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A Novel Instrument for the Measurement of the Thermal Conductivity of Molten Metals. Part II: Measurements

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New measurements of the thermal conductivity of molten mercury, gallium, tin, and indium are reported up to 750 K. The measurements are performed in a novel transient hot-wire instrument described elsewhere. The present experimental technique overcomes problems of convection, and it is shown that it operates in an absolute way in accord with a theoretical model. The uncertainty of the thermal conductivity results is estimated to be ± 2%, which is superior to that achieved in most earlier work. The low uncertainty of the present experimental results has allowed us to test the only significant theory for the thermal conductivity of molten metals, which relates this property to the electrical conductivity. The pattern of results among the four metals indicates that further theoretical developments would be warranted.

KEY WORDS: gallium; indium; mercury; molten metals; thermal conductivity; tin; transient hot-wire.

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1. INTRODUCTION

Despite the need for accurate thermal conductivity data of molten metals in several fields such as metallurgy, ceramic engineering, glass manufacture and others, several reviews of available data [1–4] have revealed discrepancies as large as 50% between the experimental molten metal thermal conductivity values reported in the literature by various authors, over a wide range of temperature. The lack of accurate data is attributed to the difficulty of realizing an experimental technique that maintains a purely conductive regime of heat transfer particularly at high temperatures, since temperature distribution and its control becomes more difficult as the temperature increases.

In a previous paper [5] a novel instrument for the measurement of the thermal conductivity of molten metals was presented. It was shown that the instrument, based on the transient hot-wire technique, demonstrated high precision and an absolute uncertainty of $\pm 2\%$ in the measurement of the thermal conductivity of a molten metal at one temperature. This is made possible [5] because the new instrument:

(a) overcomes the problem of natural convection since the duration of the experiment is short compared with the time for the onset of significant heat transfer associated with the inevitable flow, and

(b) operates in accord with a theoretical model, which enables absolute measurements.

In this paper, the results of measurements of the thermal conductivity of four molten metals are presented in a range of temperature from 300 to 750 K at atmospheric pressure.

2. EXPERIMENTAL

The experimental method is based on the transient hot-wire technique [6]. According to the simplest version of this technique, a vertical wire is suspended in the test fluid and the temperature rise of the wire is obtained by measuring the temporal change of its resistance after the initiation of a heat pulse within it. However, for the study of electrically-conducting materials it is necessary to encase the wire in an electrical insulator.

The design of the sensor employed here is shown in Fig. 1. It has been described in detail elsewhere [5] and will only be briefly summarized here. The electrically-insulating elements are fabricated using 96% pure, green alumina substrate, and the sensing element is made from a 25-μm-diameter wire made of 99.99% pure platinum. To avoid end effects [5], the sensing element is composed of two identical wires differing only

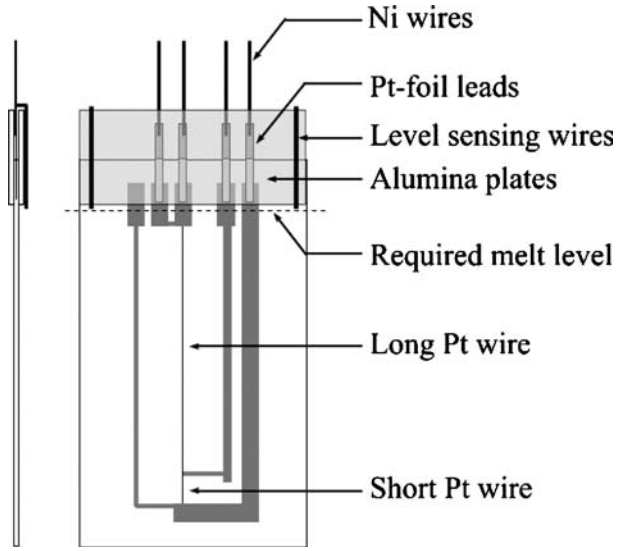

Fig. 1. The sensor.

in length, a long and a short wire, and their resistance difference corresponds to that of a central portion of a wire with no ends. The connections to the wire have been printed directly on the top of one sheet of green alumina of dimensions 100 mm length, 58 mm width, and 0.4 mm thickness, using platinum ink and a screen printing technique [7]. Platinum foils are attached at each of the ends of the connections on one sheet of alumina, and a second sheet of alumina is then placed on top of it. The sandwich is then hot-pressed at 180°C for 20 min at 35 MPa in order to guarantee the best contact between the substrate and platinum wire. After pressing, the whole assembly is placed in a programmable high-temperature furnace and baked with an appropriate temperature program up to 1600°C. This process yields a rectangular, rigid sensor 85 mm long, 50 mm wide, and approximately 650 μm thick. Finally, two nickel wires attached at each side of the sensor are employed for sensing the level of the molten metal when the sensor is immersed in it. The high temperature environment for the measurements is provided by a commercial furnace (Thermal Technology 1000–3560-FP20) specifically modified for this task [8]. The temperature measurement of the melt is performed using a thermocouple type K in a stainless steel sheath, with an uncertainty of ± 0.1 K. The thermocouple is immersed in the melt at the time of measurement and the temperature is measured at three different positions

within the melt (bottom, middle and surface), assuring that the temperature gradient is kept much lower than 0.1 K [5].

The resistance change of the central section of the wire is recorded by an automatic bridge configuration and converted to a temperature rise by an independent calibration of the temperature-resistance characteristics of the wire [5].

