

## **A Four-Probe dc Method for Measuring the Electrical Resistivities of Molten Metals**

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A four-probe dc technique for measuring liquid-metal electrical resistivities has been developed, and liquid-resistivity measurements on gallium, tin, lead, copper, a lead tin alloy, a copper tin alloy, and a zinc alloy have been presented. The Lorenz relation has been used to calculate thermal conductivities from these resistivity measurements. The thermal conductivities calculated from these resistivity measurements are (where data are available) in good agreement with recommended liquid-metal thermal conductivities.

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**KEY WORDS:** liquid metals; liquid alloys; Lorenz relation; resistivity; thermal conductivity.

### **1. INTRODUCTION**

In the past decade there has been an increased use of process modeling in the casting industry. The driving force for such process modeling is improved productivity through lower energy costs, lower scrap losses, improved product quality, and product consistency [1]. This has been recognized by the Department of Trade and Industry, U.K., who have initiated a number of programs to improve measurement methods for thermophysical properties. The aim of this present investigation was to develop an instrument capable of measuring the electrical resistivities of liquid metals at temperatures up to 1200°C. The method presented here is a four-probe potentiometric method for the measurement of electrical resistivity. Electrical resistivity is a structure-sensitive property, and while this property is important in itself, it is thermal conductivities calculated from electrical resistivities via the Lorenz relation [2] that is the focus of this study.

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Thermal conductivities of liquid metals are exceedingly difficult to measure. These difficulties are a result of the following.

- (a) Chemical reactivity (containment) problems at high temperatures required for metallic systems.
- (b) Convectonal (mass flow) heat transfer of the liquid. It is difficult to hold liquid metal at high temperatures and make thermal-conductivity measurements without there being a convectonal term associated with the measured value, as thermal instabilities in the measurement systems are enough to initiate convection.
- (c) The thermal-conductivity measurement techniques themselves usually require either a temperature gradient imposed on the sample or monitoring of the temperature response of a sample that has been perturbed by an energy pulse. These are much more difficult experiments to carry out than electrical resistivity measurements.

The relative simplicity of resistivity measurements and the fact that the measurements are independent of convective flow indicate that this technique may be a powerful tool in obtaining liquid-metal thermal conductivities. This is the driving force for this study, the ultimate aim of which is to establish whether the electrical resistivity of a liquid metal alloy can be used to calculate the thermal conductivity of the alloy. This paper has more modest aims, which are to establish a resistivity apparatus at NPL and measure the resistivities of some pure liquid metals and liquid-metal alloys.

## 2. EXPERIMENTAL

A dc four-probe potentiometric technique similar to that used by Mera et al. [3] was used to measure the liquid-metal resistivities. As this apparatus has not been previously presented, the method is explained in detail.

### 2.1. Method

The silica resistivity cell, shown in Fig. 1, was designed to enable resistance changes to be measured as a function of temperature. The resistivity ( $\rho$ ) of a metal, as defined in Eq. (1),

$$\rho = R \frac{A}{l} \quad (1)$$

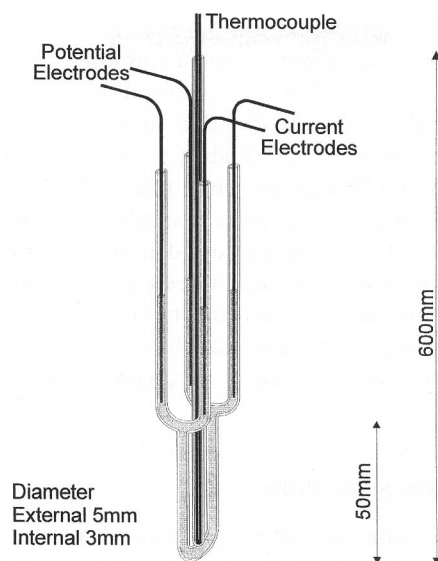


Fig. 1. Schematic of silica cell.

