

## **Deviation from Wiedemann–Franz Law for the Thermal Conductivity of Liquid Tin and Lead at Elevated Temperature<sup>1</sup>**

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The thermal conductivities of tin and lead in solid and liquid states have been determined using a nonstationary hot wire method. Measurements on tin and lead were carried out over temperature ranges of 293 to 1473 K and 293 to 1373 K, respectively. The thermal conductivity of solid tin is  $63.9 \pm 1.3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 293 K and decreases with an increase in temperature, with a value of  $56.6 \pm 0.9 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 473 K. For solid lead, the thermal conductivity is  $36.1 \pm 0.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 293 K, decreases with an increase in temperature, and has a value of  $29.1 \pm 1.1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 573 K. The temperature dependences for solid tin and lead are in good agreement with those estimated from the Wiedemann–Franz law using electrical conductivity values. The thermal conductivities of liquid tin displayed a value of  $25.7 \pm 1.0 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 573 K, and then increased, showing a maximum value of about  $30.1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 673 K. Subsequently, the thermal conductivities gradually decreased with increasing temperature and the thermal conductivity was  $10.1 \pm 1.0 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 1473 K. In the case of liquid lead, the same tendency, as was the case of tin, was observed. The thermal conductivities of liquid lead displayed a value of  $15.4 \pm 1.2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 673 K, with a maximum value of about  $15.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 773 K and a minimum value of about  $11.4 \pm 0.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 1373 K. The temperature dependence of thermal conductivity values in both liquids is discussed from the viewpoint of the Wiedemann–Franz law. The thermal conductivities for Group 14 elements at each temperature were compared.

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**KEY WORDS:** lead; liquid; thermal conductivity; tin; Wiedemann–Franz law.

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## 1. INTRODUCTION

From the viewpoint of materials, tin, lead, germanium, and silicon in Group 14 of the periodic table are some of the most important materials for the development of recent industries such as information technologies. Tin and lead are the matrix materials for solders, and germanium and silicon are those for many solid-state devices. The mathematical modeling of heat flow in high temperature processes, at the design stage, has led to improvements in process control, product quality, conservation of energy and natural resources, and prediction of the physical properties of the products. In the on-going development of these models, one of the primary requirements at the moment is for accurate values for the thermal conductivities of the materials in the liquid state. The paucity of reliable thermal conductivity data for commercial materials involved in these processes is a reflection of the difficulties in measuring accurate values for molten metals, especially at high temperatures.

It would be also interesting to compare thermal conductivities of Group 14 elements in the liquid state from the viewpoint of the construction of the theory of liquid-state physics. For example, the applicability of the Wiedemann–Franz law in the liquid state has been discussed for a long time. To clarify the situation, the data described above are expected to be fundamental. However, there have been few thermal conductivity data reported for the thermal conductivities for liquid tin, lead, germanium, and silicon. Furthermore, if they did exist, these reported data at high temperature are not accurate enough to discuss the heat transfer mechanisms thoroughly.

Table I shows the sources of published data for liquid tin and lead [1–10]. In the table, P, C, L, and N represent the periodic heat flow method, the comparative method, the longitudinal heat-flow method, and the nonstationary hot wire method, respectively. It can be found from the table that almost all of the data were determined using steady-state methods. However, it has been known that in steady-state methods convection has a significant effect on thermal conductivities of liquids even at room temperature, leading to an overestimation of thermal conductivity values. The effect of convection is much more serious at higher temperatures since accurate temperature control becomes progressively more difficult with increasing temperature. Yurchak and Filippov [3] and Filippov [4] have used the periodic heat flow method which is one of the nonsteady-state methods that gives thermal diffusivity values. However, precise measurements of the heat capacity and density are difficult for molten metals at high temperatures, although these data are required to determine the thermal conductivity. Nakamura et al. [7] measured the thermal conductivity of molten lead as a test liquid for measurements of InSb and GaSb

Table I. Published Data for Liquid Lead and Tin

Pb			
First Author	Method <sup>a</sup>	Temperature (K)	Reference
Berman	L	387–874	[1]
Powell	C	623–873	[2]
Yurchak	P	850–1250	[3]
Filippov	P	560–1355	[4]
Dutchak	C	474–870	[5]
Duggin	L	600–900	[6]
Nakamura	N	600–1000	[7]
Sn			
First Author	Method <sup>a</sup>	Temperature (K)	Reference
Brown	L	323–620	[8]
Nikolskii	L	570–833	[9]
Pashaev	L	337–610	[10]
Filippov	P	870–1230	[11]
Yurchak	P	465–1365	[3]

<sup>a</sup> P, periodic heat-flow method; C, comparative method; L, longitudinal heat-flow method; N, nonstationary hot wire method.

using the nonstationary hot wire method with an alumina-coated probe formed on an alumina substrate. In this study, a platinum layer was deposited as the heating element on the alumina substrate and then the heating element was coated with alumina. Accordingly, an accurate value for the thermal conductivity of alumina is required in order to determine values for lead, but there is no description of this.

