al.*(29) do not either show any irregularity in the structure factor of liquid lead. The problem of the nature of the extended melting and, possibly, the plausibility of a two-component model of liquid lead can be solved only by a more accurate determination of the liquid structure factor. These data are also absolutely necessary if we are to obtain meaningful results concerning the TCR from the nearly-free-electron theory of the electron transport properties of liquid metals.(20,21) In the meantime, however, it will be very valuable to gain further information about the curvature of the resistivity/temperature curves for other liquid metals. Attention should be concentrated preferably on those metals which have exhibited a pronounced aftermelting effect (e.g. tin) and/or have shown some irregularities in their structure factors (e.g. tin and gallium). Further work along these lines is in progress.

Acknowledgements

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