where  $\rho$  has units of  $\Omega \cdot m$ ,  $R$  is the resistance of the sample in  $\Omega$ ,  $A$  is the cross-sectional area of the sample in  $m^2$ , and  $l$  is the distance between the potential measuring electrodes in  $m$ , which was measured with a precalibrated silica probe. The probe was calibrated by measuring the resistance ( $R_{cal}$ ) of triple-distilled mercury (Hg) at  $20 \pm 0.2^\circ C$ , which has an electrical resistivity of  $0.956 \times 10^{-6} \Omega \cdot m$  at  $20^\circ C$  [4] ( $\rho_{cal}$ ) and an estimated uncertainty of 1% [5]. The calibrated probe would then be used to measure the electrical resistance of a sample ( $R_s$ ) and the resistivity calculated from Eq. (2).

$$\rho_s = R_s \frac{\rho_{cal}}{R_{cal}} \quad (2)$$

To perform the resistance measurements, the potential drop across the probe (from potential electrode to potential electrode shown in Fig. 1), for a given current through the sample, was measured. The applied current was obtained by measuring the potential drop across a resistor of known resistance, in series with the sample. Fluke 8840 multimeters were used to measure the potential drops. The power was supplied by a Thurlby power pack which has a maximum 10-A and 35-V output. Each resistivity measurement is averaged from two successive resistance measurements (less than 0.5 s apart), where the current polarity is reversed. A Pt/Pt13%Rh

thermocouple, situated in the central tube of the probe shown in Fig. 1, is used to measure the temperature. The maximum working temperature of the current setup is 1200°C. This temperature limit is a result of using silica as the probe material. It is envisaged that in the near-future the technique will be developed to operate at a higher temperature. This will require a new probe design and a change of probe material.

A PC is used to control the power supply, both multimeters, and the current relay and, also, log the measured data. Computer control of the measurement is such that all critical circuit parameters (current, voltage, power on time, temperature measurement step, time measurement step, and measurement integration time) can be set on the PC, and resistivity measurements can be made at either a constant temperature or constant time intervals.

## 2.2. Calibration of the Silica Probe

A glass beaker containing approximately 70 ml of triple-distilled Hg is placed in a water bath and stabilized at  $20 \pm 0.2^\circ\text{C}$ . Inserting the silica probe into the Hg, the lower U tube in the probe schematic shown in Fig. 1 fills from the bottom up through an opening in the base. A resistance thermometer is used to measure the temperature. The electrode material is Pt/Pt10%Rh. Once the system temperature has stabilized (usually after approximately 30 min), the resistance of the probe is measured.

## 2.3. Experimental Setup/Resistance Measurement

The calibrated probe is cleaned and placed in an environmental chamber, which, in turn, is situated in a Pt furnace, as shown in the setup schematic in Fig. 2. The electrical resistivity sample is measured within the environmental chamber. When the sample is molten, the crucible is raised until the electrodes contact the liquid-metal sample and a current is registered on the multimeters. The crucible is then raised an additional 5 mm to ensure that the liquid metal sample has "good" contact with the electrodes. Electrode and crucible materials are chosen to ensure minimum reaction with the sample. With the exception of the gallium measurements, all measurements presented were made in an argon atmosphere with tungsten electrodes and graphite crucibles. It should be noted that the chamber design is such that measurements can be made under vacuum or other gas atmospheres.

The gallium measurements were made in a silica crucible, with Pt10%Rh electrodes, and heated in a water bath. A resistance thermometer was used to measure the temperature.

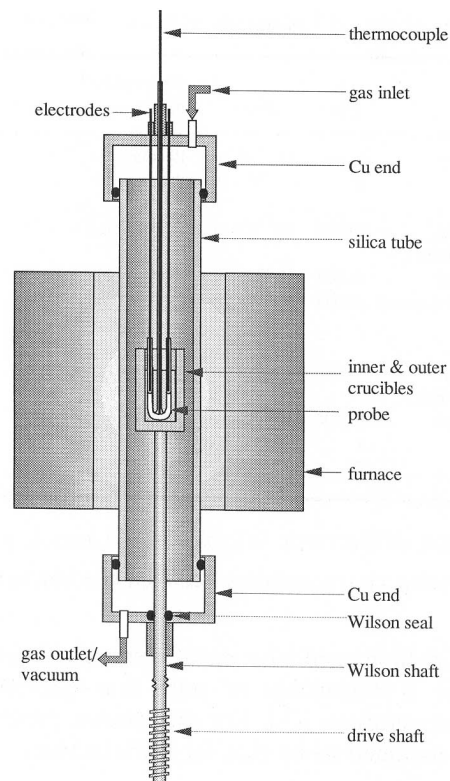


Fig. 2. Schematic of furnace setup.