The theoretical analysis of the experiment [5] employs the solution of the non-steady-state heat transfer equation in (a) the wire, (b) the alumina substrate, and (c) the melt. At the two interfaces, an interfacial heat transfer resistance is allowed. To solve these equations for the actual geometry of the sensor, a two-dimensional finite-element program has been employed. The thermal conductivity of the molten metal has been derived from a comparison of the measured and simulated temporal temperature rises of the platinum wire. For further details, the reader is referred to our previous paper [5] which fully describes this procedure.

In this paper, we report results of measurements of the thermal conductivity of four molten metals over a range of temperature from 300 to 750 K at atmospheric pressure. In all analyses the interfacial heat transfer resistance described briefly above, and in detail elsewhere [5], has been applied. The thickness and properties of the interface between the alumina and the platinum wire would be expected to be essentially independent of the fluid studied and dependent only on the temperature of the system. This turned out to be the case to a very high degree and was accounted for entirely by the effect of temperature on the properties of the materials. For the interface between the alumina and melt, the characteristics were still mainly governed by the properties of the different materials at the different temperatures although small adjustments to the characteristics of the interface were needed over the complete range of conditions [8].

The measurements of the four different materials and their results are presented separately in what follows, because each material has different physical and chemical properties and, therefore, different problems, which have to be considered and discussed separately. However, the elements of the experimental procedure are common and they are described below.

2.1. General Experimental Procedure

As described elsewhere [5], the sensor is placed in a crucible filled with the molten metal inside the oven. For metals that are in the liquid phase at room temperature, the filling of the crucible is straightforward; for the other metals the particular procedure employed is described later for each metal. Once the crucible is filled and the material is molten, it is placed in the furnace and raised with the aid of a stepper motor

drive until the melt entirely covers the working part of the sensor. The furnace is set to the desired temperature and brought to equilibrium over a period of 24h while monitoring the temperature in the melt. A flow of argon (99.999% pure) is maintained through the furnace at all times and a cold trap at the gas exhaust in the bottom cap of the furnace using liquid nitrogen condenses the metal vapor as soon as it leaves the furnace and before it enters the fume extract system. Once the melt has reached a steady temperature, a transient heating measurement is conducted, and it is repeated three times for each experimental temperature before the furnace is moved to a new set point. In general, measurements were made with increasing set temperatures but were repeated while decreasing the temperature to ensure there had been no degradation of the sensor. In order to assist with an estimate of the precision of each measurement, a sensitivity analysis was carried out. This was combined with other known effects to allow an evaluation of the uncertainty of the results for each material.

3. MEASUREMENTS

3.1. Mercury

The mercury used for the measurements was 99.9994 % pure, supplied by Alfa. The measurements were carried out in the range of temperature from ambient up to 520 K. Since mercury is liquid at room temperature, the filling of the crucible to the required level to surround the working elements of the sensor was straightforward. Because mercury is a highly toxic material with a very high vapor pressure, it was necessary, as a safety measure, to employ at all temperatures a cold trap at the gas exhaust of the furnace. Indeed, in the present configuration, the toxic nature of mercury and its high vapor pressure (2.23×10^{-3} mm Hg at 300 K) limited the temperature range that could be studied. For analysis of the experiment, the density and isobaric heat capacity of mercury were obtained from the literature [9–15]. Figure 2 shows an example of the comparison between the measured and simulated temperature rise data for a measurement at 407.7 K. The deviation of the experimental temperature rise from that predicted is seldom more than 0.1% because the total temperature rise of the wire during a run is about 5 K. The sensitivity to the thermal conductivity is illustrated in Fig. 3 where the fluid thermal conductivity has been changed by $\pm$ 1%; the effect of this small alteration is clearly discernible. The optimum fit between experiment and simulations was provided by using a thermal conductivity of 10.8 $W \cdot m^{-1} \cdot K^{-1}$ for mercury at 407.7 K. The same analysis was performed for all the measurements

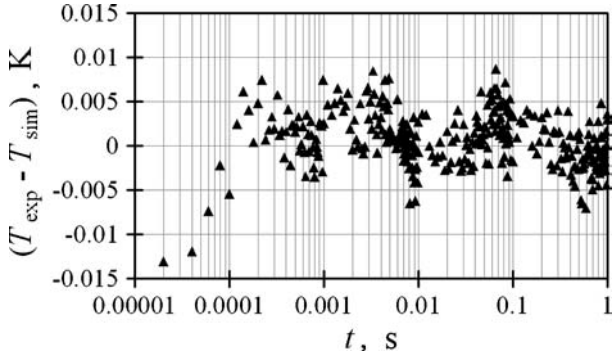

Fig. 2. Comparison between measured and simulated temperature rise data for mercury at 407.7 K.

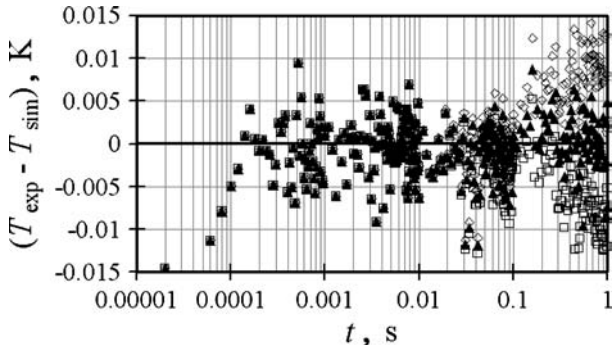

Fig. 3. Sensitivity to the thermal conductivity of mercury at 407.7 K, (▲)$\lambda_{Hg} = 10.8$ W · m^{-1} · K^{-1}; (□) $\lambda_{Hg} = 10.692(-1\%)$ W · m^{-1} · K^{-1}; (◇)$\lambda_{Hg} = 10.908(+1\%)$ W · m^{-1} · K^{-1}

made at the different temperatures, and the results for the thermal conductivity of mercury are shown in Table I.