The authors [11] have also previously developed the nonstationary hot wire method to measure thermal conductivities of molten metals, where mercury and lead were used as test liquids. Following this, the thermal conductivities of liquid silicon and germanium were successfully measured [12]. In these measurements, the reliability of the results was confirmed in detail. Consequently, the aim of this study is to measure the thermal conductivities of liquid tin and lead at higher temperatures using the developed method and to discuss heat transfer mechanisms in liquid states.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Sample

Specimens of 99.9 mass% tin and lead were used. The major impurities for tin and lead were lead and antimony, and bismuth, respectively: these impurity concentrations were 0.002 mass% maximum.

### 2.2. Measurement

In the nonstationary hot wire method, electrical power is supplied to a thin metal wire (hot wire) placed in the sample, which serves as both a heating element and a temperature sensor, and the temperature rise ( $\Delta T$ ) of the hot wire is recorded continuously. The thermal conductivity of the sample ( $\lambda$ ) is obtained from Eq. (1) [13],

$$\Delta T = \frac{Q}{4\pi\lambda} (\ln t + A) \quad (1)$$

where  $Q$  is the heat generation rate per unit length of the wire,  $t$  is the time, and  $A$  is a constant, respectively. In practice, the thermal conductivity of the sample is determined using the slope of the linear portion of the relation between  $\Delta T$  and  $\ln t$  in Eq. (2),

$$\lambda = \frac{Q}{4\pi} \frac{d \Delta T}{d \ln t} \quad (2)$$

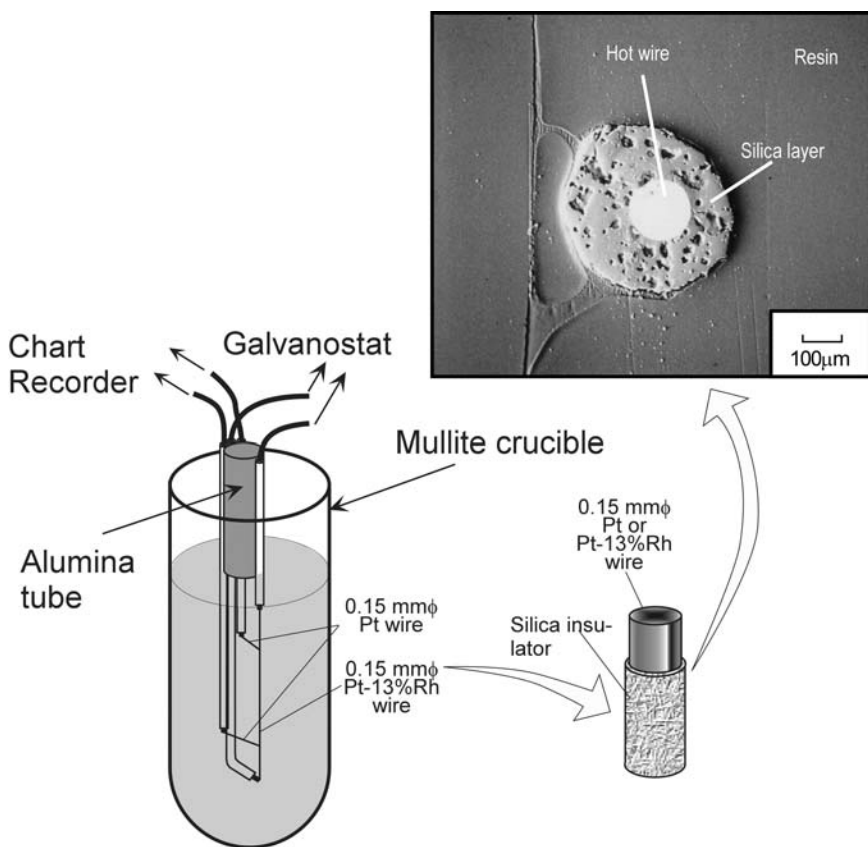
When measurements are carried out on electrically conducting specimens such as liquid metals, considerable difficulty can be encountered since there is electrical leakage to the sample from the hot wire. This problem, however, can be overcome by forming a silica insulation layer of less than 100  $\mu\text{m}$  in thickness on the wire [11].