#### 2.4. Error Analysis of the Four-Probe Technique

An analysis of possible errors is given in Table I. The uncertainty is calculated as recommended in the NAMAS publication NIS 3003 [6] and is  $\pm 1.7\%$  for low electrode reactivity and  $\pm 2.7\%$  for high electrode reactivity. The reported uncertainties are based on a standard uncertainty multiplied by a coverage factor of 2, providing a level of confidence of approximately 95%.

The judgment for high or low electrode reactivity is a difficult one to make. Electrode reactivity refers to the factors that are difficult, if not impossible, to quantify that involve the electrode. Such factors could include

- (1) oxidation of electrodes prior to immersion in the liquid metal sample,

**Table I.** Sources of Uncertainty in Resistivity Measurements

Source of uncertainty	$\pm$ value	Units	Probability distribution	Divisor	Sensitivity coefficient	$\pm$ $10^{-8} \Omega \cdot m$
Recommended value of Hg	0.956	$10^{-8} \Omega \cdot m$	Rectangular	1.73	1	0.552
Temperature of standard	0.3	$^{\circ}C$	Rectangular	1.73	$8.90 \times 10^{-10}$	0.015
Resolution in voltage measurement of calibrant	0.0159	$10^{-8} \Omega \cdot m$	Rectangular	1.73	1	0.009
Resolution in voltage (current) measurement of calibrant	0.0004	$10^{-8} \Omega \cdot m$	Rectangular	1.73	1	0.000
Standard deviation of cell constant	0.0033	$10^{-8} \Omega \cdot m$	Type A	1.00	1	0.003
Temperature of sample	3	$^{\circ}C$	Rectangular	1.73	$8.90 \times 10^{-10}$	0.154
Resolution in voltage measurement of sample	0.0396	$10^{-8} \Omega \cdot m$	Rectangular	1.73	1	0.023
Resolution in voltage (current) measurement of calibrant	0.0006	$10^{-8} \Omega \cdot m$	Rectangular	1.73	1	0.000
Electrode reactivity (low)	1	%	/	/	1	0.595
Electrode reactivity (high)	2	%	/	/	1	1.189

- (2) dissolution of electrode into the liquid metal, and
- (3) poor wetting characteristics between the electrode and the liquid metal.

Experience with handling particular metal systems aids in quantifying such intangibles, and it is reasonable to state that electrode problems will increase at high temperatures [7]. For the systems presented in this paper the uncertainty is assumed to be that for low reactivity.

## 2.5. Material Composition

Sample identification, composition, and electrodes used to make the measurements are given in Table II.

**Table II.** Sample Identification, Composition, and Electrode Material Used in Measurements

NPL identifier	Material	Composition (wt%)	Electrode material
CGQ	Electrolyte Cu	99.98	W
ENP and ARY	Sn	99.9995	W
ENN	Ga	99.9999	Pt(10%Rh)
ENQ	Pb	99.95	W
ENQ1	Pb + Sn alloy (ENQ + ENP)	69.4 + 30.6	W
CGQ1	Cu + Sn alloy (CGQ + ENP)	90 + 10	W
ENH	Zn alloy (commercial alloy)	Zn + 4Al + 0.53 Mg	W

### 3. RESULTS AND DISCUSSION

In order to assess the ability of the NPL four-probe dc potentiometric method for the measurement of liquid-metal resistivities, a number of liquid metals for which there is critically assessed data available [8] were measured. The technique was then used to measure the electrical resistivities of three alloys. These liquid-metal resistivity results are given in Figs. 3–6. The referenced data shown in Figs. 3–6 are the recommended values given by Iida et al. [8] and are given in Table III. The recommended resistivities are given in the form of Eq. (3),

$$\rho = a + bT \quad (3)$$

where  $a$  and  $b$  are constants given in Table III and  $T$  is the temperature in K. Table III also includes the range over which the equations are valid.  $T_m$  denotes the melting temperature.