To permit a comparison of the present data with those produced in other studies, the results for the thermal conductivity of mercury, λ_{Hg} (W · m^{-1} · K^{-1}), shown in Table I, were fitted to the equation,

$$\lambda_{Hg} = -0.4682 + 8.92909\,(T/273.15) - 0.92908\,(T/273.15)^2 \qquad (1)$$

The maximum deviation of the current data from this fit is 1.8%, while the standard deviation of the fit is 0.45% (at the 95% confidence level).

The correlation of the present results is compared with the results reported by other authors in Fig. 4. It is possible to discern the good agreement with the results of Hall [16, 17] with differences between

Table I. Thermal Conductivity of Liquid Mercury, λ_{Hg}, and Liquid Gallium, λ_{Ga}, as a Function of Temperature, T.

T (K)	λ_{Hg} ($W \cdot m^{-1} \cdot K^{-1}$)	T (K)	λ_{Ga} ($W \cdot m^{-1} \cdot K^{-1}$)
295.6	8.05	321.3	29.3
312.2	8.50	367.7	33.5
319.5	8.80	416.3	37.0
332.0	9.05	465.6	41.1
352.0	9.50	520.4	45.0
370.7	9.90	565.0	47.7
390.0	10.20	614.3	50.9
407.7	10.80		
425.9	11.20		
476.6	12.40		
515.2	13.00		

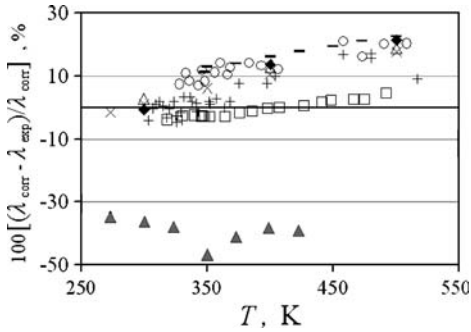

Fig. 4. Comparison of the results of earlier measurements of the thermal conductivity of liquid mercury with the correlation of the present work: (□) Hall [16, 17]; (+) Powell and Tye [18], (×) Prabhuram Saksena [20], (◯) Vel'tishcheva et al. [21], (—) Duggin [22], (△) PTB [19], (♦) Vukalovich et al. [23], (▲) Gehlhof and Neumeier [24].

± 5%. Similar differences are observed for temperatures up to 350 K for the data reported by Powell and Tye [18] and for the recommended values by PTB [19], as well as for the data reported by Prabhuram Saksena [20]. The differences from the current data for the work of these three groups increase for temperatures from 350 to 400 K rising to 15% and then increasing to 20% from 400 to 500 K. The differences from the data reported by Vel'tishcheva et al. [21], Duggin [22], and Vukalovich et al. [23] are within 5 to 15% for temperatures from 330 to 400 and up to

about 20% for temperature from 450 to 500 K. There is a large difference between the results here and those reported by Gelhoff and Neumeier [24] and those of the remainder of the previous studies; discrepancies increase to as much as 60% at about 430 K

3.2. Gallium

The gallium used for the measurements was supplied by Mining and Chemical Products Ltd. (MCP) with a minimum purity of 99.99%. The metal was supplied in plastic bottles, and it was melted in the bottles before filling the crucible. For the analysis, known values for the density and isobaric heat capacity of gallium were taken from the literature [9, 25–29]. Figure 5 shows a plot of the deviations between measured and simulated temperature rises for 614.3 K; this figure also demonstrates that the deviation is seldom larger than 0.1% given that the total temperature rise is about 5 K.

Figure 6 serves as an example to demonstrate the sensitivity to the thermal conductivity of gallium for a measurement at 367.7 K where simulations were performed varying the thermal conductivity with values 1% greater and smaller than the optimal value. Here it is clearly illustrated that the sensitivity to this small amount is generally the same as for mercury despite the fact that the thermal conductivity is four times larger. From this analysis it is possible to ascertain that the thermal conductivity of gallium at 367.7 K is 33.5 $W \cdot m^{-1} \cdot K^{-1}$. The same analysis was made for all the measured temperatures, and the results obtained are listed in Table I.

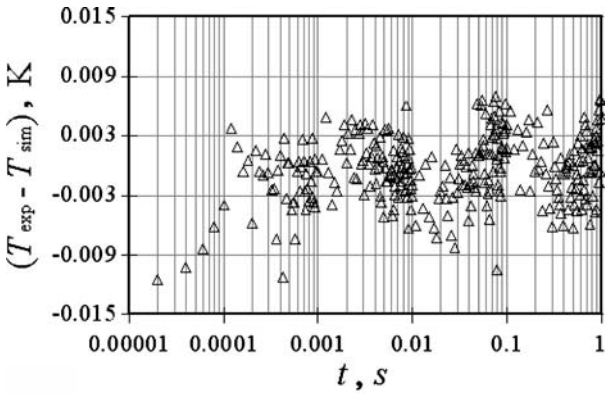

Fig. 5. Comparison between measured and simulated temperature rise data for liquid gallium at 614.3 K.