Figure 1 shows a schematic diagram of the experimental apparatus for liquid tin and lead used in this study. The silica-coated probe used in this study consisted of a hot wire (0.15 mm diameter  $\times$  30 to 40 mm length) of platinum-13% rhodium, serving as a sensor wire as well, which is connected to 0.5 mm diameter lead wires of platinum. Potential leads (0.15 mm diameter) of platinum were attached at an interval of 20 to 25 mm to the sensor wire, to allow four-terminal resistance measurements of the sensor wire. The lead and potential wires were supported by mullite tubing. To form a silica layer on the wires, the probe was dipped into silica slurry (Toh-a Gousei Kagaku: Aron Ceramic CC) several times and then dried in

ambient atmosphere for 24 h to remove moisture, followed by sintering at 423 K for 2 h. The thickness of the silica layer ranged between 80 and 100  $\mu\text{m}$ . It has been confirmed in previous work [11] that silica films with these thicknesses give rise to no effects on the thermal conductivity values. The effect of the coating layer can be determined by modifying Eq. (1):

$$\Delta T = \frac{Q}{4\pi\lambda} \left[ \ln t + A + \frac{1}{t} (B \ln t + C) \right] \quad (3)$$

where  $A$ ,  $B$ , and  $C$  are constants that can be calculated from the thermal conductivity, thermal diffusivity, etc. of the hot wire, for the coating layer, and specimen, respectively. Comparison of Eqs. (1) and (3) indicates that



**Fig. 1.** Schematic diagram of experimental apparatus for thermal conductivity measurements on liquid metals.

the latter term in Eq. (3) represents the effect of the coating layer. For the case of liquid tin at 1473 K, the values of  $A$ ,  $B$ , and  $C$  are  $1.62 \times 10^2$ ,  $-1.83 \times 10^{-4}$ , and  $-1.13 \times 10^{-1}$ , respectively. For the case of liquid lead at 1373 K, the values of  $A$ ,  $B$ , and  $C$  are  $1.10 \times 10^2$ ,  $-5.02 \times 10^{-4}$ , and  $6.63 \times 10^{-2}$ , respectively. These calculations were computed using published physical property data [14, 15]. The physical property values for the silica coating layer at high temperature (1473 K) were assumed to be one tenth of those at room temperature which were supplied by the production company. Although this is a very extreme assumption, the latter term of Eq. (3) is small enough to be negligible. Consequently, the presence of the silica layer has no serious effect on the measurement and the thermal conductivity can be derived from Eq. (1).

The measurements were carried out in the following manner. The sample was held in a 34 mm inner diameter cylindrical mullite crucible and placed in a furnace having a SiC heating element. The temperature of the furnace was controlled within  $\pm 1$  K by means of a PID (proportional integral derivative) controller. To suppress convection, the surface temperature of the molten sample was kept at a temperature about 2 K higher than the bottom temperature. The probe was dipped vertically into the center of the liquid sample after melting, as shown in Fig. 1.

Generally, in experiments where a small current is supplied to the hot wire, the temperature rise of the hot wire is smaller. A smaller temperature rise may have advantages since it could result in less convection as well as a delay of its onset. However, when the temperature rise is too small, it is very difficult to measure it accurately and the effect of the heat capacity of the hot wire and silica layer cannot be ignored. On the other hand, the experiment using larger currents brings about convection at an earlier stage of the measurement. From the results of previous work [11, 12], it was found that a current of 3.0 A provides suitable conditions. Consequently, the same conditions have been employed in this study. The voltage change between the potential wires was monitored continuously using a chart recorder, and was converted to the resistance change of the hot wire based upon the principle of four-terminal resistance measurements. The temperature rise ( $\Delta T$ ) was calculated from the resistance change of the hot wire. On the other hand, the heat generation rate ( $Q$ ) per unit length of the hot wire was calculated from the current and the resistance per unit length of the hot wire at each temperature.