There are some generalities that apply to all the data in Figs. 3–6.

- (1) With the exception of the Zn alloy, which shows a decrease in resistivity with increasing temperature in the liquid phase, the resistivity of the liquid metals increases linearly with temperature.
- (2) At the melting point (or liquidus for alloys), there is an abrupt change in resistivity associated with the phase change.
- (3) With the exception of gallium, all the reported resistivities increase when transforming from solid to liquid.

#### 3.1. Gallium

The resistivity measurements of gallium shown in Fig. 3 were made as follows:

- (1) cooling from the liquid and stabilizing the temperature for 15 min, denoted static  $T$ ;
- (2) cooling from the liquid at a cooling rate of approximately  $1^\circ\text{C} \cdot \text{min}^{-1}$  while making measurements, denoted cooling;
- (3) heating from solid into the liquid at approximately  $1^\circ\text{C} \cdot \text{min}^{-1}$  while making measurements, denoted heating.

It can be seen in Fig. 3 that the resistivity measurements are in good agreement (better than  $\pm 1\%$ ) with those recommended by Iida [8] and also that, regardless of how the measurement is made (heating, cooling, or static temperature), the resistivity value in the liquid agrees with that recommended by Iida [8]. On cooling, the gallium exhibited a small

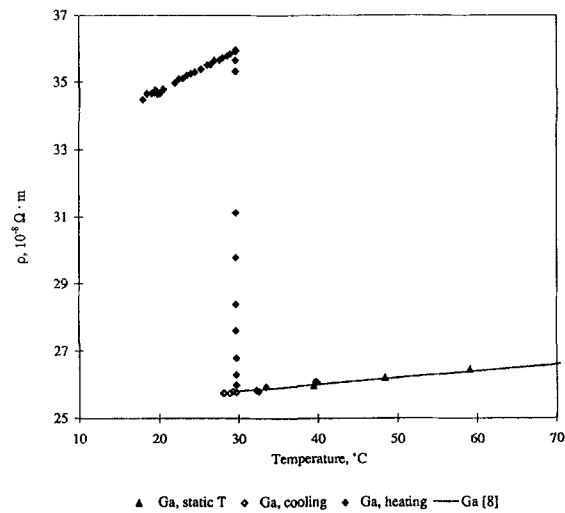


Fig. 3. Resistivity of gallium.

degree of undercooling, approximately  $2.5^{\circ}\text{C}$  below its melting point of  $29.8^{\circ}\text{C}$  [9]. The resistivity behavior on undercooling was as would be expected if the Iida [8] liquid resistivity were extrapolated below the melting point. This indicates that the liquid structure above the melting point persists into the undercooled state.

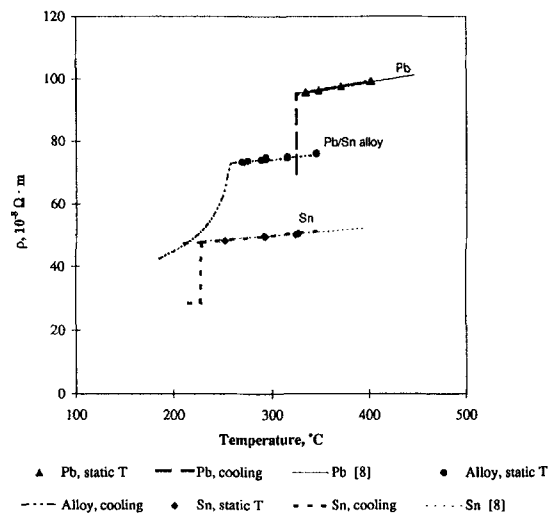


Fig. 4. Resistivities of lead, tin, and a lead-tin in alloy.