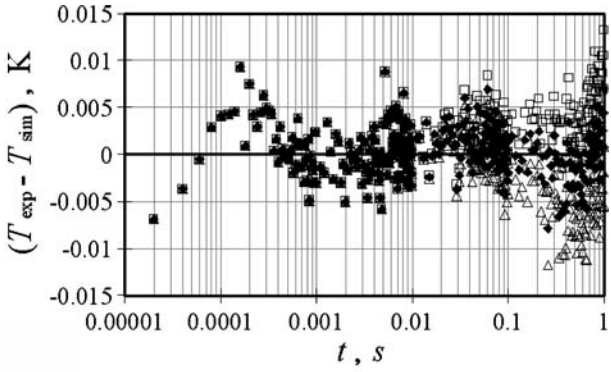

Fig. 6. Sensitivity to the thermal conductivity of liquid gallium at 367.7 K, (▲)$\lambda_{Ga} = 33.5\ W \cdot m^{-1} \cdot K^{-1}$; (□) $\lambda_{Ga} = 33.8(+1\%)$ $W \cdot m^{-1} \cdot K^{-1}$, (Δ)$\lambda_{Ga} = 33.1(-1\%)\ W \cdot m^{-1} \cdot K^{-1}$.

To permit comparisons with other studies, the results for the thermal conductivity of gallium, $\lambda_{Ga}(W \cdot m^{-1} \cdot K^{-1})$, shown in Table I, were fitted to the equation,

$$\lambda_{Ga} = -4.30691 + 33.11917\,(T/273.15) - 3.82542\,(T/273.15)^2 \qquad (2)$$

The maximum deviation of the present data from the correlation was one of 0.8%, while the standard deviation of the fit is 0.27% (at the 95% confidence level).

This correlation is compared in Fig. 7 with the results of earlier measurements found in the literature. The results obtained in this work are in good agreement with the results from the most recently reported measurements. The new measurements support the work of Magomedov [30] and Bush et al. [31] with deviations of ± 5%. Similar deviations are found for the data reported by Dutchak and Panasyuk [32] from 300 to 400 K. The recommended values by Ho et al. [33] are within ± 10% of the reported data, while those reported by Duggin [34] differ from the present results by 10% at 350 K rising to 20% at 550 K. There are large differences from the results of Yurchak and Smirnov [35] and Pashaev [36] at temperatures of 600 K; the differences amounted to as much as 60% from the correlation given in this work.

3.3. Tin

The tin used for the measurements was supplied by MCP with a stated purity of 99.99%. The metal was supplied in the form of ingots, and they

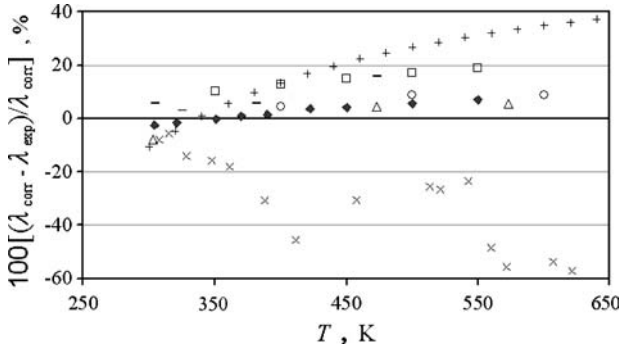

Fig. 7. Comparison of the correlation of the present thermal conductivity data for liquid gallium with the data from different authors, (Δ) Magmedov [30]; (♦) Bush et al. [31]; (—) Dutchak and Panasyuk [32]; (◯) Ho et al. [33]; (□) Duggin [34]; (+) Yurchak and Smirnov [35], (×) Pashaev [36].

were cut into small pieces to fill the crucible; once the crucible was filled it was placed in the furnace and the latter heated slowly to achieve melting. After melting, the crucible was moved up in the furnace using the levitation platform and the sensor dipped into the melt. At this stage the level of the melt was measured and, if found to be too low to cover the active region of the sensor, the crucible was then lowered and cooled. Once it was cooled, it was removed from the furnace and further small pieces of tin added. The procedure described above was again performed and the level of the melt measured again. Further, smaller additions of tin could, if necessary, then be added through the support tube of the sensor from the top of the furnace. Measurements were then carried out in a range of temperature from 530 to 730 K. In this case the measurements were stopped at 730 K because the molten tin started to react with the alumina of the sensor.

For the analysis we employed reported values of density and isobaric heat capacity of tin [9, 19, 37]. Figure 8 shows the comparison between measurement and simulation at the transient temperature of 603.2 K. It illustrates that the deviation seldom exceeds about 0.1% of the temperature rise which is comparable with the resolution of the measurements for mercury and gallium. A similar sensitivity analysis has again been carried out for this metal [8] but we omit details here.