The measurements on tin and lead were started in the homogeneous liquid state at about 573 K and 673 K, respectively, using argon that was deoxidized by passing in phosphorous pentoxide and magnesium at 773 K. Measurements on tin and lead were made during the heating cycle at intervals of about 100 K until temperatures of 1473 and 1373 K were attained,

respectively, and were also made to room temperature during the cooling cycle to confirm the reproducibility of the measurements. Accordingly, measurements were made in both liquid and solid states. At least three different probes were used for each sample, and three runs were carried out at each temperature. After the measurements on both elements, no accretions between each sample and the mullite crucible were observed. This indicates that there was no reaction between the crucible and each of the samples.

### 3. RESULTS

In the thermal conductivity measurements by the hot wire method, it is very important that there is no electrical leakage from the hot wire to the sample. To confirm this, the resistance of the hot wire between the potential wires was measured and compared with that measured in air. Figure 2 shows the resistances of the hot wires with coating in the experiments on tin and lead, while the solid line represents the resistance of the hot wire with no coating, which was calculated from the values specified by the Japanese Industrial Standards Committee [16]. The closed and open triangles represent the values measured during the heating and cooling cycles, respectively, for tin. The closed and open squares represent values measured during the heating and cooling cycles, respectively, for lead. These results are in very good agreement with one another, which indicates that there was no electrical leakage from the hot wire to the melts.

Figures 3 and 4 show typical cross-sectional views of the hot wire after the measurements on tin and lead, respectively, along with X-ray mapping

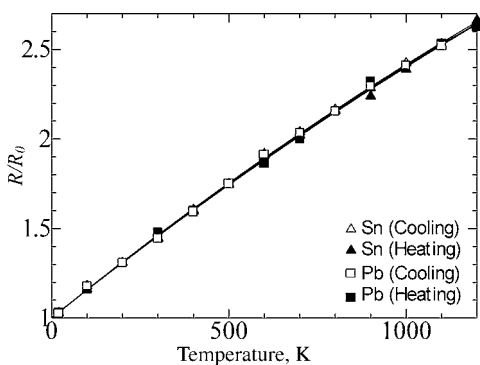


Fig. 2. Reduced electrical resistance ( $R/R_0$ ) of the hot wire at each temperature, where  $R$  and  $R_0$  indicate the electrical resistance at each temperature and  $0^\circ\text{C}$ , respectively.

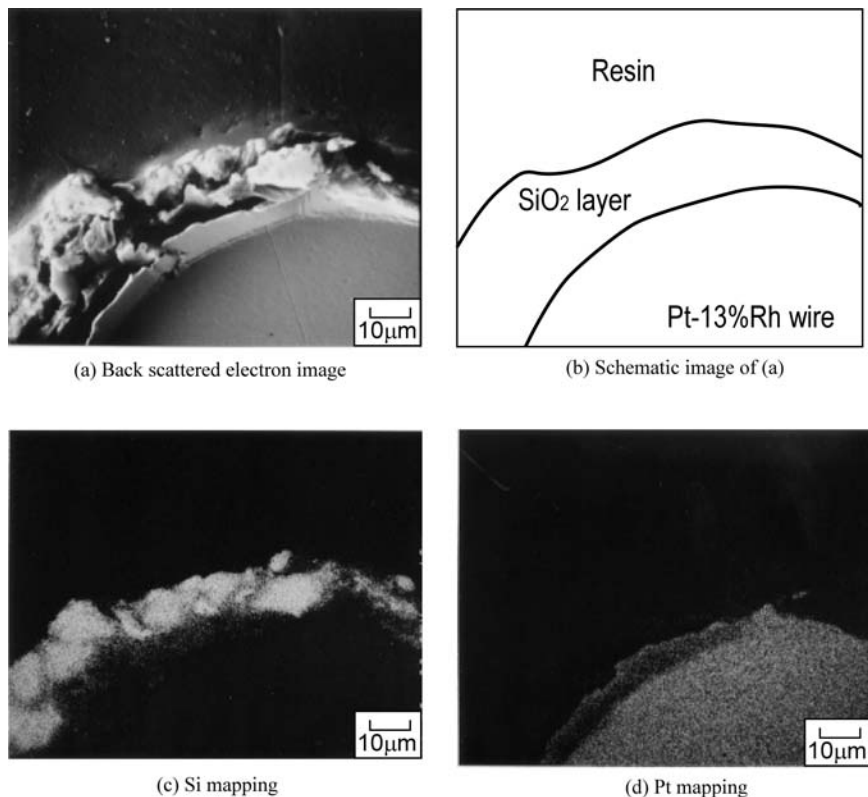


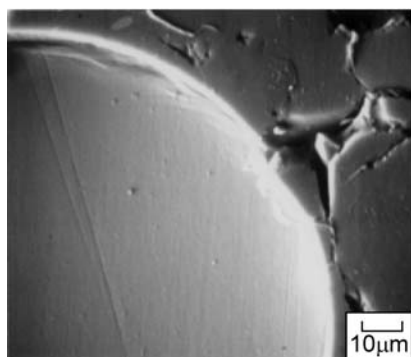
Fig. 3. Typical cross-sectional view of the hot wire after the experiment with tin along with X-ray mapping for Si and Pt.

for silicon and platinum. The cracks were formed during the polishing process. These figures revealed that the coating layer of silica did not react with the samples and that the sample was not oxidized.