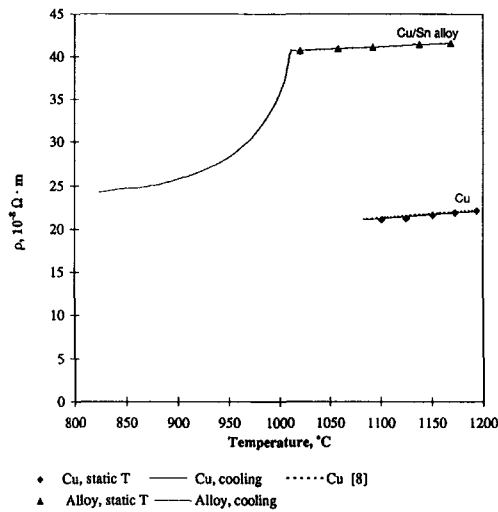


Fig. 5. Resistivities of copper and a copper-tin alloy.

Little can be made of the solid results, as it is impossible to evaluate whether or not the gallium had filled the lower U-tube or solidified, leaving voids. Solid gallium has an orthorhombic structure [9] at these temperatures and its resistivity is anisotropic. The approximate resistivity values per axis  $c$ ,  $a$ , and  $b$  are  $0.56 \times 10^{-6}$ ,  $0.18 \times 10^{-6}$ , and  $0.08 \times 10^{-6} \Omega \cdot m$ , respectively [8]. The experimental solid resistivity values shown in Fig. 3 can be considered a measure of the relative amounts of gallium in a

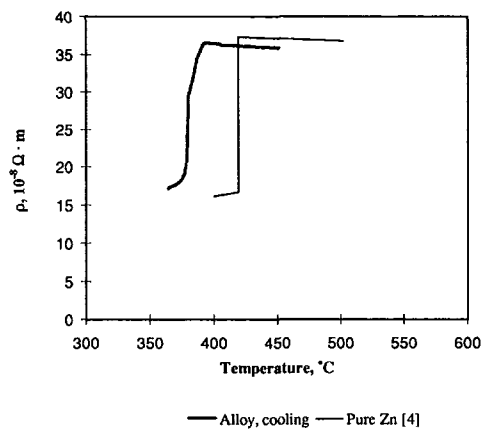


Fig. 6. Resistivities of zinc [4] and a zinc alloy.

Table III. Recommended Resistivity Values for Liquid Metals [8] Using Eq. (3)

Material	$a$ ( $\Omega \cdot \text{m}$ )	$b$ ( $\Omega \cdot \text{m} \cdot \text{K}^{-1}$ )	$T_m$ (K)	Range (K)
Cu	$9.10 \times 10^{-8}$	$8.90 \times 10^{-11}$	1357.75	$T_m$ to 1473
Ga	$1.99 \times 10^{-7}$	$1.95 \times 10^{-10}$	302.95	$T_m$ to 670
Pb	$6.66 \times 10^{-7}$	$4.79 \times 10^{-10}$	600.55	$T_m$ to 1273
Sn	$3.54 \times 10^{-7}$	$2.49 \times 10^{-9}$	505.15	$T_m$ to 1473

particular orientation with respect to the resistivity cell. The “open” orthorhombic structure is responsible for the high (relative to the liquid) resistivity of the gallium in the solid as well as the drop in resistivity as gallium transforms from solid to liquid. This is typical for metals that increase in density on melting [10].

### 3.2. The Tin–Lead System

The resistivity measurements of tin, lead, and a lead–tin alloy (69.4% Pb + 30.6% Sn), shown in Fig. 4, were made as follows:

- (1) cooling from the liquid and stabilizing the temperature for 15 min, denoted static  $T$ ; and
- (2) cooling from the liquid at a cooling rate of approximately  $1^\circ\text{C} \cdot \text{min}^{-1}$  while making measurements, denoted cooling.

Providing that the silica probe survived solidification, measurements were also made on heating. As no deviations from the cooling measurements were observed, and in the interest of clarity of Fig. 4, the heating results are not shown.