To permit comparisons with other studies, the results for the thermal conductivity of tin, $\lambda_{Sn}(W \cdot m^{-1} \cdot K^{-1})$, shown in Table II, were fitted to the equation,

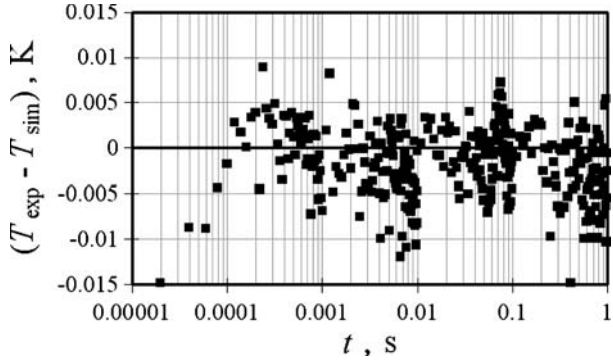

Fig. 8. Comparison between measured and simulated temperature rise data for liquid tin at 603.2 K.

Table II. Thermal Conductivity of Liquid Tin, λ_{Sn}, and Liquid Indium, λ_{In}, as a Function of Temperature, T.

T (K)	λ_{Sn} ($W \cdot m^{-1} \cdot K^{-1}$)	T (K)	λ_{In} ($W \cdot m^{-1} \cdot K^{-1}$)
534.3	30.7	453.0	34.0
571.2	32.0	491.5	38.0
603.2	33.0	521.9	39.0
630.0	33.5	554.2	40.5
678.2	34.3	587.1	42.3
703.0	34.5	617.1	43.5
730.2	35.0	660.9	45.0
		700.4	46.5
		743.6	47.5

$$\lambda_{Sn} = -10.20393 + 32.06273\,(T/273.15) - 5.68583\,(T/273.15)^2 \qquad (3)$$

The maximum deviation is 0.5%, while the standard deviation of the fit is 0.22% (at the 95% confidence level).

Figure 9 compares the present correlation with the data of earlier studies. Here, good agreement with the recommended values by Ho et al. [33] can be seen with differences within ± 3%. The deviations from the results of other studies [36, 38] are usually within ± 10 %.

3.4. Indium

The indium used for the measurements was supplied by Lowden Metals Ltd. (LM) with a stated purity of 99.99%. As for tin, indium was

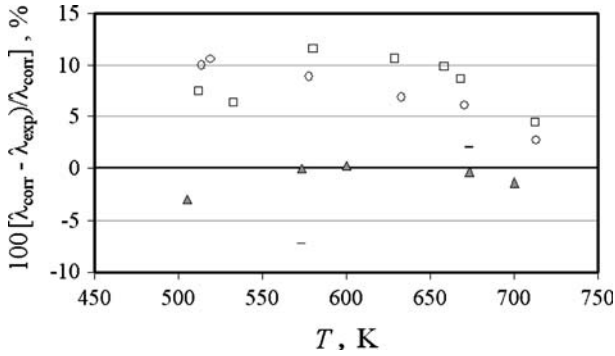

Fig. 9. Comparison of the correlation of the present thermal conductivity data for tin with the data from other authors, (▲) Ho et al. [33]; (□), (◯) Hemminger [38]; (—) Pashaev [36].

supplied in the form of ingots, and thus it was also cut into small pieces in order to fill the crucible. The procedure for filling and for measurements as was adopted for tin, was followed for indium; the measurements were carried out in the range of temperature from 450 to 750 K.

For the analysis we have employed reported values of density and isobaric heat capacity of indium [39–41]. Figure 10 shows a comparison between measured and simulated temperature rises of the wire for an experiment at 521.9 K; the chart illustrates that the maximum scatter is ± 0.1%, taking in account that the total temperature rise in the measurement was about 5 K.

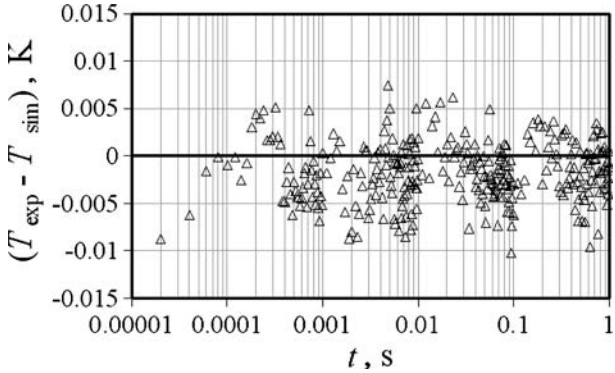

Fig. 10. Comparison between measured and simulated temperature rise data for liquid indium at 521.9 K.

Table II shows the results of measurements of the thermal conductivity of indium. As for the other metals, in order to permit a comparison with earlier work, the present results were represented by the equation,

$$\lambda_{\mathrm{In}} = -1.80546 + 29.11637\,(T/273.15) - 4.03036\,(T/273.15)^2 \qquad (4)$$

The maximum deviation is 2%, while the standard deviation of the fit is 0.60% (at the 95% confidence level).

Figure 11 illustrates comparisons of the correlation of these results with data reported in the literature by other authors. Here we can discern that the present work support the data reported by Goldratt and Greenfield [43] with deviations within ± 5%. Similar deviations are observed for the recommended values by Ho et al. [33] and Yurchak and Smirnov [35]. Larger deviations are found from the data reported by Duggin [42] and the recommended values given by Touloukian et al. [44], where the deviations are about ± 5% at 500 K rising to 15% at 700 K.