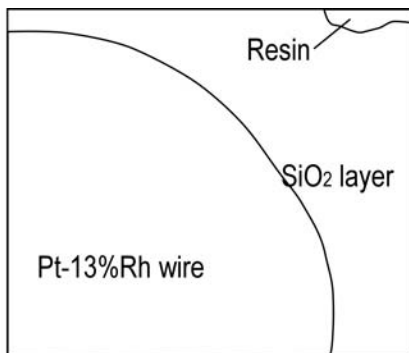
Figure 5 shows a typical temperature rise ( $\Delta T$ ) as a function of logarithm of time obtained during measurements on liquid tin at 1473 K. Similar curves were also observed in the case of liquid lead. It can be seen that there is a linear relation between  $\Delta T$  and  $\ln t$  for the time period, 0.7 to 2 s, and the temperature rise deviates from linearity in the time period above 2 s. This deviation is due to the onset of convection [11]. The thermal conductivity is calculated from the slope of only the linear portion using Eq. (2).

Table II gives a summary of average values, standard deviations, and scatter of thermal conductivity values for tin and lead in the solid and

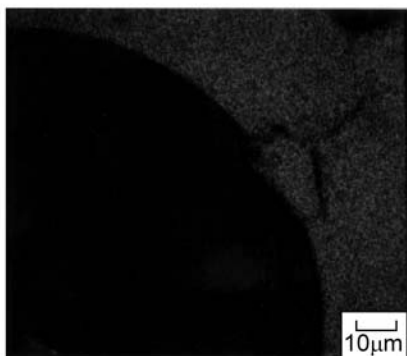




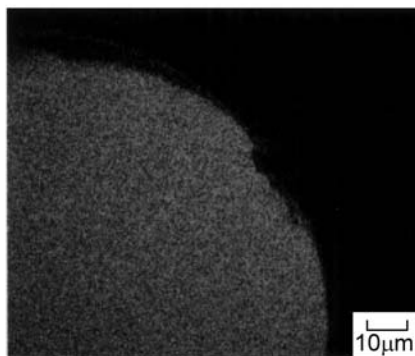
(a) Back scattered electron image



(b) Schematic image of (a)

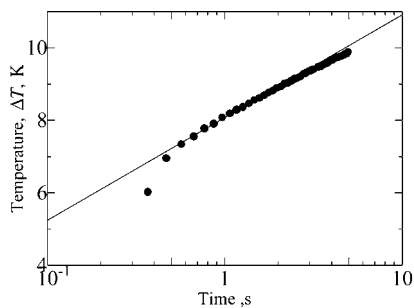


(c) Si mapping



(d) Pt mapping

**Fig. 4.** Typical cross-sectional view of the hot wire after the experiment with lead along with X-ray mapping for Si and Pt.



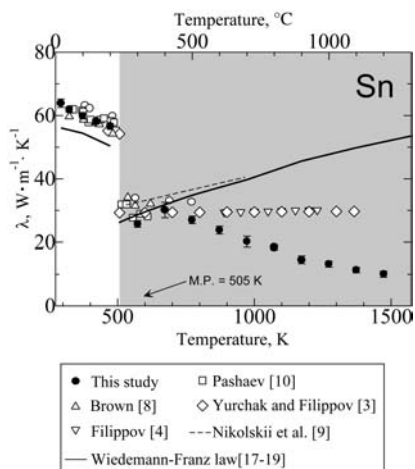
**Fig. 5.** Typical plot of temperature rise as a function of logarithm of time for liquid tin at 1473 K.