It can be seen in Fig. 4 that the resistivity measurements of tin and lead are in good agreement (better than  $\pm 1\%$ ) with those recommended by Iida [8] and also that regardless of whether the measurement is made at a stabilized temperature or on cooling, the resistivity values agree with those recommended by Iida [8]. The resistivity of liquid lead was greater than that of the lead–tin alloy, which in turn was greater than that of the liquid tin. Only the pure tin showed any signs of undercooling, approximately  $15^\circ\text{C}$  below its melting point of  $232^\circ\text{C}$  [9]. As with the gallium data, the resistivity behavior on undercooling was as would be expected if the Iida [8] liquid resistivity results were extrapolated below the melting point. This indicates that the liquid structure above the melting point persists into the undercooled state.

The point of deviation from linearity in the lead/tin system is considered to be the liquidus temperature, i.e., the point when the alloy begins to solidify. Below the liquidus temperature, the resistivity behavior is no longer linear with temperature. The resistivity in this region will be affected by the changing composition of the alloy, in terms of the relative amount of the liquid and solid alloy present as well as the solidifying species [11]. This will also be affected by the cooling rate of the alloy [11].

### 3.3. The Copper–Tin System

The resistivity measurements of copper and a copper/tin alloy (90% Cu + 10% Sn), shown in Fig. 5, were made as follows:

- (1) cooling from the liquid and stabilizing the temperature for 15 min, denoted static  $T$ ; and
- (2) cooling from the liquid at a cooling rate of approximately  $1^{\circ}\text{C} \cdot \text{min}^{-1}$  while making measurements, denoted cooling.

Providing that the silica probe survived solidification, measurements were also made on heating. As no deviations from the cooling measurements were observed and in the interest of clarity of Fig. 5, the heating results are not shown.

It can be seen in Fig. 5 that the resistivity measurements of pure copper are in good agreement (better than  $\pm 1\%$ ) with those recommended by Iida [8] and also that, regardless of whether the measurement is made at a stabilized temperature or on cooling, the resistivity values agree with that recommended by Iida [8]. The resistivity of the copper/tin alloy was greater than that of liquid copper. Neither the copper nor the copper alloy showed any signs of undercooling.

The point of deviation from linearity in the copper/tin system is considered to be the liquidus temperature. As with the lead/tin alloy, for cooling past the liquidus point, the resistivity behavior is no longer linear with temperature. As mentioned previously this nonlinear behavior was dependent on the changing composition of the alloy as it solidified, which in turn was affected by the cooling rate. To assess the effect of cooling rate on the resistivity, the measurement was repeated at a cooling rate of approximately  $6^{\circ}\text{C} \cdot \text{min}^{-1}$  (cf.  $1^{\circ}\text{C}$  per min previously) through the semi-solid region. No measurable differences in resistivity as a function of temperature between the two cooling rates were observed. For reasons of clarity, this is not shown in Fig. 5. This lack of effect of cooling rate is probably a result of the change in cooling rate being too small to affect substantially the alloy's solidifying microstructure and therefore its resistivity.

### 3.3. Zinc Alloy

The resistivity measurements made on a zinc alloy are shown in Fig. 6. The measurements were made on cooling from the liquid at a cooling rate of approximately  $1^{\circ}\text{C} \cdot \text{min}^{-1}$  while making measurements and are denoted cooling.

On cooling it was found that the resistivity of the liquid alloy increased as the temperature decreased. This is typical of divalent metals Cd, Zn, and Mg [12] and, as can be seen in Fig. 6, is similar, although lower in resistivity, to that reported for pure zinc [4].

The point of deviation from linearity in the zinc alloy is considered to be its liquidus temperature. As with the lead/tin and copper/tin alloys, for cooling past the liquidus point, the resistivity behavior is no longer linear with temperature. As mentioned previously this nonlinear behavior was dependent on the changing composition of the alloy as it solidified.