4. DISCUSSION

In the present work, a new technique has been developed for measurement of the thermal conductivity of molten metals with a claimed uncertainty of ± 2%. The accuracy of the present results makes it of interest to compare the measurements of the thermal conductivity of the four molten metals presented here with the Wiedemann and Franz (W-F) law. Although this law was derived as early as the second half of the 19th century, it is often used today for estimation of the thermal conductivity of

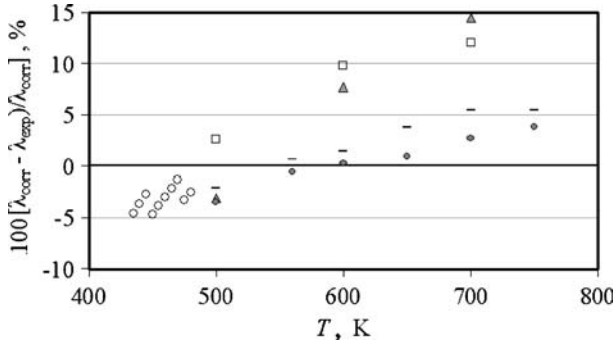

Fig. 11. Comparison of the results of earlier measurements of liquid indium with the correlation of the present work, (•) Ho et al. [33]; (—) Yurchak and Smirnov [35]; (▲) Duggin [42]; (◯) Goldratt and Greenfield [43]; (□) Touloukian et al. [44].

metals (liquid and solid) in the absence of experimental data. It must be stressed that the W-F law is based upon a simple approximate theory even for perfect crystals of solid metals. Its application to the molten state metals is therefore distinctly unsound but represents still the only available theoretical approach.

According to the Wiedemann–Franz relationship [46], the thermal conductivity of a perfect crystal of a metal, λ_e, is proportional to its electrical conductivity σ, via the relation,

$$\frac{\lambda_e}{\sigma} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T = L_0 T. \tag{5}$$

In the above relation, k_B is Boltzman's constant, e is the electron charge, T is the absolute temperature, and the constant of proportionality, L_0, is known as the Lorenz number, given as

$$L_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.445 \times 10^{-8}\ \mathrm{V}^{-2} \cdot \mathrm{K}^{-2} \tag{6}$$

The relationship, Eq.(6), even for pure crystalline metals, relies upon several unproven and quite significant assumptions [46]; its application to the liquid state is even more questionable. It is therefore not surprising that recent studies in solid and molten metals [42,47–48] have led to considerable doubts as to the validity of the theory. In the solid state [49, 50] the electronic contribution to the thermal conductivity of metals ranges from 90 to 99% of the total thermal conductivity. Thus, in these cases, departures from the W-F law have been attributed almost exclusively to the phonon (lattice vibrations) contribution. This implies that the phonon contribution to the thermal conductivity of a metallic solid cannot be neglected if it is desired to have an accurate approximation for the total thermal conductivity. For the case of the liquid state, the ions are no longer constrained to fixed lattice positions about which they vibrate so that the notion of the phonon contribution to the thermal conductivity is inappropriate. Instead, the ions will move in a more random fashion and then, as is the case for non-ionized liquids, the contribution to the total thermal conductivity has no theoretical basis. Specifically, for the case of molten metals, this matter has received no attention whatsoever.

The discussion above makes it clear that no matter what its limitations, the only available theory for the thermal conductivity of molten metals resides within the W-F law. Thus, we use the present results for the thermal conductivity of several molten metals to examine how well this simple relationship performs. To do this, we use the reported values of the electrical resistivity, ρ_e, for mercury [51–53], gallium [50, 51, 53, 54], tin

[50, 52, 54], and indium [50, 52] and evaluate a parameter L_T from the relationship,

$$L_T = \frac{\lambda \rho_e}{T} \tag{7}$$

If the W-F law was valid and there were no contributions to the total thermal conductivity except the electronic one, this would yield the Lorenz number, L_0. The results obtained are shown in Fig. 12 where the thick line represents the theoretical Lorenz number. It is important to note that here we are using the total thermal conductivity instead of only the electronic contribution so that the calculated L_T could be expected to be higher than the value of L_0 obtained using only the electronic contribution.

Figure 13 shows the deviations of L_T from L_0, for the four different metals. It can be seen in Fig. 12 that the measured L_T number for mercury increases as a function of temperature, and from Fig. 13 that the deviations from L_0 are about 9% at room temperature, increasing to 15% at 500 K. For gallium, the temperature dependence is similar to that for mercury, where the L_T number increases as a function of temperature but, in this case, the deviations from L_0 are much smaller than for mercury, being about -2% at room temperature increasing to 8% at 620 K. For gallium a different temperature dependence has been observed by other investigators, for example, Duggin [42] found that L_T is almost constant in the range of temperature from 350 to 600 K but the deviations from L_0 are about -16%. Yurchak and Smirnov [47] show a value of L_T for gallium that decreases as temperature increases, the deviations from L_0 being about $+8\%$ at 350 K dropping to -20% at 700 K.

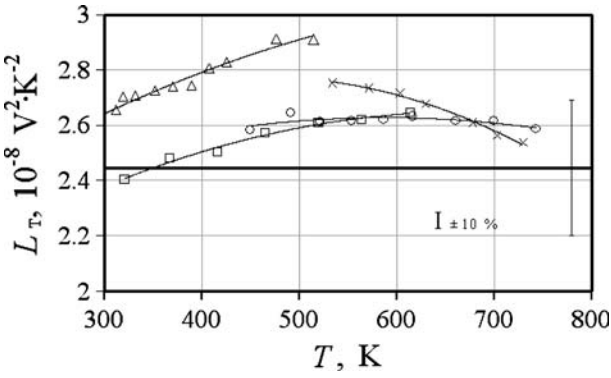

Fig. 12. Dependence of the measured L_T, with temperature for (△) mercury, (□) gallium, (◯) indium, and (×) tin.