**Table II.** Average Values, Standard Deviations and Scatter for Thermal Conductivities of Liquid Tin and Lead

Sn			
Temperature (K)	Average value ( $W \cdot m^{-1} \cdot K^{-1}$ )	Standard deviation ( $W \cdot m^{-1} \cdot K^{-1}$ )	Scatter (%)
293	63,9	1,33	2,1
323	61,9	0,86	1,4
373	59,9	1,02	1,7
423	58	0,64	1,1
473	56,6	0,90	1,6
573	25,7	1,04	4,1
673	30,1	2,44	8,1
773	27	1,18	4,4
873	23,8	1,23	5,2
973	20,2	1,74	8,6
1073	18,4	0,74	4,0
1173	14,6	1,23	8,4
1273	13,2	0,95	7,2
1373	11,3	0,85	7,5
1473	10,1	0,97	9,6
Pb			
Temperature (K)	Average value ( $W \cdot m^{-1} \cdot K^{-1}$ )	Standard deviation ( $W \cdot m^{-1} \cdot K^{-1}$ )	Scatter (%)
293	36,1	0,57	1,6
323	34,8	0,51	1,4
345	34,4	1,05	3,1
373	34,4	1,75	5,1
423	33,4	1,01	3,0
473	32,2	0,93	2,9
523	32,4	2,15	6,6
573	29,1	1,13	3,9
673	15,4	1,20	7,8
773	15,6	1,00	6,4
873	14,4	0,93	6,5
973	14	0,49	3,5
1073	13,9	0,45	3,3
1173	12,7	0,58	4,6
1273	11,9	0,52	4,4
1373	11,4	0,58	5,1

liquid states. The thermal conductivities of solid tin are  $63.9 \pm 1.3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 293 K and decrease with increasing temperature and exhibit a value of  $56.6 \pm 0.9 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 473 K. The thermal conductivities of solid lead are  $36.1 \pm 0.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 293 K and decrease with increasing temperature giving a value of  $29.1 \pm 1.1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 573 K. The thermal conductivities of liquid tin displayed a value of  $25.7 \pm 1.0 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 573 K, and thereupon increased with increasing temperature before attaining a maximum value of about  $30.1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 673 K. Subsequently, the thermal conductivities gradually decreased with increasing temperature and the thermal conductivity was  $10.1 \pm 1.0 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 1473 K. In the case of liquid lead, the tendency was identical with that of tin. The thermal conductivities of liquid lead displayed a value of  $15.4 \pm 1.2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 673 K, a maximum value of about  $15.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 773 K, and a minimum value of about  $11.4 \pm 0.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 1373 K. The experimental uncertainties are within 9.6% and 7.8% for the measurements on liquid tin and lead, respectively, and the reproducibility of these measurements is very good.

Figures 6 and 7 show the thermal conductivities of liquid tin and lead, respectively, as a function of temperature together with the reported values [1–11]. The closed circles refer to the data recorded in the present work, and the solid lines refer to values estimated from the Wiedemann–Franz law using reported electrical conductivity values [17–19], where the value of  $2.45 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$  was employed as the Lorenz number.



**Fig. 6.** Thermal conductivity of tin compared with literature values and those obtained with Wiedemann–Franz law.

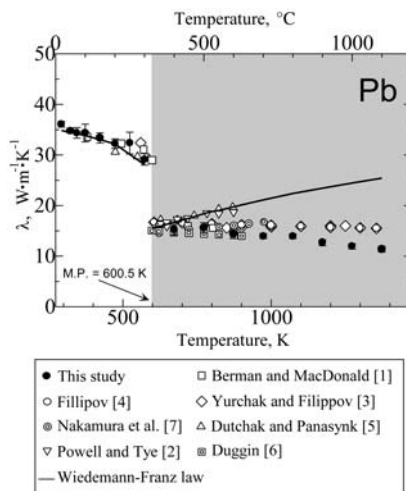


Fig. 7. Thermal conductivity of lead compared with literature values and those obtained with Wiedemann–Franz law.

## 4. DISCUSSION

### 4.1. Comparison with Literature Data

In the solid state, thermal conductivities for both metals are in good agreement with values previously reported [1–10]. Although almost all of the previous values were measured by using steady-state methods, it can be said that these values were relatively reliable for the solid samples since these methods were well-established at lower temperatures where the effect of radiation can be regarded as negligible. This agreement provides strong evidence that the method developed in the present work can apply to the solid samples.

In the liquid state, the measured values are in good agreement with literature values around the melting points for both elements, but the present measured values at higher temperatures are lower than the literature values. It can be explained as follows; almost all of the literature values were also determined using steady-state methods, even in the measurements of liquids as described in Section 1. In every method, temperature gradients are introduced into a sample to measure its thermal conductivity, but when the sample is in the liquid state, convection is usually initiated.