### 3.4. Lorenz Thermal Conductivities

There is an absence of reliable thermal-conductivity data for the commercial alloys used in the casting industry [1, 2]. This is a reflection of the difficulties of obtaining accurate experimental values, especially at high temperatures. In particular, there is difficulty in obtaining accurate values of the thermal conductivity of liquid metals, since convection can contribute strongly to the transport of heat. In general, convection flow will tend to increase the measured thermal conductivity, leading to an erroneously high (apparent) value for the thermal conductivity [2]. While it may be possible to eliminate convection at ambient temperatures, at higher temperatures this becomes increasingly more difficult because of the problems in eliminating thermal gradients, and hence, convection, in the liquid sample. In contrast, accurate electrical conductivities are simpler to obtain experimentally and, more importantly, are unaffected by convection.

The Lorenz [8] relation relates the thermal conductivity  $\lambda$  to the electrical resistivity  $\rho$  by Eq. (4),

$$\lambda = \frac{L_0 T}{\rho} \quad (4)$$

where  $T$  is the temperature in K and  $L_0$  is a constant with a value of  $2.445 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$  [8], and therefore, may be used to obtain liquid thermal conductivities that are unaffected by convection. The Lorenz relation is valid only if the heat conduction in the metal is carried by electrons. This is likely to be the case near or above the melting point of a metal, where the metal is in a highly energized state.

In a review carried out by Mills et al. [2] on the thermal conductivities for all pure metals for which data were available, it was found that experimentally evaluated Lorenz values at the melting point, in both the solid and the liquid were always within  $\pm 10\%$  of the theoretical value  $L_0$ . The review was not definitive, as it was impossible to rationalize this  $\pm 10\%$  difference in deviations from the Lorenz value in terms of failings in the Lorenz relation or experimental errors in the reported data. Nevertheless, liquid-metal thermal conductivities with an error of  $\pm 10\%$  are of value, particularly if it could be shown that liquid-alloy thermal conductivities calculated via the Lorenz relation from electrical resistivity measurements exhibited the same behavior.

The liquid thermal conductivities calculated from the Lorenz relation are shown in Fig. 7. For comparison, also shown in Fig. 7 are the recommended liquid thermal-conductivity values given in the review by Mills et al. [2] for gallium, tin, lead, and copper. These recommended values are based on liquid thermal-conductivity data, and not on electrical-resistivity measurements. Where comparisons can be made, the thermal conductivities from resistivity measurements are in reasonable agreement with the recommended thermal conductivities, the deviation being at most 7%. The deviations between the thermal conductivities may be as a result of failings in the Lorenz relation or errors associated with both the resistivity and the thermal-conductivity measurements. This deviation is small enough to show that, for these pure metals at least, the thermal conductivity of the liquid phase can be calculated from the resistivity. There are as yet no

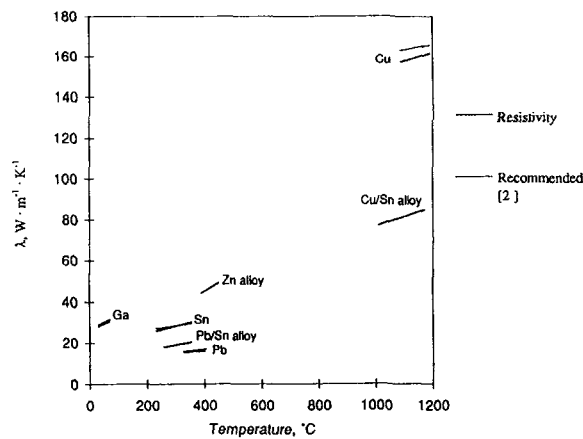


Fig. 7. Thermal conductivities of a number of liquid metals calculated from resistivities and compared with recommended [2] values.

thermal-conductivity data for the alloys to make a similar comparison. This will be addressed in the near-future, when it is planned to measure the thermal diffusivity, specific heat ( $C_p$ ), and density of these alloys to make a comparison.

#### 4. CONCLUSIONS

A method for measuring electrical resistivities of liquid metals has been presented and shown to be able to yield the electrical resistivity to better than  $\pm 1\%$  of the recommended values of gallium, tin, lead, and copper.

Liquid-metal thermal conductivities calculated from resistivities via the Lorenz relation for gallium, tin, lead, and copper show deviations of less than 7% from recommended values.

#### ACKNOWLEDGMENT

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