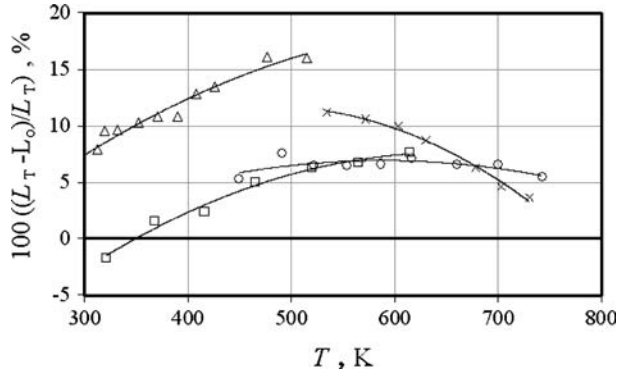

Fig. 13. Deviation of the measured L_T, from L_0 for (△) mercury, (□) gallium, (○) indium, and (×) tin.

The cases of indium and tin are different in the sense that the dependence on the temperature is different to that observed for mercury and gallium. For indium, the L_T number is broadly constant as a function of temperature, whereas for tin it tends to decrease as temperature increases. The behavior observed here for indium is very similar to that observed in the measurements of Goldratt and Greenfield [56], but here the deviations from L_0 are about 5 to 6% while the earlier authors found deviations of 9%. However, the results reported by Yurchak and Smirnov [47] and Duggin [42] show a tendency of L_T to decrease as temperature increases. For the case of tin, the tendency of L_T to decrease as temperature increases has also been observed by Brown [45] and Filippov [45].

It is believed that the present measurements of the thermal conductivity of molten metals enjoy a higher level of confidence than those of earlier measurements on the basis of the study reported here. Thus, the deviations of the value of L_T from the Lorenz value, L_0, are large enough to be significant. This results is not surprising perhaps given the simplistic origin of the theory, but does demonstrate the need for improvement.

5. CONCLUSIONS

The thermal conductivity of mercury, gallium, tin, and indium have been measured over a wide range of temperature. It has been demonstrated that the practical behavior of measurements performed in a transient hot-wire instrument conformed to a theoretical model. This result supports the idea that the experiment is free from systematic errors caused by an inadequacy in the theory. An assessment of the random errors of measurement suggests that the absolute uncertainty of the results for

the thermal conductivity of the molten metals is approximately $\pm 2\%$; an uncertainty which is superior to that enjoyed by earlier techniques. It is thus believed that the experimental data reported in this work represent the most accurate values of the thermal conductivity of molten metals reported to date.

The highly accurate thermal conductivity measurements presented here confirm that there is no existing theory for this property of a molten metal that can explain within experimental uncertainty what is observed. Only if a very crude estimate ($\pm$ 20%) of the thermal conductivity of a molten metal is required should the W-F law be employed. Furthermore, the relationship of the thermal conductivity to the electrical conductivity is worthy of further investigation.

REFERENCES

1. R. Tufeu, J. P. Petitet, L. Denielou, and B. Le Neindre, *Int. J. Thermophys.* **6**:315 (1985).
2. Y. Nagasaka and A. Nagashima, *Int. J. Thermophys.* **12**:769 (1991).
3. N. Nagazawa, Y. Nagasaka, and A. Nagashima, *Int. J. Thermophys.* **13**:753 (1992).
4. E. P. Sakonidou, M. J. Assael, C. A. Nieto de Castro, H. R. van den Berg, and W. A. Wakeham, *Thermal Conductivity* **24**:516 (1999).
5. M. V. Peralta-Martinez, M. J. Assael, M. Dix, L. Karagiannidis, and W. A. Wakeham, *submitted to Int. J. Thermophys.*
6. M. J. Assael, C. A. Nieto de Castro, H. M.Roder, and W. A. Wakeham, "Transient Methods for Thermal Conductivity," in *Experimental Thermodynamics, Vol. III, Measurement of the Transport Properties of Fluids*, A. Nagashima, J. V. Sengers, and W. A. Wakeham, eds. (Blackwell Scientific Pubs., London, 1991), Chap. 7, pp.161–195.
7. M. Dix, I. W. Drummond, M. Lesemann, M. V. Peralta-Martinez, W. A., Wakeham, M. J. Assael, L. Karagiannidis, and H. R. van den Berg, *Proc. 5th Asian Thermophysical Properties Conference*, Seoul, Korea (1998), p.113.
8. M. V. Peralta-Martinez, *Ph.D. Thesis* (University of London, 2000).
9. *Handbook of Chemistry and Physics*, 76th Ed. (CRC Press, Boca Raton, Florida, 1995–1996).
10. F. Simon, *Ann. Physik.* **68**:241 (1992).
11. A. L. Dixon and W. A. Rodebusch, *J. Am. Chem. Soc.* **49**:11162 (1927).
12. L. G. Carpenter and L. G. Stoodley, *Philos. Mag.* **10**:249 (1930).
13. T. B. Douglas, A. F. Ball, and D. C. Ginnings, *J. Res. Nat. Bur. Stand.* **46**:334 (1951).
14. R. H. Busey and W. F. Giauque, *J. Am. Chem. Soc.* **75**:806 (1753).
15. E. B. Amitin, E. G. Ledeva, and I. E. Paukov, *Russ. J. Phys. Chem.* **53**:1528 (1979).
16. W. C. Hall, *Phys. Rev.* **2**:1004 (1938).
17. W. C. Hall, *Ph.D. Thesis* (University of Kansas, Lawrence, Kansas, 1936).
18. R. W. Powell and R. P. Tye, *Intern. Devel. Heat Transf. ASME* **103**:856 (1961).
19. *Report on Mercury*, Physikalisch-Technische Bundesanstalt (PTB), ISSN 0942–7821, Braunschweig and Berlin (1995).
20. M. P. Prabhuram Saksena, *Ind. Eng. Chem. Fundam.* **21**:484 (1982).
21. V. A. Vel'tishcheva, N. A. Kalakutskaya, and N. A. Nikol'skii, *Teploenergetika* **5**:80 (1958).