With respect to tin and lead, the melting points are relatively low, therefore, the ideal temperature gradient that makes the temperature of the upper part of the liquid sample higher than that of the lower part can be easily achieved around the melting point. Furthermore, since the densities of tin and lead were high, the velocity of convection would be slow. Accordingly, it can be assumed that the measurements were carried out under ideal conditions around the melting point.

However, as the temperature rises, it becomes more difficult to produce ideal conditions and then thermal conductivity tends to be overestimated. Yurchak and Filippov [3] and Filippov [4] have used the periodic heat-flow method which is a nonsteady-state method. The basic principle of this method is that if one end of a sample is heated periodically, then the temperature along the sample also varies with the same period but with diminishing amplitude, from which the thermal diffusivity and heat capacity can be determined. However, for the case of a liquid sample, the temperature response could also be delayed or disappear due to the convection. In addition, because of a lack of precise values for the density and heat capacity of liquid tin and lead, the thermal conductivity derived from the thermal diffusivity would be less reliable than values obtained without requiring a knowledge of other physical properties of the sample. Nakamura et al. [7] have measured the thermal conductivity of lead as a test liquid for measurements on InSb and GaSb. In these measurements, they developed the nonstationary hot wire method, in which a hot wire having a length of 100  $\mu\text{m}$  and a width of 15  $\mu\text{m}$  was printed on the alumina substrate having 94% purity, and, subsequently, alumina of 60  $\mu\text{m}$  thickness was deposited on it to prevent electrical leakage to the sample. In order to determine an accurate value for the thermal conductivity of the sample, an accurate value of the thermal conductivity of the alumina substrate is necessary, but there is no description in the paper how this was achieved. Moreover, although the electrical resistivity of the alumina progressively increases as temperature increases, no investigation of the electrical leakage was made. Comparisons with values estimated from the Wiedemann–Franz law are described in the following section.

#### **4.2. Temperature Dependence and its Deviation from the Wiedemann–Franz Law**

The Wiedemann–Franz law applies to solid metals and can be used to predict reasonable values of the thermal conductivity from electrical conductivity as shown in Figs. 6 and 7. This law has been derived from the free electron model on the assumption that the relaxation times are identical for electric and thermal processes. The Wiedemann–Franz law states that the

thermal conductivity is proportional to the product of the electrical conductivity ( $\sigma$ ) and the absolute temperature ( $T$ ) as follows:

$$\lambda = L\sigma T \quad (4)$$

where  $L$  is the Lorenz number which is reduced to  $2.45 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$  based upon the free electron model. But in the actual metals, this value is not always suitable because the electron is not perfectly free but nearly free. For the nearly free electron model, the Lorenz number would have a value different from  $2.45 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$ . This indicates that the absolute value of the measured thermal conductivity is different from that calculated from the electrical conductivity using the free electron model but both temperature dependences are the same as shown in Fig. 6. Accordingly, we assume that the Wiedemann–Franz law applies when the temperature dependence of the measured thermal conductivity is in good agreement with the estimated thermal conductivity.

It has not been clear whether or not this law can be applied to the thermal conductivity of liquid metals. For example, Cook [20] has reported that the Wiedemann–Franz law based upon only electron-phonon scattering cannot reasonably explain thermal conductivity values of liquid alkali metals. It has also been pointed out that the law should be modified in order to include the effect of electron-electron scattering. Around the melting point, the measured thermal conductivity values for liquid tin and lead are in good agreement with the values obtained using the Wiedemann–Franz law. It indicates that liquid metals have a free-electron structure. This fact was also confirmed from the results of Hall coefficient measurements by Greenfield [21]. At higher temperatures, the measured thermal conductivity deviates downward from those obtained with the Wiedemann–Franz law. It is interesting that even when the thermal conductivities of melts were measured using steady-state methods, in which thermal conductivity values tend to be overestimated, the reported values are still lower than those estimated by the law. To explain this, an inelastic scattering process which contributes as a resistance to only the heat conduction must be assumed. This process has little effect on the electrical conductivity, but for the thermal conductivity, it reduces heat conduction, which means that the inelastic scattering process does not obey the Wiedemann–Franz law [22]. It does not occur for electron-phonon scattering and impurity scattering, which give rise to a thermal resistance that obeys the Wiedemann–Franz law.