22. M. J. Duggin, *Phys. Lett. A* **27**:257 (1968).
23. M. P. Vukalovich, A. I. Ivanov, L. R. Fokin, and A. T. Yakovlev, *Thermophysicial Properties of Mercury* (State Committee for Standards at the Board of Minister of the Soviet Union, Publisher for Standards, Moscow, 1971), Monograph No. 9, pp. 203.
24. G. Gehlhoff and F. Neumeier, *Verhandl. Deut. Physik. Ges.* **21**:201 (1919).
25. E. Boitard, J. P. Bross, and M. Laffite, *J. Chim. Phys.-Chim. Biol*. **66**:166 (1969).
26. Y. Takahashi, H. Kadokura, and H. Yokokawa, *J. Chem. Thermodyn.* **15**:65 (1983).
27. H. S. Chen and D. Turnbull, *Acta Metall*. **6**:369 (1968).
28. G. B. Adams Jr., H. L. Johnston, and E. C.Kerr, *J. Am. Chem. Soc*. **74**:4784 (1952).
29. E. B. Amitin, Yu. F. Mimekov, O. A. Nabutovkaya, I. E. Paukov, and S. I. Sokolova, *J. Chem. Thermodyn.* **16**:431 (1984).
30. A. M. Magmedov, *Tezisy Nauchn. Soobn Vses Konf. Str. Suoistvan Met. Shlak Rasp*. **3**:21 (1978).
31. G. Bush, H. J. Guntherodt, and P. Wyssmann, *Physica Letter A* **41**:49 (1972).
32. Ya I. Dutchak and P. V. Panasyuk, *Soviet Phys.-Solid State* **8**:2244 (1967).
33. C. Y. Ho, R. W. Powell, and P. E. Liley, *J. Phys. Chem. Ref. Data* **1**:279 (1972).
34. M. J. Duggin, *Phys. Lett. A* **29**:470 (1969).
35. R. P. Yurchak and B. P. Smirnov, *Soviet Phys.-Solid State* **10**:1065 (1968).
36. B. P. Pashaev, *Soviet Phys.-Solid State* **3**:303 (1961).
37. S. N. Banchila and L. P. Filippov, *High Temperatures* **11**:602 (1973).
38. W. Hemminger, *High Temp. High Press.* **17**:465 (1985).
39. O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry*, 5th Ed. (Pregamin Press, Oxford, 1979).
40. A. I. Kaznoff, R. L. Orr, and R. Hultgren, U. S. Dept. Comm., Office Tech. Serv., 1, (1961).
41. F. Gronvold, *J. Thermal Anal*. **13**:419 (1978).
42. M. J. Duggin, *J. Phys. F. Metal Phys.* **2**:433 (1972).
43. E. Goldratt and A. Greenfield, *J. Phys. F. Metal Phys.* **10**:195 (1980).
44. Y. S. Touloukian, R. W. Powell, C. Y. Ho, and P. G. Klemens, *Thermophysical Properties of Matter*, Vol. 1, *Thermal Conductivity of Metallic Elements and Alloys* (IFI/Plenum, New York, 1970).
45. N. W. Ashcroft and N. D. Mermin, Solid State Physics (Saunders College Publishing, Philadelphia, Pennsylvania, 1976).
46. G. Wiedemann and R. Franz, *Ann. Phys.* 2 **89**:497 (1853).
47. R. P. Yurchak and B. P. Smirnov, *High Temp.* **7**:163 (1969).
48. R. W. Powell, M. J. Woodman, and R. P. Tye, *Philos. Mag*. **7**:1183 (1962).
49. P. G. Klemens and R. K. Williams, *Int. Met. Rev*. **31**:197 (1986).
50. P. G. Klemens, *Thermal Conductivity* **20**:63 (1988).
51. R. W. Powell and R. P. Tye, *ASME* **103**:856 (1961).
52. G. V. Samsonov, ed., *Handbook of the Physicochemical Properties of the Elements* (Plenum Press, New York, 1968).
53. G. T. Dyos and T. Farrell, eds., *Electrical Resistivity Handbook, IEEE Materials and Devices Series* (Institution of Electrical Engineers, London, 1992).
54. G. Ginter, J. G. Gasser, and R. Kleim, *Philos. Mag. B* **54**:534 (1986).
55. V. E. Zinovyev, *High Temperature Transport Properties of Metals* (Publ. Metallurgiya, Moscow, 1984).
56. E. Goldratt and A. J. Greenfield, *J. Phys. F. Metal Phys.* **10**:L95 (1980).