The electron-electron scattering mentioned above is one of the inelastic scattering processes. This process, especially at low temperatures, rarely occurs for solid metals because of the screening effect between electrons

and the Pauli exclusion principle. However, for the case of liquid metals, the situation assumes a new aspect. Anderson [23] reported that the disordered structure of atoms brings about electron localization. Furthermore, Altshuler et al. [24] pointed out that the frequency of electron-electron scattering increases under electron localization. In other words, the frequency of electron-electron scattering, which is one of the inelastic processes, progressively increases as the arrangement of the atoms in the liquid becomes disordered with increasing temperature. Although Anderson discussed the electron localization only at very low temperatures, it would be reasonable to assume the occurrence of electron localization based upon its principle.

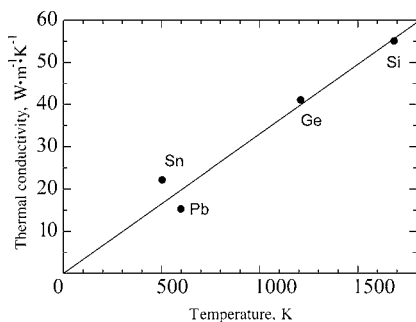
Electron-electron scattering is one of the probabilities. There is a possibility that an other kind of inelastic scattering process occurs, but nevertheless, the inelastic scattering process could be one of the keys to explain deviations from the Wiedemann–Franz law.

#### 4.3. Comparison with the Thermal Conductivities for Liquid Silicon and Germanium

Since silicon and germanium belong to the same group of the periodic table as tin and lead, it would be expected to find a new relationship by comparing the thermal conductivities for them. The simplest way is to serialize their thermal conductivities in the periodic table order. Figure 8 shows thermal conductivities for liquid silicon, germanium, tin, and lead at each melting point [12]. Since the thermal conductivities at the melting point were not measured directly in this and previous studies [12], they are estimated by extrapolation. The estimated thermal conductivities for liquid silicon, germanium, tin and lead at each melting point are about 55.0, 41.0, 22.1, and 15.2  $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ , respectively. The plot shows good linearity across the origin. Thus, the theoretical thermal conductivity of metals can be expressed as follows, based upon the free electron model:

$$\lambda = \frac{\pi^2 n k_B^2 \tau}{3m} T \quad (5)$$

where  $n$  is the electron density,  $k_B$  is the Boltzmann constant,  $\tau$  is the relaxation time, and  $m$  is the mass of an electron. A comparison between Fig. 8 and Eq. (5) indicates that the value of  $(nk_B^2 \tau / (3m))$ , namely, the product of the electron density and the relaxation time, is constant. This means that the higher the electron density is, the shorter the relaxation time is, and *vice versa*. It would be reasonable to expect that the product of the electron density and the relaxation time has the same value for elements



**Fig. 8.** Thermal conductivities of liquid tin, lead, germanium, and silicon at the melting point.

belonging to the same group. With respect to applicability to other groups' elements, further work should be done to analyze the validity of this idea. At higher temperature, although it is not clear whether or not the free-electron model can be applied to melts, such a linear relation could not be obtained due to the same reason as the inapplicability of the Wiedemann–Franz law described above.

## 5. CONCLUSION

The thermal conductivities of tin and lead have been measured in both solid and liquid phases using a nonstationary hot wire method with a silica-coated probe.

- The thermal conductivities of solid tin are  $63.9 \pm 1.3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 293 K and decrease with increasing temperature, giving a value of  $56.6 \pm 0.9 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 473 K.
- The thermal conductivities of solid lead are  $36.1 \pm 0.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 293 K and decrease with increasing temperature, giving a value of  $29.1 \pm 1.1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 573 K.
- The temperature dependences for solid tin and lead are in good agreement with those estimated from the Wiedemann–Franz law using electrical conductivity values.
- The thermal conductivities of liquid tin have a value of  $25.7 \pm 1.0 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 573 K, and thereupon increase with increasing temperature, until a maximum value of about  $30.1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at



673 K is attained. Subsequently, the thermal conductivities gradually decrease with increasing temperature and the thermal conductivity is  $10.1 \pm 1.0 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 1473 K.

- The thermal conductivities of liquid lead have a value of  $15.4 \pm 1.2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 673 K, and thereupon increase, until a maximum value of about  $15.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 773 K is attained. Subsequently, the thermal conductivities gradually decrease with increasing temperature and the thermal conductivity is  $11.4 \pm 0.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at 1373 K.
- Deviations from the Wiedemann–Franz law can be explained in terms of an inelastic scattering process.
- The plot of thermal conductivities against melting point for each element shows good linearity and passes through the origin.

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